

Chemical and Isotopic Database for McHenry County Study on Groundwater Quality and Land Use

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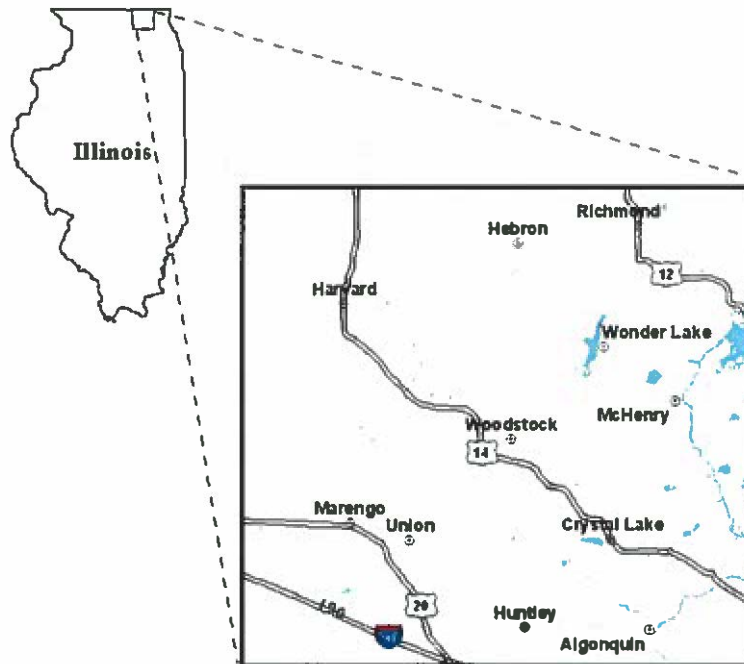
INTRODUCTION

This document provides the database for an investigation of the effects of land use on groundwater quality in McHenry County, northeastern Illinois. The document provides a complete set of chemical and isotopic data for 31 samples during this study as well as the figures that were generated from this and 38,000 historical water quality data obtained. Interpretation and discussion of the data may be found in Hwang et al. (in preparation). The historical groundwater quality data used in this investigation are available from much more extensive databases maintained by the MCDH (McHenry County Department of Health) and ISWS (Illinois State Water Survey).

Expansion of urbanized areas is inevitable with population growth. Urban activities, however, often produce contaminants that end up in groundwater. The Chicago metropolitan area in northeastern Illinois recently has seen a more rapid increase in population and land development than the rest of Illinois. Kelly and Wilson (2002) discovered that the groundwater quality in the Chicago metropolitan area has degraded since the early 1990's, and the change appeared to be most rapid in the outlying counties. McHenry County, located on the edge of the Chicago metropolitan area (figure 1), has experienced the fastest

growth of any county in Illinois (U.S. Census Bureau, 2000). The population of McHenry County increased from 35,000 in 1930 to 183,000 in 1990 and grew to 260,000 in 2000 and 303,990 in 2005 (U.S. Census Bureau, 2000, McHenry County Department of Planning and Development, 2006). Figure 2 displays the population growth in McHenry County from 1900 to 2000 in ten-year intervals.

McHenry County is an excellent region to study the anthropogenic impacts on groundwater resources because of this rapid growth and because its water supplies are almost entirely from groundwater. About 75% of its groundwater supply comes from shallow sand and gravel aquifers which are vulnerable to surface-borne contamination (Curry et al., 1997). About 13 percent of the 280 McHenry County wells in the ISWS water quality database contained nitrate concentrations at or exceeding the drinking water standard of 10 mg/L (as nitrogen) set by the USEPA (Meyer, 1998). Water quality records from the MCDH between 1986 and 2002 also indicated that nitrate concentrations were at or exceeded 10 mg/L in more than 800 wells (about 6% of the total record).



McHenry County

Figure 1. Location of study area. A blown-up map displays the major municipalities in McHenry County.

On a global basis, nitrate (NO_3^-) pollution in groundwater is a common problem in the modern world. The most common nitrate sources in surface water and groundwater are naturally-occurring atmospheric nitrate and soil organic matter, septic effluent, animal waste, and synthetic and organic fertilizers (Hallberg and Keeney, 1993). Increasing

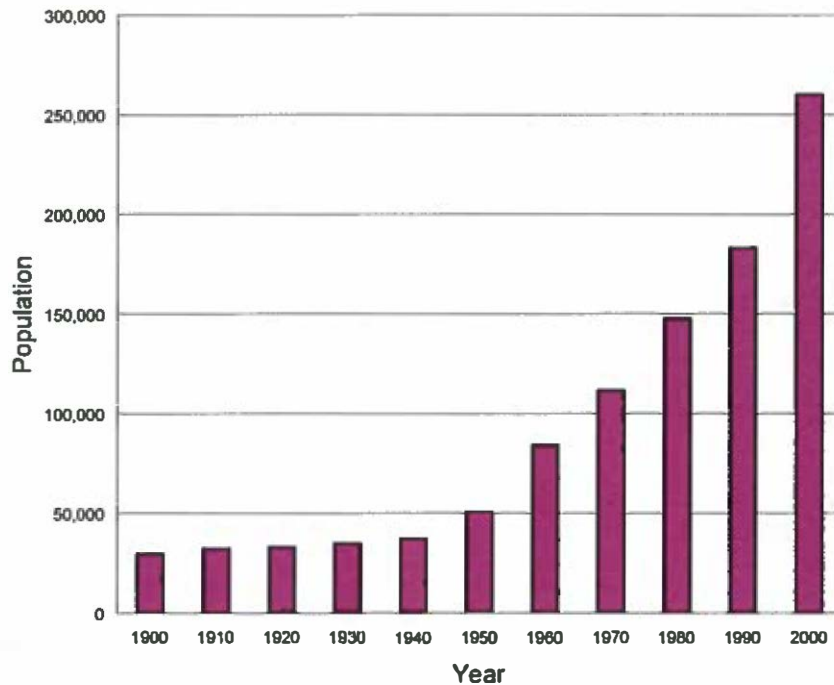


Figure 2. Population growth in McHenry County from 1900 to 2000 (U.S. Bureau of Census, 2000).

applications of fertilizer and large amounts of sewage disposal in the past few decades have contributed to the amount of N loading into surface water and shallow groundwater. High nitrate levels in drinking water are hazardous to human health and have been linked to blue-baby syndrome and stomach cancer (O’Riordan and Bentham, 1993). Thus, it is important to understand the extent of nitrate pollution in shallow groundwater and to identify its source.

The groundwater contaminant most associated with urbanization is chloride (Eisen and Anderson, 1979). One of the major sources for chloride (Cl-) is road salt used as deicer in urban areas. Other sources of chloride include leachate from leaking landfills, septic effluent, animal waste, and basin brine seeps (Panno et al., 2006). Other contaminants typically found in urban areas include sulfate, heavy metals, and volatile organic compounds (Kelly and Wilson, 2002).

STUDY AREA

McHenry County, in northeast Illinois near Chicago, is bounded by the Illinois-Wisconsin state line and five Illinois counties: Lake County to the east, Boone County to the west, and Kane, DeKalb and Cook Counties to the south. The population growth has been greatest in the southeastern part of the county. For example, the population in the municipality of Algonquin grew 76% from 10,376 in 1990 to 18,254 in 2000 (data compiled by Leonore Buckley, McHenry County Planning and Development Bureau).

The geology and groundwater resources of the McHenry County area have been characterized by the Illinois State Geological Survey and the Illinois State Water Survey (Suter et al., 1959; Csallany and Walton, 1963; Woller and Sanderson, 1976; Curry et al., 1997; Meyer, 1998). In general, the county is covered by glacial sediments deposited during the last 730,000 years from at least three separate glacial episodes, i.e. pre-Illinois, Illinois and Wisconsin

episodes (Curry et al., 1997). The physiography of the county is referred to as the Wheaton Morainal Country and consists of a series of glacial moraines and lowlands made up of very permeable sand, or sand and gravel layers, and much less permeable diamicton layers (Horberg, 1950; Curry et al., 1997). The glacial deposits in this county are a few tens of meters to up to 150 m thick and overlie bedrock composed of dolomite, limestone and shale of the Ordovician Galena and Maquoketa Groups (Herzog et al., 1994; Curry et al., 1997).

Glacially-deposited sand and gravel layers comprise relatively shallow, productive aquifers that are used extensively for water resources. An aquifer sensitivity map (Keefer, 1995) showed that the uppermost sand and gravel aquifers in many places in McHenry County are highly susceptible to contamination by NO_3^- leaching; soil leaching indices in many areas were described as “very fast” to “fast”. Consequently, many of the sand and gravel aquifers of this county can easily be sullied with surface-borne contaminants. Curry et al. (1997) noted that greater than 70% of the private and municipal wells in the county are less than 30 m deep. Where the sand and gravel deposits intersect the surface, many of the private wells are sand point wells with depths typically less than 5 meters. Somewhat more deeply buried sand and gravel aquifers, generally lying beneath a sandy diamicton unit, are slightly more protected from contamination. Even deeper, and probably even more protected are the sand and gravel aquifers that include the Pearl Formation deposited during the Illinois Episode, and the pre-Illinois Episode basal drift aquifer of the Banner Formation. The underlying bedrock is dolomite, which is highly fractured, and it is used as a water resource in those areas of the northeast where glacial deposits are too thin to serve as useable aquifers (Visocky et al., 1985; Curry et al., 1997).

OBJECTIVES

The main objective of this investigation was to evaluate the change in groundwater quality throughout the history of urban development during the last few decades in McHenry County, Illinois, based on available groundwater quality data. The second objective was to identify the origin of NO_3^- in the shallow groundwater of a few selected areas in McHenry County where high-nitrate levels were detected in well water samples. The third objective was to assess the general timing of aquifer recharge in the area based on tritium analyses of selected groundwater samples.

METHODS

This study consisted of two phases. Phase one focused on searching the Water Quality Database of the ISWS and the water analysis records of the McHenry County Department of Health (MCDH) for groundwater with NO_3^- concentrations greater than 10 mg/L (as N). The Water Quality Database of the ISWS is based on township and range, and the water quality records of the MCDH are sorted by address. Computer software, ArcGIS, was used to analyze both databases to delineate the change of groundwater quality through time and in different areas of McHenry County. Drilling records stored in the Geological Record Library at the Illinois State Geological Survey were used to provide depth and stratigraphic information of the wells of interest and to make cross sections. Population data for several townships were collected and analyzed to assess the population growth rate. The land cover map of the County (Illinois Department of Agriculture, 2000) and aerial photos were used to understand types of land usage.

