ground water

Case Study/

Long-Term Trends in Chloride Concentrations in Shallow Aquifers near Chicago

by Walton R. Kelly

Abstract

The rapid expansion of major cities throughout the world is resulting in the degradation of water quality in local aquifers. Increased use of road deicers since the middle of the 20th century in cities in the northern United States, Canada, and Europe has been linked to degraded ground water quality. In this article, Chicago, Illinois, and its outlying suburban areas are used as an example of the effects of urbanization in a historical context. A statistical study of historical water quality data was undertaken to determine how urbanization activities have affected shallow (<60 m) ground water quality. Chloride (Cl^-) concentrations have been increasing, particularly in counties west and south of Chicago. In the majority of shallow public supply wells in the western and southern counties, Cl^- concentrations have been increasing since the 1960s. About 43% of the wells in these counties have rate increases greater than 1 mg/L/year, and 15% have increases greater than 4 mg/L/year. Approximately 24% of the samples collected from public supply wells in the Chicago area in the 1990s had Cl^- concentrations greater than 100 mg/L (35% in the western and southern counties); median values were less than 10 mg/L before 1960. The greater increase in Cl^- concentrations in the outer counties is most likely due to both natural and anthropogenic factors, including the presence of more significant and shallower sand and gravel deposits, less curbing of major highways and streets, and less development in some parts of these counties.

Introduction

Rapid urbanization is occurring in many major metropolitan areas throughout the world, and this can be a serious stress on water resources (Jenerette and Larsen 2006; Villholth 2007). Increased water demand can put a strain on limited water sources, and many urban activities can degrade water quality. Urbanization has long been recognized as a threat to shallow ground water quality (e.g., Long and Saleem 1974; Eisen and Anderson 1979; Eckhardt and Stackelberg 1995; Bruce and McMahon 1996; Murray et al. 2004). Contamination is often linked to land-use changes and the presence of numerous pollutant sources such as landfills, sewage treatment plants, industrial effluents, septic systems, gasoline storage tanks, road runoff, and so forth. The list of potential contaminants is extensive, including various organic classes (e.g., petroleum compounds, solvents, and pesticides), toxic metals, mercury, chloride (Cl^-), sulfate (SO_4^{2-}), nitrogen (nitrate, ammonium), and total dissolved solids.

Chloride is a particularly useful indicator of aquifer contamination. Although not a primary threat to human health, elevated concentrations of Cl^- make water nonpotable and thus there is a secondary drinking water standard of 250 mg/L. Chloride is a common contaminant that behaves conservatively in the environment and has numerous sources in urban areas. Increases in Cl^- concentrations in urban areas are generally the result of anthropogenic inputs, usually road salt runoff, sewage effluent, or brine waste disposal. Road salt has been linked to ground water degradation in many urban and roadside areas in snowy climes (Huling and Hollocher 1972; Pilon and Howard 1987; Amrhein et al. 1992; Howard and Haynes 1993, Williams et al. 2000; Bester et al. 2006). Significant application of road salt began after World War II and accelerated rapidly from the 1960s (Figure 1) (Salt Institute 2006). Once in ground water, Cl^- and other contaminants can persist for many years if travel times are slow. Howard et al. (1993) estimated that, even if road salting was

Center for Groundwater Science, Illinois State Water Survey, Champaign, IL 61820; (217) 333-3729; fax: (217) 244-0777; kelly@sws.uiuc.edu
Received November 2007, accepted April 2008.

doi: 10.1111/j.1745-6584.2008.00466.x

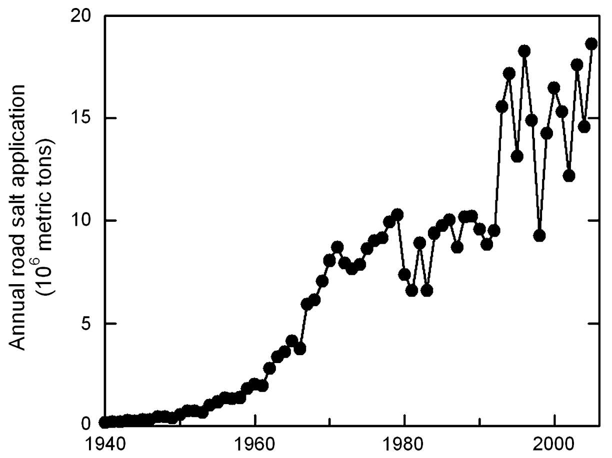

Figure 1. Annual road salt application in the United States (data from Salt Institute 2006).

stopped immediately in the Toronto area, it would be decades before the Cl^- concentrations returned to pre-1960 levels in shallow ground water.