Approximately 38,000 groundwater quality records from McHenry County were retrieved from the ISWS and the MCDH. The ISWS database contained records from 1913 to 1996. The MCDH database contained records from 1986 to 2002. Merging of the two databases was not feasible because the MCDH database was based on street addresses and the ISWS database was based on township, range and sections. To overcome this problem, we used the computer software, ArcGIS, to display and analyze records from the two databases on the same map. Initially the databases had to be cleaned up before they could be analyzed. Erroneous records - wells located outside of McHenry County, or with wrong or incomplete addresses, without depth information, and those that were not groundwater - were removed from the database. Records that did not report actual concentrations were also

removed (eg, less than values were removed). In the ISWS database, nitrate data were reported in three different ways, as dissolved nitrate, total nitrate, or nitrate + nitrite. Because nitrite is rarely detected in shallow groundwater, its amount was assumed to be negligible. For comparison purposes, we assumed that the value of nitrate + nitrite was equal to the dissolved nitrate concentration.

In the second phase of this project, we selected wells with high historical NO_3^- concentrations to identify the sources of NO_3^- using nitrate isotopes. We collected 30 groundwater samples from private wells in Marengo-Union, Wonder Lake, McHenry, and near Woodstock and one manure leachate sample between December 2002 and August 2003. Both $^{18}\text{O}/^{16}\text{O}$ ratios and D/H (deuterium/hydrogen) ratios of groundwater samples from several shallow aquifers were analyzed to help provide hydrogeochemical information on the groundwater. The concentration of the radioactive isotope tritium was used to determine whether recharge to the sampled aquifers occurred within the recent past (45 to 50 years). The chemical composition of groundwater samples was also determined.

Analytical Procedures

Groundwater samples from 30 wells were analyzed for cations, anions, total Kjeldahl N (TKN), ammonia, D/H, $^{18}\text{O}/^{16}\text{O}$, nitrate- ^{15}N , and nitrate- ^{18}O analyses. Groundwater samples from 10 selected wells were also analyzed for tritium content. One additional leachate sample (sample 25) collected next to a horse manure storage area was analyzed as an end member sample for animal waste. Water samples with comparatively high $^{15}\text{N}/^{14}\text{N}$ ratios and low $^{18}\text{O}/^{16}\text{O}$ ratios were analyzed for their caffeine content to help distinguish human sewage effluent sources from livestock manure sources. All of the water samples were analyzed in the field for temperature, pH, Eh and specific conductance with techniques described by Wood (1981). Water samples were filtered through 0.45- μm membranes and stored in polyethylene bottles. Cation samples were acidified in the field with ultra pure nitric acid to a pH of less than 2. All samples were transported in ice-filled coolers to the laboratory, and kept refrigerated until analysis.

Cation concentrations in water samples were determined with a Thermo-Jarrell Ash Model ICAP 61e using ThermoSPEC/AE 6.20 software. Anion concentrations in the water samples were analyzed using a Dionex 211i ion chromatograph following USEPA Method 300.0 (Pfaff, 1993). Both cation and anion concentrations were analyzed at the Illinois State Geological Survey. Concentration of total organic carbon was analyzed at the Waste Management and Research Center. Total organic carbon (TOC) analysis was performed on a Shimadzu PC-Controlled Total Organic Carbon Analyzer, Model TOC-VCN. Total organic carbon contents were determined by difference between total carbon and inorganic carbon using the method of oxidative combustion-infrared analysis (U.S. EPA 9060A, 2004). Selected groundwater samples were analyzed by the Illinois State Geological Survey (ISGS) for tritium content, $^{18}\text{O}/^{16}\text{O}$, and D/H isotopic ratios. Tritium content in water samples was enriched by an electrolytic enrichment process (Ostlund and Dorsey, 1977) and analyzed by a liquid scintillation counter. The $^{18}\text{O}/^{16}\text{O}$ analysis of water samples was measured by a method described in Epstein and Mayeda (1953) with modification described in Hackley et al. (1999). The D/H analysis of water samples were analyzed by a method described in both Coleman et al. (1982) and Vennemann and O'Neil (1993), with modifications described in Hackley et al. (1999). Ammonium concentrations were determined at the Illinois Natural History Survey using the Berthelot Reaction, which involves the formation of a blue-colored indolphenol compound in a solution of ammonia salt, sodium phenoxide and sodium hypochloride (Greenburg et al., 1987). Following enhancement of color using sodium nitroprusside, the color intensity is measured by a Bran & Luebbe TRAACS 2000 colorimeter at 660nm. Total Kjeldahl Nitrogen (defined above) was determined at the Illinois Natural History Survey by oxidation of the organic material in the water, followed by digestion by NaOH to convert all organic nitrogen compounds to NH_3 . Ammonia was then analyzed as above. A separate analysis of nitrite and nitrate yielded TKN by difference (Raveh and Avnemelech, 1979).

Nitrate isotopic analyses were performed at the Isotope Geochemistry Laboratory of the ISGS using an improved ion-exchange method developed by Hwang et al. (1999), which is modified from Silva et al. (2000). Anion exchange columns pre-packed with Bio-Rad Ag1-X8 anion exchange resin in the chloride form were used to extract NO_3^- from the water samples. After passing a groundwater sample through the columns, 1-M HBr solution was introduced to the column to elute the NO_3^- . Then, $\text{Ag}_2\text{O}(\text{s})$ was slowly added into the effluent to neutralize the solution and convert the NO_3^- in the effluent into AgNO_3 solution. The neutralized solutions were filtered by 0.45 μm Millipore-type HNWP filter papers and transferred into Teflon beakers. The beakers were placed in an oven at 80°C to reduce the volume of the solution to around ten milliliters. The concentrated solutions were then trans-

ferred into Petri-dish and frozen in a freezer. Later on the frozen solution were freeze-dried overnight to form $\text{AgNO}_3(\text{s})$. The $\text{AgNO}_3(\text{s})$ was stored in amber vials.

For nitrate-oxygen isotopic analyses, the dried AgNO_3 was weighed into 9-mm quartz tubes for combustion. One gram of graphite was mixed with every 4 grams of AgNO_3 in the tube. The sample tubes were heated in a vacuum oven at 100°C overnight to remove residual moisture (Revesz et al., 1997) and sealed the next morning for combustion. A furnace connected to a programmable temperature controller was used for the combustion procedure. Samples were heated at 650°C for one hour, followed by 600°C for ten hours, and slowly cooled to room temperature in ten hours. When tested on reagent grade AgNO_3 , 97% to 100% recovery of CO_2 was usually obtained. After combustion, the quartz sample tubes were connected to a vacuum system for purification of the CO_2 . The purified CO_2 sample was then analyzed for oxygen isotope ratios. For nitrate-N isotopic analyses, dried AgNO_3 was weighed into 9-mm quartz tubes with prebaked CaO , Cu metal turnings and Cu_2O . To convert the AgNO_3 to N_2 gas, the sample tubes were heated at 850°C for 2 hours and slowly cooled to 650°C , then cooled naturally to room temperature. Isotopic analyses of the CO_2 and N_2 gas were performed on a Finnigan Mat Delta E mass spectrometer.

RESULTS

Database Analysis (GIS results)

Historical groundwater records from both ISWS and MCDH databases were analyzed to delineate temporal and spatial trends.

TDS History. Total Dissolved Solids (TDS) is the sum of all dissolved constituents in water. The secondary standard of TDS for drinking water suggested by USEPA is 500 mg/L. Among the two databases analyzed, only the ISWS database contained TDS information. TDS records were divided into four time interval (1913-1950, 1951-1965, 1966-1980, and 1981-1996) to check temporal trend (figure 3). It was also divided into four depth intervals (0 to 50 ft, 51 to 100 ft, 101 to 200 ft, and greater than 200 ft) to delineate any correlation between TDS concentration and well depth (figure 4).

Chloride History. For comparison, chloride concentrations in precipitation, soil water, and uncontaminated aquifer in northeastern Illinois are usually less than 15 mg/L (Panno et al., 2006). The historical records for chloride concentration were divided into four time intervals as shown on figure 5. The chloride records were also divided into four depth intervals between 0 and 200 ft (0 to 61m, see figure 6).

Nitrate History. The temporal trend of historical nitrate concentration record is shown in figure 7. Figure 8 displays nitrate concentrations in four depth intervals between 1 and 200 ft (0 to 61m). Figure 9 displays the distribution of high NO_3^- concentration records on a land cover map (Illinois Department of Agriculture, 2000). Figure 10 displays high nitrate (greater than 10 mg/L) records on a map that ranks the degree of sensitivity of the aquifers to nitrate leaching.

Chemical Analysis

Table 1 and 3 show the results of chemical and isotopic analysis of thirty one samples collected in this study. One additional leachate sample (sample 24) collected next to a horse manure storage area was analyzed as an end member sample for animal waste. Table 2 shows the range, mean, and median concentration for specific ions for samples associated with the different environments (Urban, Urban/rural, rural, and livestock facilities).

Caffeine. Five samples with suspected septic influence (Table 1) were chosen for caffeine analysis. All of their results were below detection limit.

Isotope Analysis

δD and $\delta^{18}\text{O}$ of Water. The δD values of groundwater samples ranged from -41.6 to -61.4 permil, and the $\delta^{18}\text{O}$ values from -6.7 to -9.1 permil (Table 3). Most of the data fall on the meteoric water line on a δD versus $\delta^{18}\text{O}$ plot except the surface water sample collected next to the horse manure pile (figure 11).

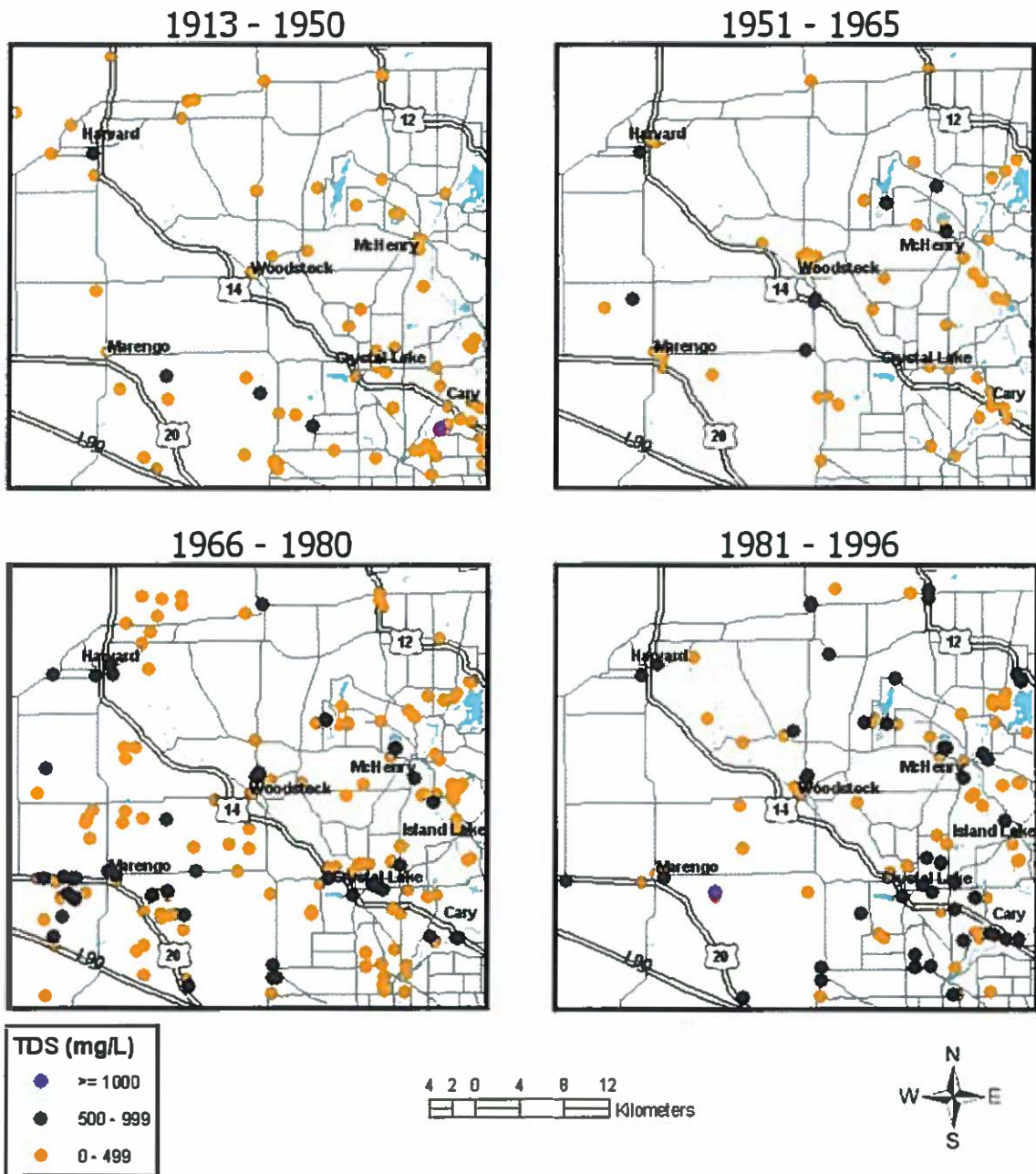


Figure 3. Historical records of TDS (total dissolved solids) concentrations for McHenry County during 1913 to 1996.

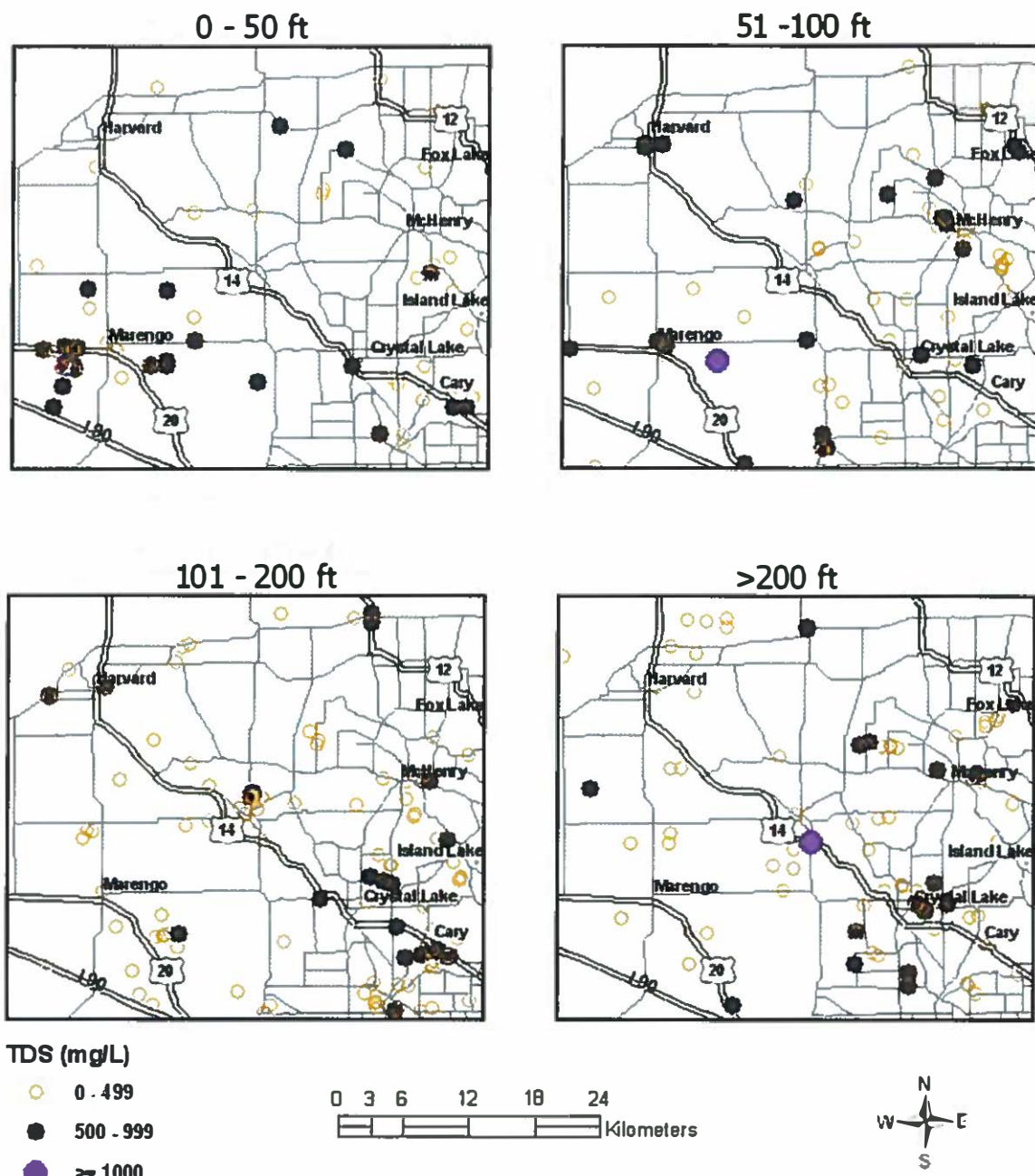


Figure 4. Distribution of historical TDS concentrations at different depth intervals for McHenry County.

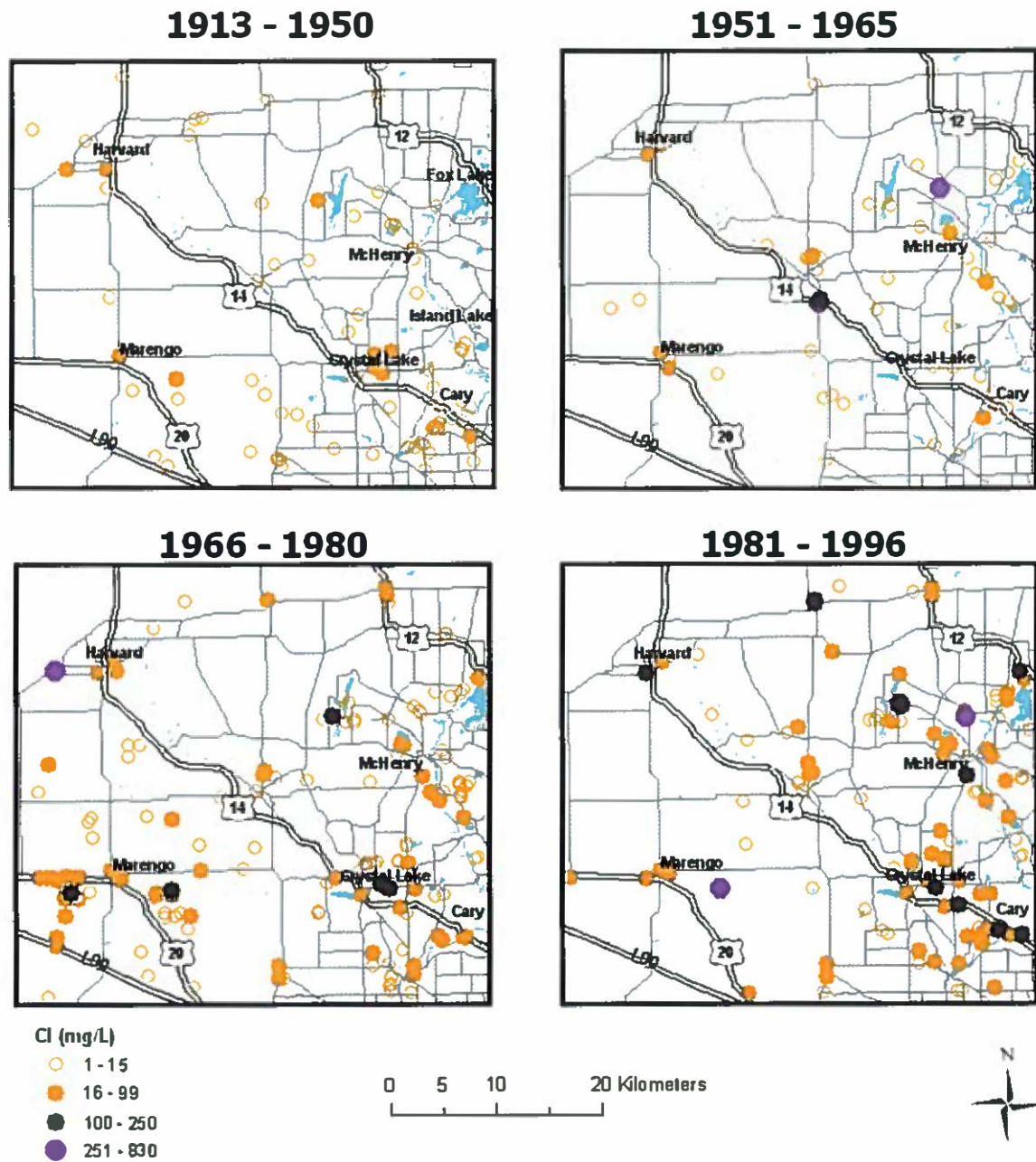


Figure 5. Historical records of chloride concentrations for McHenry County during 1913 to 1996.