In this investigation, the Chicago, Illinois, metropolitan area is used as an example of the effects of rapid urbanization on ground water quality. Like many other major cities in North America, the Chicago area is undergoing a rapid increase in population, increasing from about 5 million to nearly 8 million from 1950 to the present, and is projected to increase by 25% by 2020 (NIPC [Northeastern Illinois Planning Commission] 1999). Most of the growth is occurring in the outer counties to the west and south (DuPage, Kane, McHenry, and Will [Figure 2]), where the projected population increase is 70% to 100% by 2020 (NIPC 1999). The amount of developed land also has been expanding; residential acreage increased by 46% between 1970 and 1990 (NIPC 1996). The growth in population and development has placed a heavy demand on water resources. Water use has increased by more than 25% since 1980, and demand is expected to continue to grow as the population of the region increases (Kirk et al. 1982; Avery 1999). Because there are legal constraints on withdrawals by Illinois from Lake Michigan (capped at 3200 cubic feet per second [7.8 billion L/d] by the U.S. Supreme Court in 1967) and deep bedrock aquifers are estimated to be at or near their sustainable limits, shallow bedrock and overlying sand and gravel aquifers are expected to be the main sources of additional water to meet the increased demand. They are, however, vulnerable to surface contamination.

Unconsolidated aquifers of glacial origin are common in the north-central and northeastern parts of the conterminous United States and often exposed at the surface (USGS 1999). Ground water withdrawals from these states are about one-third of total public supply withdrawals, and ground water withdrawals are increasing (Hutson et al. 2004). Because these shallow aquifers will most likely be heavily used in the coming decades, it is important to determine if their water quality has been or is being degraded and to what extent. A baseline of information is necessary in the development of strategies to protect these aquifers. The purpose of this study was

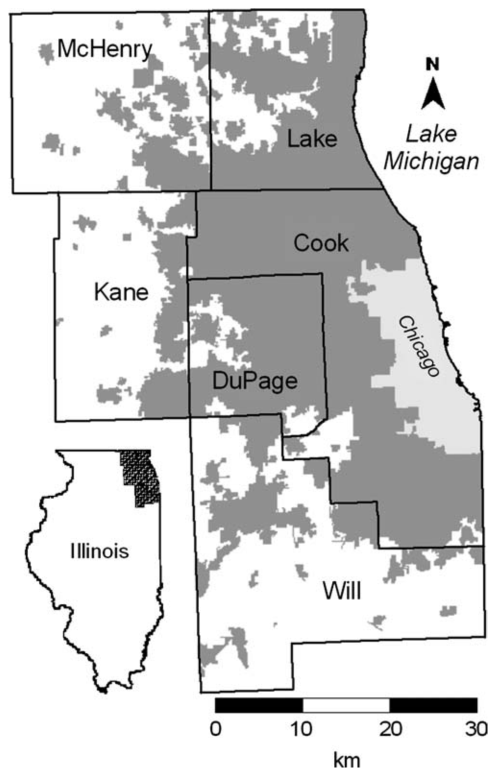

Figure 2. Chicago metropolitan area. Light gray area indicates Chicago city limits. Dark gray areas are incorporated municipalities.

twofold: (1) to determine temporal changes in ground water quality over the past several decades in the Chicago metropolitan area using historical ground water quality data and (2) to determine spatial variability in ground water quality, particularly as a function of urbanization activities. Chloride was used as the primary indicator of ground water quality.

Methods

Study Area

For the purposes of this study, the Chicago metropolitan area is considered to encompass six counties in northeastern Illinois: Cook, DuPage, Kane, Lake, McHenry, and Will (Figure 2). This is an area of approximately 9,580 km^2 (3,700 square miles) with a population of almost 8 million. We limited our evaluations to wells less than 60 m (200 feet) deep, which we assumed would encompass the wells most vulnerable to surface contamination.

The aquifers being evaluated are in shallow bedrock and overlying sand and gravel units. The shallow bedrock in northeastern Illinois is primarily Silurian, Devonian, and Pennsylvanian sedimentary rock, with the most productive aquifers being fractured Silurian dolomites. The surficial deposits belong to the Wedron Formation and consist of unconsolidated deposits of Wisconsinan-age glacial till and outwash ranging in thickness from less than 0.3 to more than 120 m (Willman and Frye 1970). The glacial deposits are thickest in northwestern McHenry County, but deposits in excess of 60 m are also found in central and eastern McHenry County, most of Lake County, northern Kane County, north-central DuPage County, and northwestern and west-central Cook County. The thinnest deposits generally are found in the central part of the study area, notably central DuPage and Cook Counties and northern and western Will County. Moderate to large supplies of ground water can be found in unconsolidated sands and gravels in the Wedron Formation. These units can be exposed at the surface or underlying or interbedded with till. The most productive water-producing units tend to be basal sand and gravel deposits, just above and in contact with shallow bedrock.