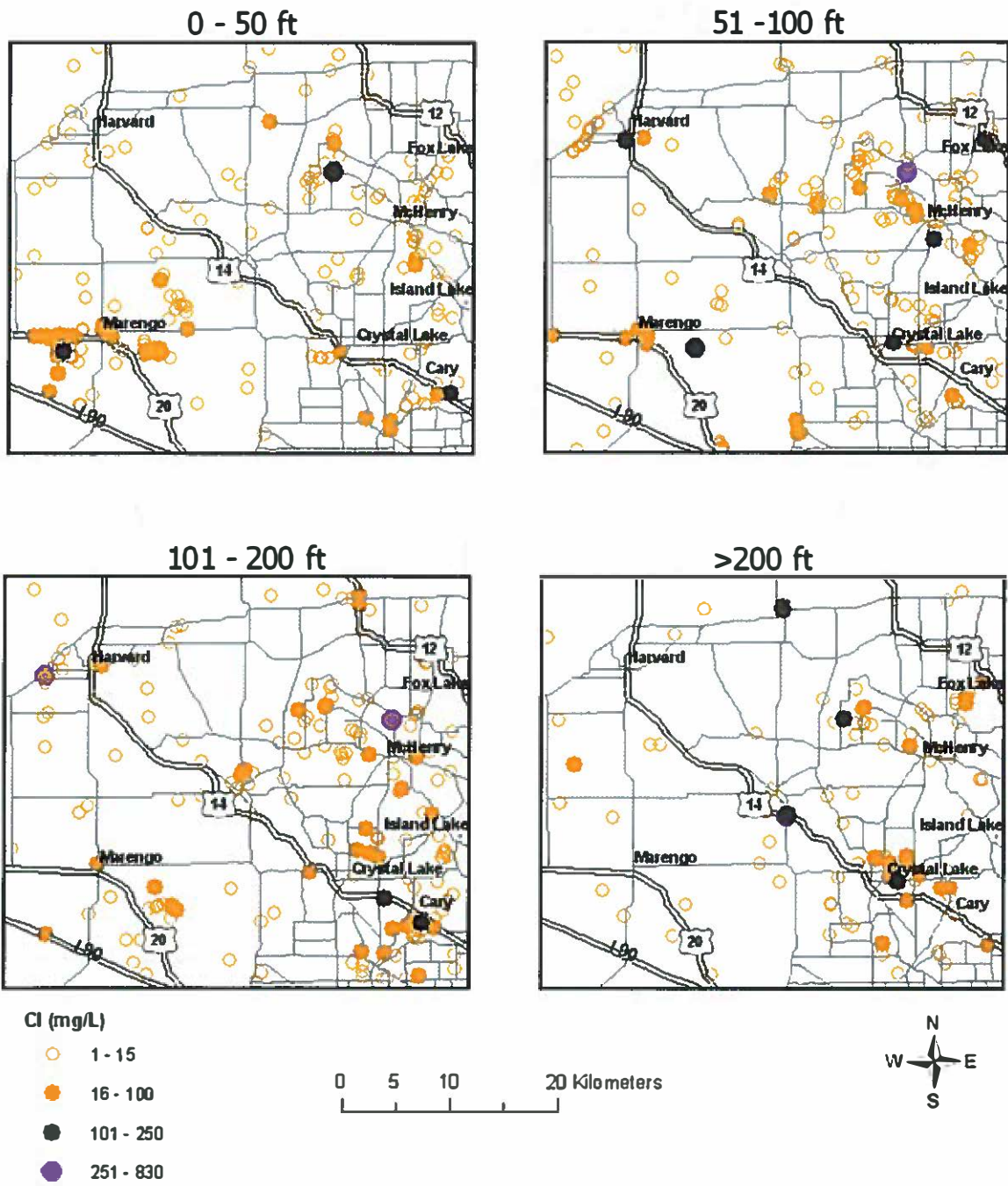


Figure 6. Distribution of historical chloride concentrations at different depth intervals for McHenry County.

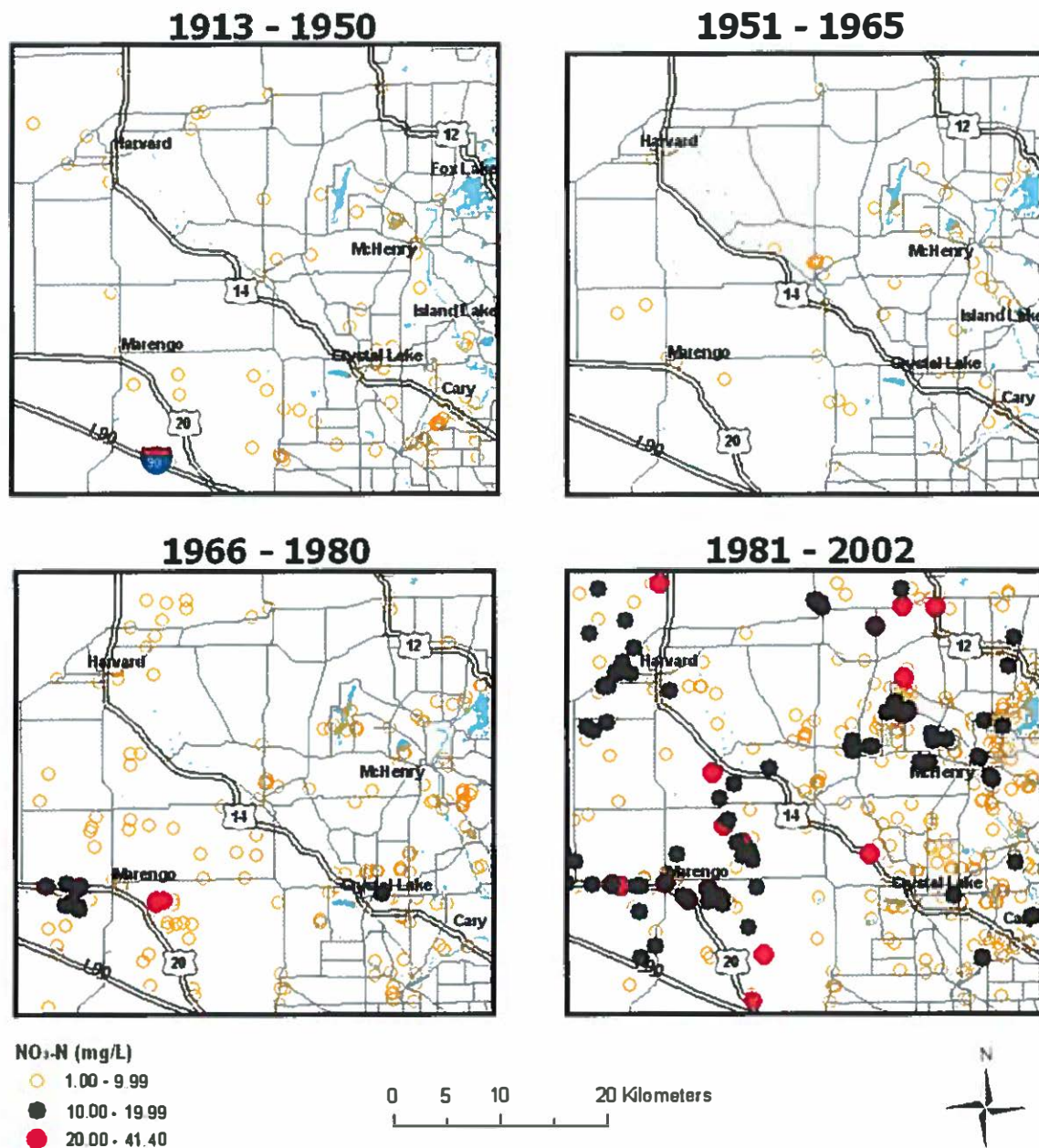


Figure 7. Historical records of nitrate concentrations for McHenry County during 1913 to 2002.

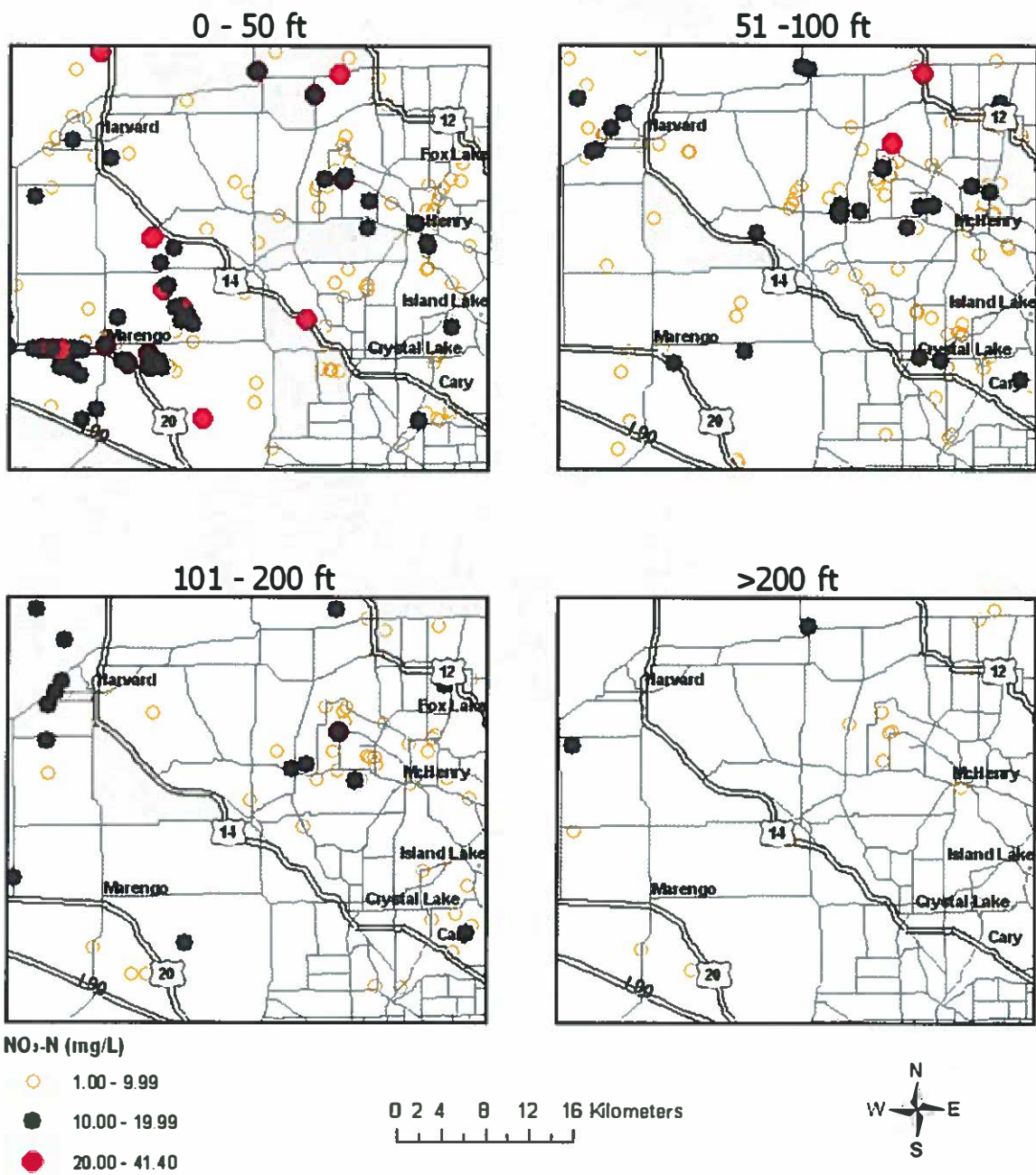
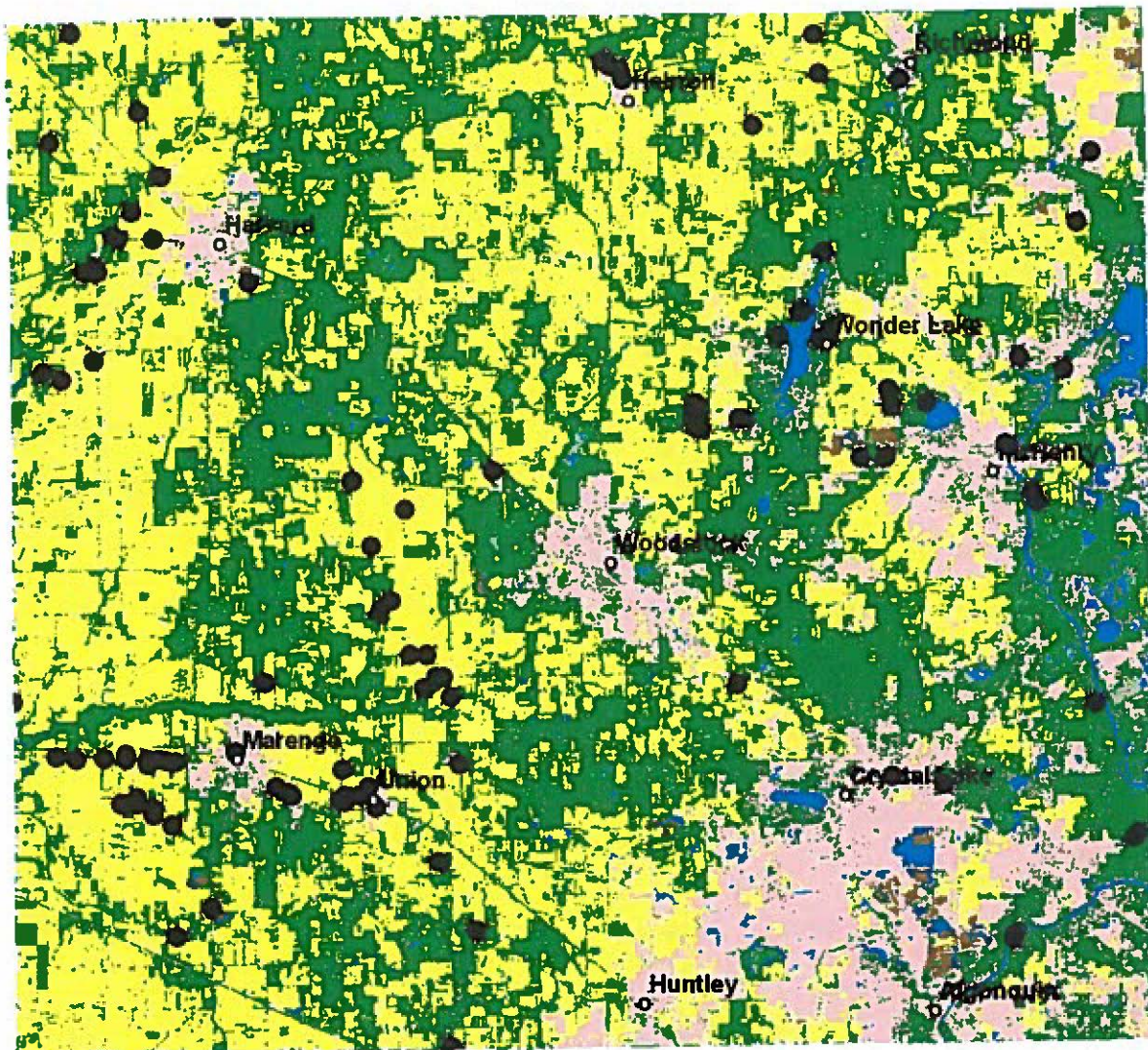


Figure 8. Distribution of nitrate concentration in shallow groundwater at different depth intervals.



- NO3 (mg/L)**
 ● > 10
- Class_Names**
- Background
 - Barren & Exposed Land
 - Cloud Shadows
 - Clouds
 - Coniferous
 - Corn
 - Deep Marsh
 - Floodplain Forest
 - High Density
 - Low/Medium Density
 - Other Agriculture
 - Other Small Grains & Ha
 - Partial Canopy/Savannah
 - Rural Grassland
 - Seasonally/Temporarily f
 - Shallow Marsh/Wet Meac
 - Shallow Water
 - Soybeans
 - Surface Water
 - Swamp
 - Upland
 - Urban Open Space
 - Winter Wheat
 - Winter Wheat/Soybeans

Figure 9. A map shows types of land cover (Illinois Department of Agriculture, 2000) in McHenry county area. Black circles represent wells with historical nitrate concentration greater than 10mg/L. Color symbols for the land cover map: yellow-cropland; green-grassland and forest; pink-urban areas; blue-lakes and rivers.

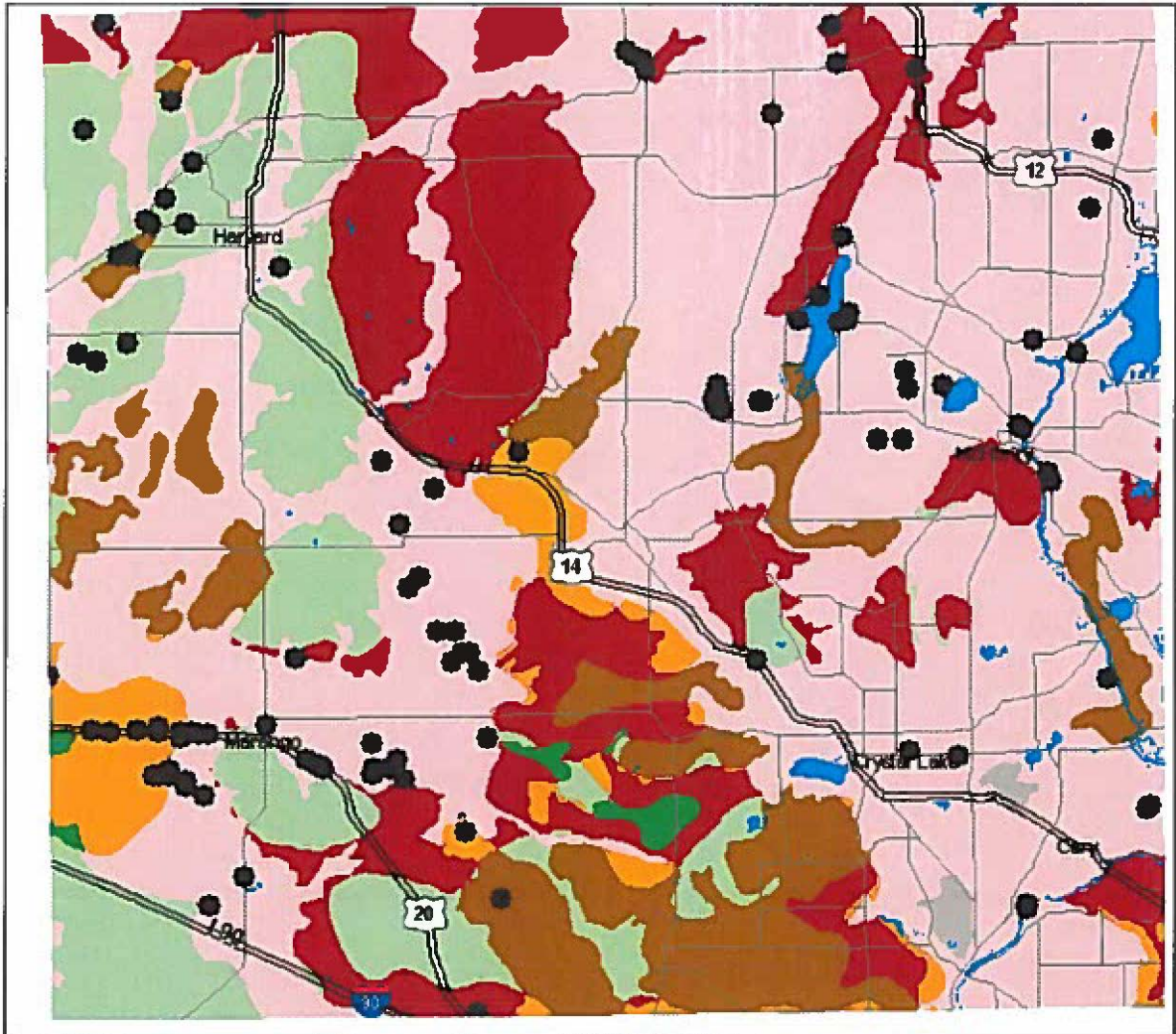


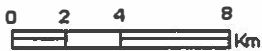
Figure 10. Nitrate concentrations >10 mg/L (solid circles) on an aquifer sensitivity map (Keefer, 1995).

NO₃ (mg/L)

● > 10

Aquifer Sensitivity to NO₃

- Excessive
- High
- Moderate
- Somewhat limited
- Limited
- Very limited
- Disturbed land
- Surface water



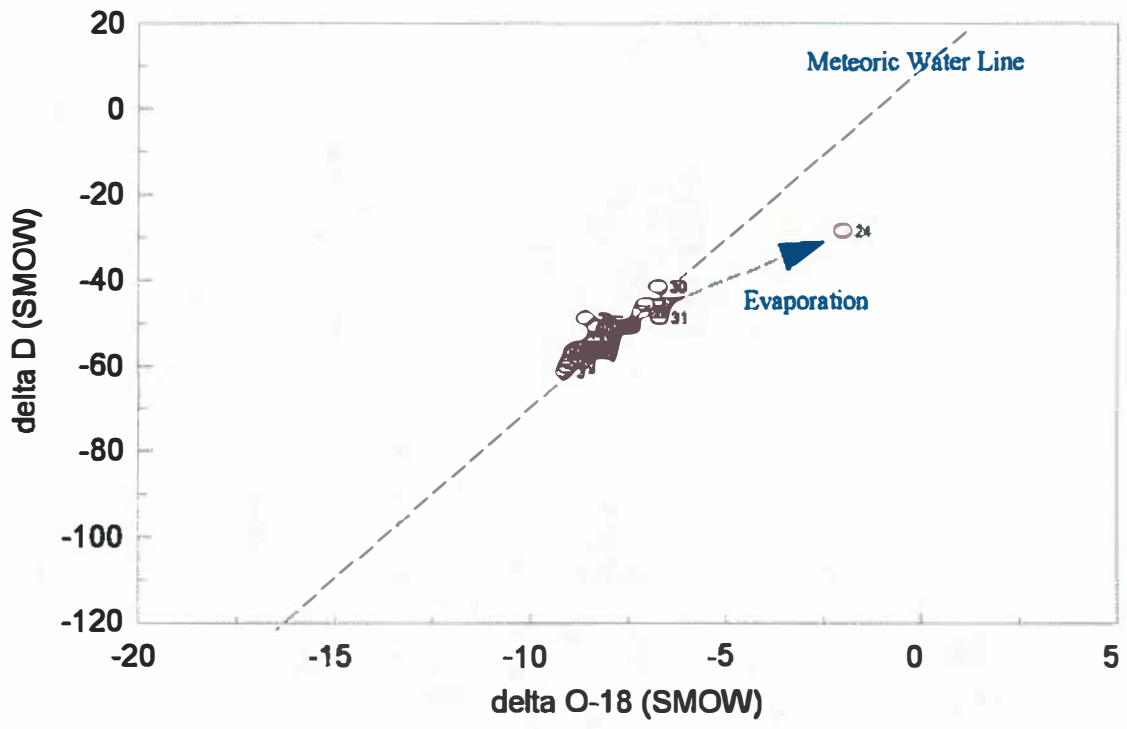


Figure 11. Delta D versus delta ¹⁸O diagram showing most of the shallow groundwater samples fall on the meteoric water line.

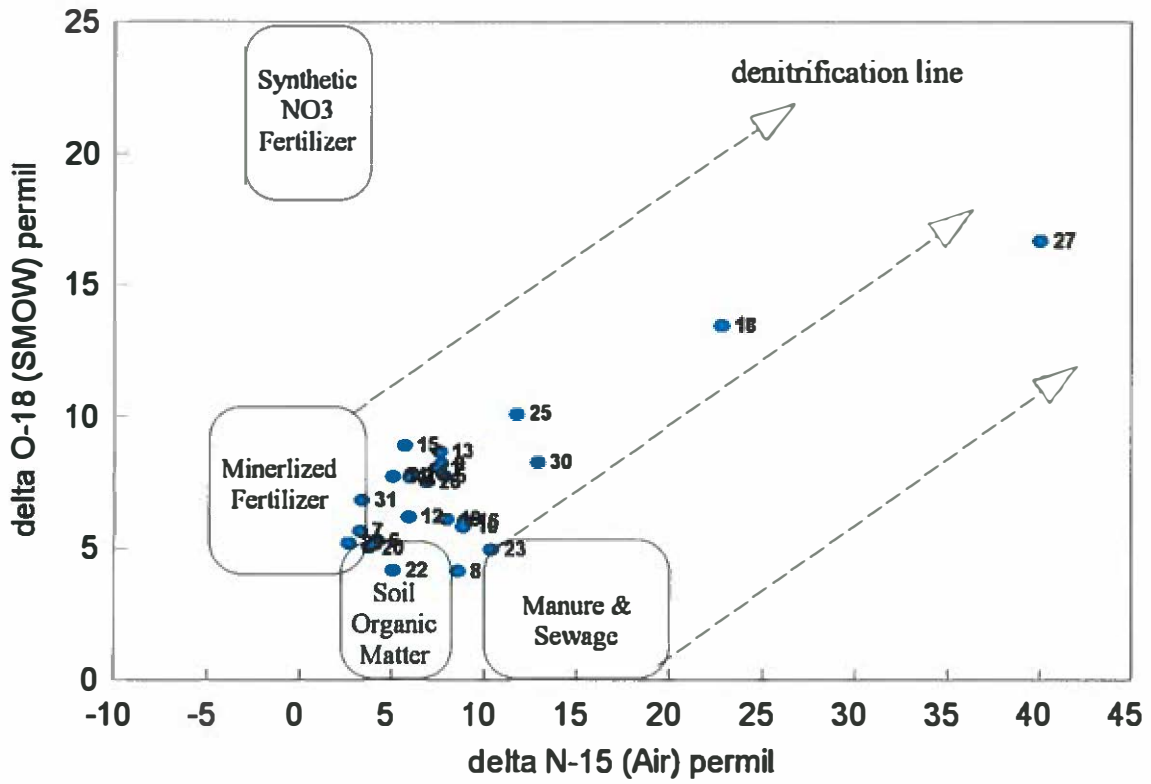


Figure 12. A $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ diagram displays nitrate isotope data with the typical ranges of common end-members (Clark and Fritz, 1997).

Table 1. Field Measurements and Ionic Concentrations (unit: mg/L)

Sample ID	Sample Type *	Depth (ft)	Temp(°C)	pH	Eh(mV)	Cl ⁻	NO ₃ ⁻ -N	SO ₄ ²⁻	DOC	NH ₄ ⁺ -N	TKN	Caffeine
1	urban	20	15.9	7.07	456	219	7.25	30	1.8	0.01	0.01	nd
2	urban	20	14.0	7.16	156	229	0.08	35.3	0.83	0.03	0.19	nd
3	rural	15	14.6	7.18	476	15.6	2.26	24.9	1.5	0.04	0.02	nd
4	rural	38	11.3	7.28	92	43.2	<0.02	24.9	0.85	nd	nd	nd
5	rural	15	12.6	7.02	445	27.1	49.4	57.9	8.1	0.02	0.04	nd
6	rural	20	15.4	7.19	473	23.7	0.08	4.8	1.8	0.04	<DL	nd
7	rural	28	12.0	7.19	491	15.5	14.6	18.4	2.8	<DL	20	nd
8	urban/rural	16	13.4	7.125	414	135	4.55	13.7	1.3	<DL	<DL	<0.15
9	urban/rural	80	11.5	7.12	460	59.4	4.39	34.8	0.58	<DL	<DL	nd
10	urban	110	11.2	6.96	507	169	7.53	26.2	0.65	<DL	0.19	<0.15
11	urban	90	11.2	7.18	487	41.6	7.21	46	0.87	<DL	1.35	nd
12	urban	88	11.1	7.14	499	43.9	9.12	28.8	0.53	<DL	1.04	nd
13	urban	124	12.3	6.91	538	155	10	53.6	1.4	<DL	<DL	nd
14	urban/rural	16	11.2	7.19	453	164	12.1	41.1	0.5	0.01	0.01	nd
15	rural	100	11.3	7.2	510	17	7.9	64.2	1.1	<DL	<DL	nd
16	Urban	100	13.5	7.01	413	166	6.27	48.1	0.9	<DL	<DL	<0.15
17	Urban	100	14.4	7.2	147	80.4	0.19	76.4	1.6	0.01	0.21	nd
18	urban/rural	30	12.2	7.21	290	12.7	4.63	56.3	0.7	<DL	<DL	<0.15
19	Urban	20	12.4	7.02	462	271	14.2	42.1	1.3	<DL	<DL	<0.15
20	rural	61	11.2	7.41	521	19.3	6.19	36.9	2.1	0.02	0.54	nd
21	urban/rural	25	12.1	7.48	88	2.8	<0.02	1.3	1.7	1.98	2.51	nd
22	urban/rural	53	12.3	7.16	477	83.5	7.7	34.3	0.8	0.07	0.45	nd
23	urban/rural	23	12.3	7.21	455	52.7	6.38	28.6	1.2	0.13	0.9	nd
24	manure leachate	0	nm	7.34	344	440	0.19	111	220	155	256	nd
25	animal waste	26	13.7	7.32	500	33	22.4	62.4	0.82	0.04	10.6	nd
26	animal waste	22	15.1	7.38	525	35.4	25.4	28	0.97	0.03	3.92	nd
27	animal waste	7	14.7	7.06	568	69.2	5.59	236	26	0.05	13.8	nd
28	animal waste	2.5	18.6	6.94	488	56.5	0.02	68.5	38	21.8	30	nd
29	animal waste	14	13.7	7.25	549	18.8	13	15.7	1.1	0.01	4.58	nd
30	animal waste	7	15.2	6.93	331	36.6	18.7	37.6	4.8	0.02	5.11	nd
31	animal waste	18	13.2	7.38	519	15.4	25.2	15.2	0.9	<DL	6.3	nd

nm: not measured

nd: no data

<DL: less than detection limit

*Sample type: urban - groundwater from urban area.

rural - groundwater from rural areas which are dominated by cropland.

urban/rural - groundwater from border of urban and rural areas.

manure leachate - from standing leachate next to a pile of horse manure.

animal waste - groundwater from farms with livestock such as hogs and cattle.

Table 2. Range of Ionic Concentration in Groundwater from Different Environments (unit: mg/L)

Component	Environment	Range	Mean	Median
Cl ⁻	Urban	41.6 to 271	152.8	166
	Rural	15.5 to 43.2	24.1	21.5
	Urban/Rural *	2.8 to 164	72.9	59.4
	Animal Waste	15.4 to 69.2	37.8	35.4
NO ₃ ⁻	Urban	0.1 to 14.2	6.9	7.3
	Rural	0 to 49	13.7	9.6
	Urban/Rural	0 to 12.1	5.7	5.5
	Animal Waste	0 to 25.4	15.8	18.7
SO ₄ ²⁻	Urban	26.2 to 76.4	42.9	42.1
	Rural	4.8 to 57.9	28	24.9
	Urban/Rural	1.3 to 56.3	30	34.3
	Animal Waste	15.2 to 236	66.2	37.6
TKN	Urban	0 to 1.35	0.3	0.2
	Rural	0 to 20	3.4	0.29
	Urban/Rural	0 to 2.51	0.6	0.7
	Animal Waste	3.92 to 30	10.6	6.3
Total N	Urban	0.3 to 14.2	7.2	7.7
	Rural	2.3 to 49.5	20.6	9.7
	Urban/Rural	4.4 to 12.1	6.5	4.6
	Animal Waste	17.6 to 15.8	29.5	29.4

*Urban/Rural: near the border of urban and rural areas.

Table 3. Isotope Data (Units: Permil for Stable Isotopes, TU for tritium)

Sample ID	δD	$\delta^{18}O$	$\delta^{13}C(HCO_3^-)$	$\delta^{18}O(NO_3^-)$	$\delta^{15}N(NO_3^-)$	$\delta^{15}N(NH_4^+)$	Tritium
1	-54.5	-8.35	-12.27	8.1	7.5	nd	8.29
2	-55.9	-8.45	-12.78	nd	nd	nd	6.66
3	-61.4	-9.10	-11.36	7.7	6.0	nd	nd
4	nd	nd	nd	nd	nd	nd	nd
5	-51.4	-7.80	-10.13	7.8	7.8	nd	8.73
6	-59.3	-8.98	-13.08	5.3	4.2	nd	nd
7	-50.1	-7.78	-8.63	5.6	3.3	nd	nd
8	-53.2	-8.17	-13.98	4.1	8.6	nd	7.06
9	-53.9	-8.33	-10.12	8.2	7.7	nd	nd
10	-55.9	-8.65	-13.32	5.8	8.9	nd	nd
11	-58.1	-8.78	-11.69	7.8	6.1	nd	nd
12	-60.4	-9.04	-11.92	6.2	5.9	nd	nd
13	-56.9	-8.60	-10.62	8.7	7.6	nd	nd
14	-56.9	-8.86	-10.40	7.7	5.1	nd	6.51
15	-56.5	-8.90	-9.96	8.9	5.7	nd	9.69
16	-57.6	-8.50	-13.31	6.0	9.0	nd	9.67
17	-57.1	-8.46	-11.00	nd	nd	nd	16.29
18	-56.2	-8.47	-9.03	13.5	22.9	nd	8.5
19	nd	-8.33	-13.08	6.1	8.0	nd	nd
20	-57.1	-8.84	-12.08	5.0	3.8	nd	nd
21	-53.8	-8.39	-5.22	nd	nd	-3.2	nd
22	-55.9	-8.75	-11.37	4.2	5.1	nd	nd
23	-50.9	-8.00	-12.39	5.0	10.4	nd	nd
24	-28.3	-1.99	-5.96	nd	nd	12.5	nd
25	-49.0	-8.57	-5.04	10.1	11.8	nd	nd
26	-51.3	-8.09	-4.73	7.5	6.9	nd	nd
27	-45.6	-7.06	-11.63	16.7	40.1	nd	nd
28	-47.6	-7.17	-11.46	nd	nd	7.7	nd
29	-50.9	-7.89	-8.87	5.2	2.7	nd	nd
30	-42.6	-6.74	-16.14	8.3	12.9	nd	nd
31	-48.7	-6.70	-3.82	6.8	3.4	nd	nd

nd: no data, mostly due to concentration too low to be analyzed for isotopic ratio

$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of Dissolved Nitrate. Nitrate isotope samples were collected from wells in different environments such as urban, rural, and livestock farms. The $\delta^{15}\text{N}$ values of groundwater samples ranged from 2.7 to 40.1 permil, and the $\delta^{18}\text{O}$ from 4.1 to 16.7 permil (figure 12). Several samples were collected near farms with livestock facilities (#25 to #31).

$\delta^{15}\text{N}$ of Ammonium. Three samples (sample 21, 24 and 28) which contained enough ammonium were analyzed for ammonium $\delta^{15}\text{N}$. Sample 21 was collected from a shallow well with low Eh value (88 mv). Sample 24 was the horse manure leachate. Sample 28 was from a shallow (0.8 m deep) hand-dug well down gradient from a hog farm. The $\delta^{15}\text{N}$ values are -3.2 (groundwater), +7.7 (dug well) and +12.5 permil (manure leachate).

Tritium. Tritium analyses have been completed for six groundwater samples collected from depths of 6 to 30 m. The tritium measurements ranged predominantly from 6.5 to 9.7 TU, with one sample containing 16.29 TU.

CROSS-SECTIONS

The stratigraphy of the McHenry County study area consisted of interbedded diamicton and sand and gravel deposits (30 to 90 m thick), all overlying Silurian-age dolomite (Curry et al., 1997). The sand and gravel deposits and the dolomite all served as aquifers for the region; the diamicton acts as an aquitard capable of isolating aquifers from surface-borne contaminants. Four cross sections were made across selected areas of McHenry County (figure 13) to depict the stratigraphy and to show the relationships between agricultural land and cities and their effects on groundwater quality (figures 14a, 14b, 15, 16).

Each land use should have a characteristic contaminant signature in the groundwater beneath. The tightly-clustered network of streets in urban areas typically are treated with large amounts of road salt in the winter months; rural areas have fewer roads that would result in a less intense application of road salt. Thus, one would expect a greater level of chloride contamination in the urban areas than in the rural areas. However, it is important to note that most farm wells sampled were just off the roadways that received road salt during the winter months. Given that sodium-chloride contamination would accumulate adjacent to the roadways, one would expect many farm wells to be contaminated with chloride from road salt. Conversely, land use in the rural areas is typically row-crop agriculture and as such, would receive synthetic N-fertilizer during the spring months. In these areas, one would expect more NO_3 contamination in the rural areas than in the urban areas. Groundwater contamination, of course, would depend on the local geology and whether the underlying sand and gravel aquifer was exposed at the surface or was protected by a layer of diamicton. For example, Figure 14 shows Marengo, IL having chloride concentrations in wells over 200 mg/L and nitrate concentrations of 7 mg/L or less, whereas, chloride and nitrate concentrations in wells to the southwest have

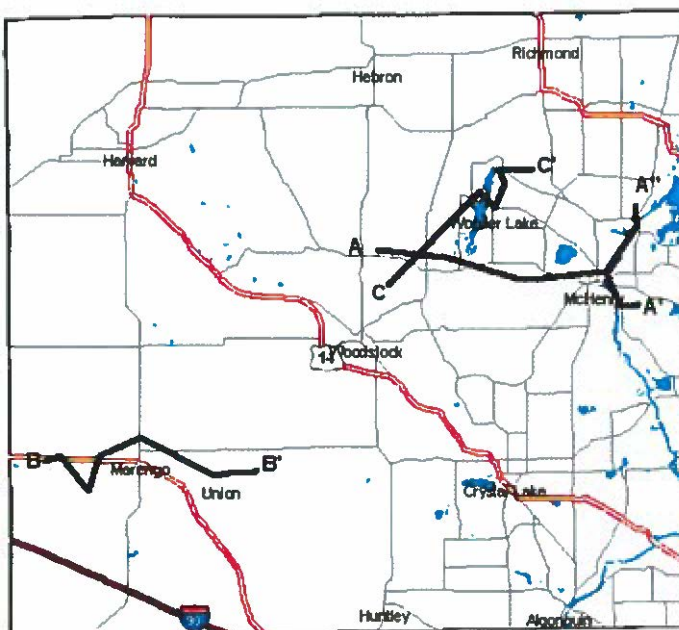


Figure 13. Location of cross section maps on a McHenry County map.

receive synthetic N-fertilizer during the spring months. In these areas, one would expect more NO_3 contamination in the rural areas than in the urban areas. Groundwater contamination, of course, would depend on the local geology and whether the underlying sand and gravel aquifer was exposed at the surface or was protected by a layer of diamicton. For example, Figure 14 shows Marengo, IL having chloride concentrations in wells over 200 mg/L and nitrate concentrations of 7 mg/L or less, whereas, chloride and nitrate concentrations in wells to the southwest have

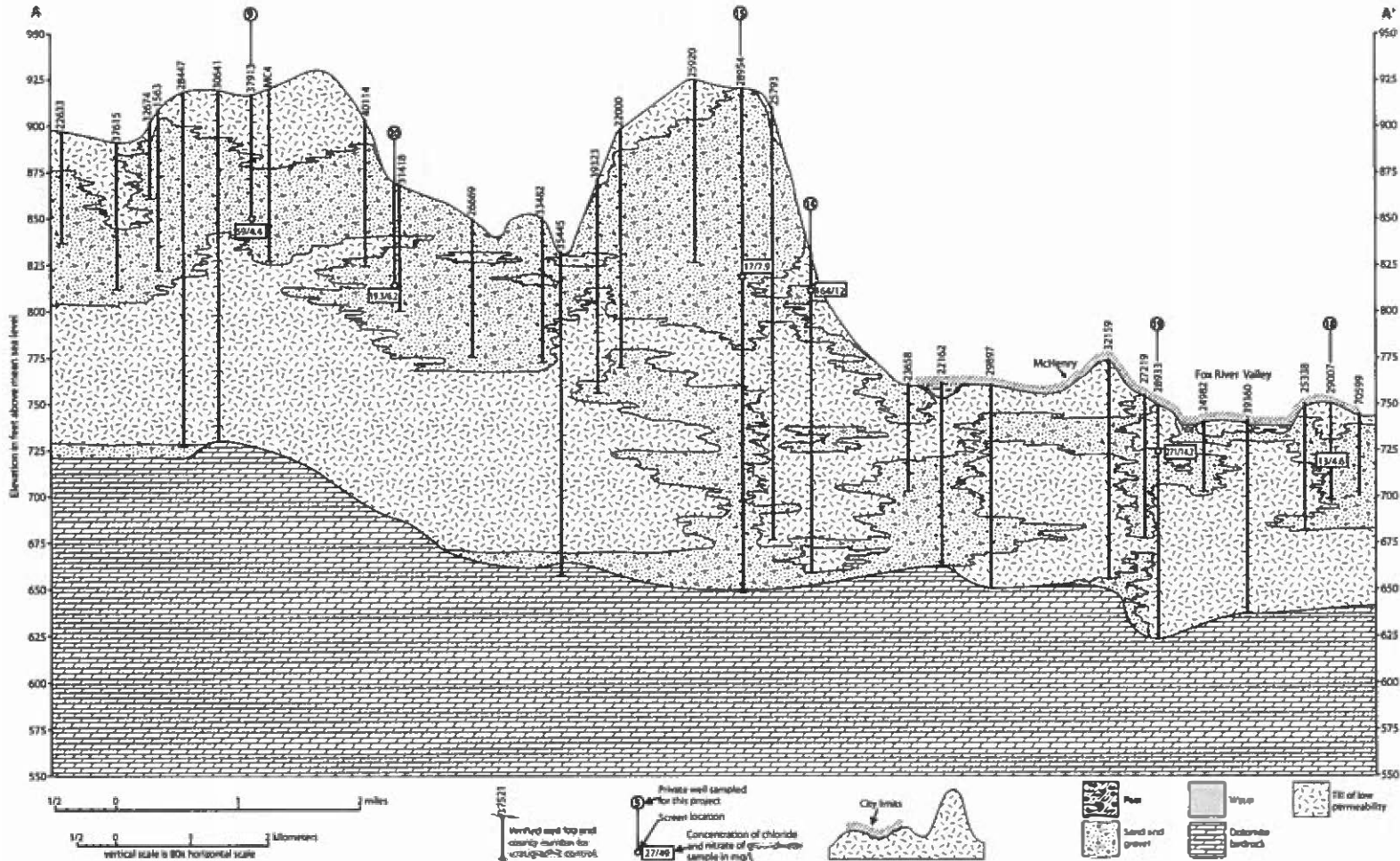


Figure 14a. Cross section A-A' across a rural area and the town of McHenry showing sand and gravel aquifers exposed at the surface in some areas and protected by finer, clay-rich glacial till in other areas.

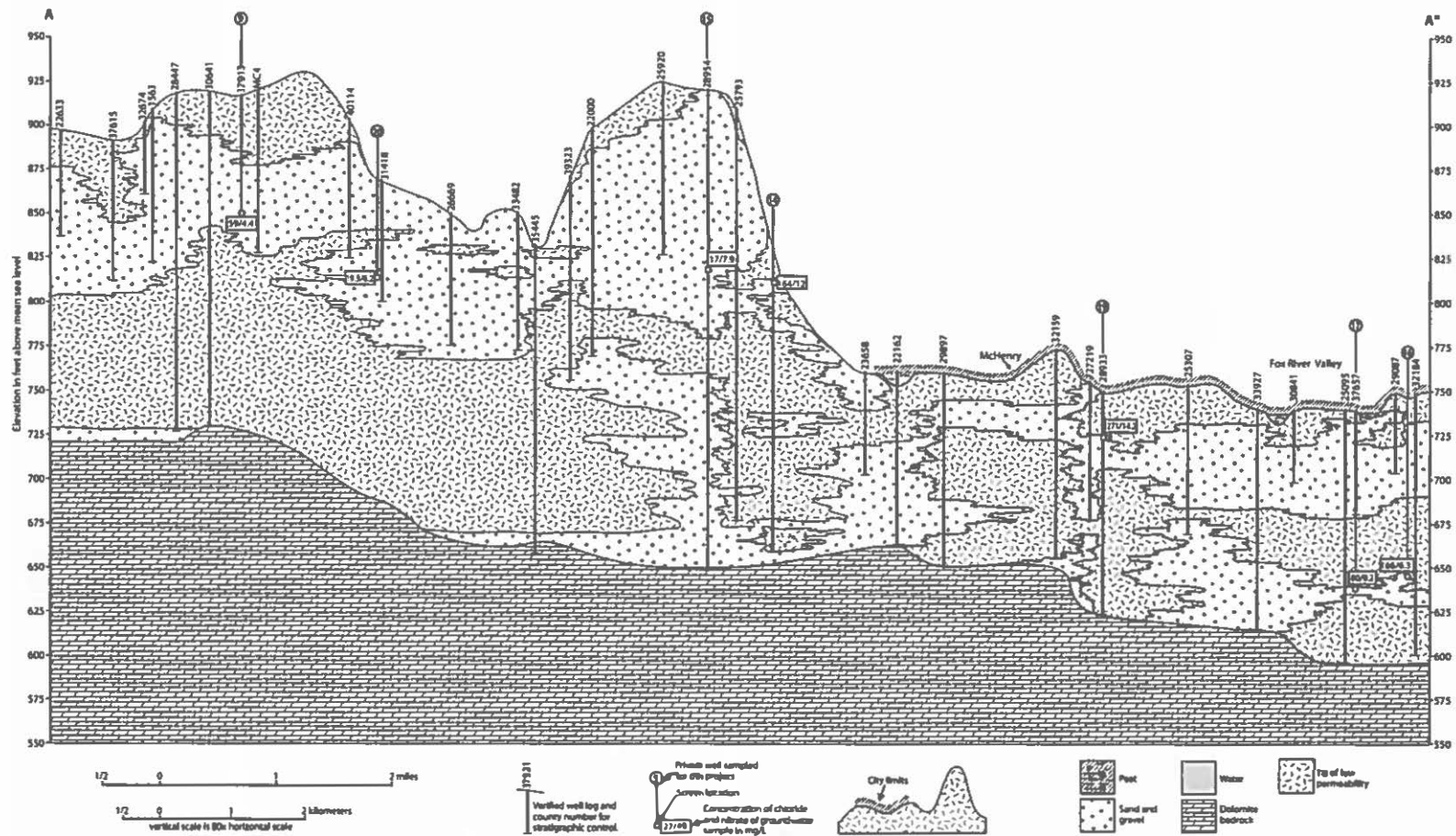


Figure 14b. Cross section A-A'' across a rural area and the town of McHenry showing sand and gravel aquifers exposed at the surface in some areas and protected by finer, clay-rich glacial till in other areas.

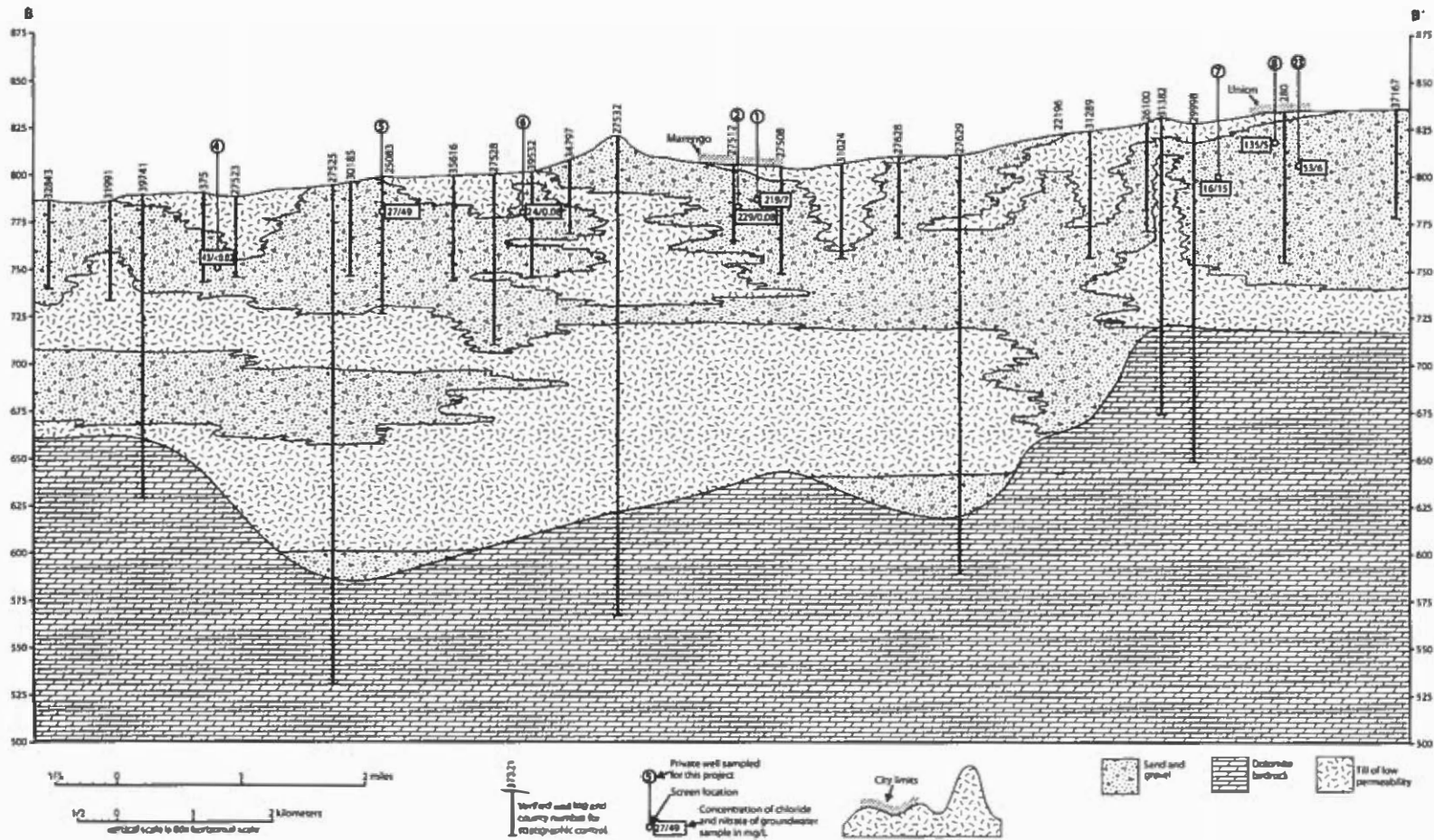


Figure 15. Cross section B-B' across rural areas and the towns of Marengo and Union showing sand and gravel aquifers exposed at the surface in some areas and protected by finer, clay-rich glacial till in other areas.

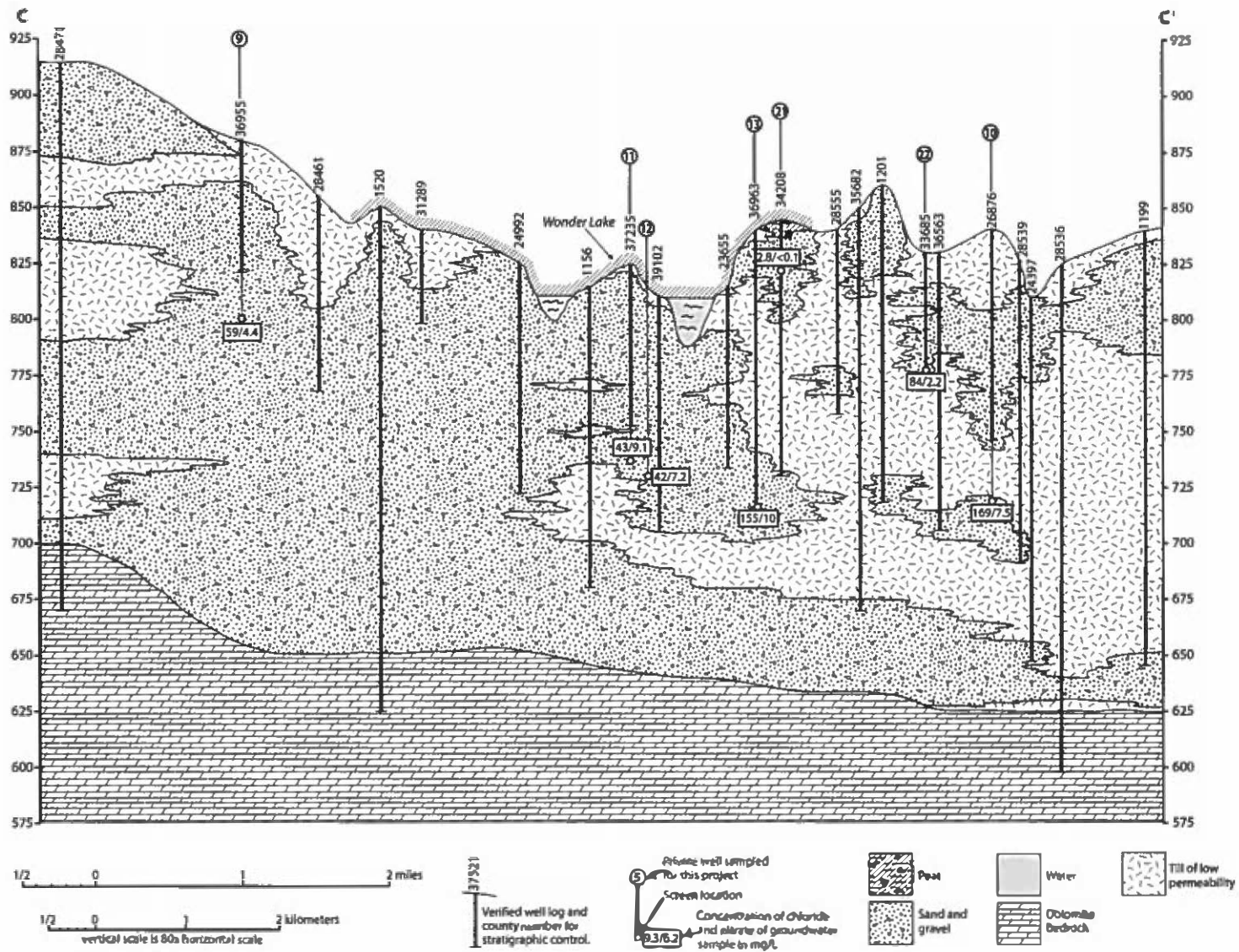


Figure 16. Cross section C-C' across rural areas and the town of Wonder Lake showing sand and gravel aquifers exposed at the surface in some areas and protected by finer, clay-rich glacial till in other areas.

chloride concentrations not exceeding 43 mg/L and nitrate concentrations as large as 49 mg/L. However, because the cross sections are two-dimensional depictions of the stratigraphy, it is possible that a well penetrating what appears to be a well-protected aquifer in a cross section could be part of a body of sand and gravel that extends to the surface only a short distance away.

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