Ground water recharge rates in the Chicago area are not known with precision but are estimated to vary between 50 and 300 mm/year (Roadcap et al. 1993; Arnold et al. 2000). The highest rates are generally in the southern and northwestern parts of the study area. Assuming an average porosity of 0.3, ground water flow rates based on the reported recharge rates vary between 0.17 and 1.0 m/year. Estimation of recharge is complicated by the fact that urban areas are generally considered to increase ground water recharge due to leaking water mains and storm water and sewer pipes (Sharp et al. 2003). Recharge from water mains would have high quality (drinking water), while storm and sewer water would tend to have poor quality. Chicago has been replacing old water mains at the rate of 80 km/year (out of a total of 6700 km) and is in the midst of a massive engineering project (generally known as "deep tunnel") to divert storm water and sewage into temporary underground storage reservoirs during large rain or snowmelt events, replacing many of the old combined sewer pipes. The replacement of old water mains between 1990 and 2001 was estimated to have reduced water losses by about 450 million L/d (City of Chicago 2003).

Historical Data Sources for Temporal Variability Analysis

A difficulty in determining temporal changes in ground water quality is the lack of long-term chemical data and thus an understanding of how water quality has changed or is changing. Because of this, the literature on long-term temporal variations in ground water quality is limited, especially in urban areas (Long and Saleem 1974; Gibb and O'Hearn 1980; Hull 1984; Montgomery et al. 1987; Yee and Souza 1987; Spruill 1990; Broers and van der Grift 2004; Drake and Bauder 2005).

Ground water quality data evaluated in this study come primarily from a ground water chemistry data base maintained by the Illinois State Water Survey (ISWS). It contains results from approximately 50,000 ground water samples from more than 25,000 wells in Illinois dating back to the late 1890s. At the time of this study, there were more than 2100 samples from private wells and more than 2500 samples from approximately 1000 public wells less than 60 m deep in the six-county area, dating from 1906 to 2005.

While Cl^- was the primary focus of this study, the other major ions (calcium [Ca], magnesium [Mg], sodium [Na], SO_4^{2-}, and bicarbonate [HCO_3^-]) and dissolved solids were also considered with respect to evaluating data quality. A complete discussion of these other major ions is found in Kelly and Wilson (2008). Complete analyses (i.e., having data for all major ions) from the data bases were evaluated using an ion balance; a percent error greater than 10% was assumed to indicate an analytical or reporting error, and the result was not considered in statistical analyses.

Chloride data were divided into six time periods for analysis: before 1950, 1950s, 1960s, 1970s, 1980s, and 1990 to 2005. When the data were subdivided by well type and depth (see subsequently), the data from the 1950s and 1960s were combined because of the relatively small number of samples from those decades. Wells were divided into two groups based on well type for additional analysis, public supply and private, primarily because public supply wells are much more likely to have been sampled multiple times. In addition, public supply wells tend to have much longer well screens than private wells and are pumped at much greater rates, and thus their water quality tends to be more representative of an aquifer as a whole because ground water from discrete intervals is often blended. Wells were also subdivided by depth, less than 30 m and between 30 and 60 m. For wells that had multiple samples from a single year, the arithmetic mean of concentrations for that particular year was used so that repeat analyses from a single year would not have an undue influence on the analyses.

The effects of geological and land-use data on Cl^- concentrations in the shallow aquifers were evaluated using well log data on file at the ISWS. Some well log information (i.e., casing length, screen location, and/or overlying till thickness) was available for 200 of 242 wells examined individually (see subsequently). All these wells had source aquifer information (shallow bedrock, unconsolidated sand and gravel, or both).

Statistical Analyses

Exploratory data analysis for both temporal and spatial data analysis included box-and-whisker plots, Kruskal-Wallis analysis of variance (ANOVA) on ranks, and Mann-Whitney rank sum tests (Helsel and Hirsch 2002). Dunn's method was used to determine whether differences between population pairs were significant when results from an ANOVA on ranks test indicated a significant difference. The spread of the data was measured by the interquartile range (IQR), the difference between the 75th and the 25th percentiles. Nonparametric analyses were used because the data generally were not normally distributed (tested using Kolmogorov-Smirnov test).

Trend analysis of data for individual public supply wells with multiple samples was done by determining the Kendall *S* statistic (Helsel and Hirsch 2002). The null hypothesis was that no trend existed, and a significance level (α) of 0.10 was used. When the number of samples exceeded 10, a large sample approximation was used (Helsel and Hirsch 2002).

In order to estimate rates of changes in Cl^- concentrations for individual wells, regressions were performed to determine the slope coefficient (β_1), which for these data gives the change in concentration in milligrams per liter per year. Although regressions are parametric tests and thus not robust for data that are not normally distributed, β_1 can be tested using the *t*-ratio test statistic, with the null hypothesis being $\beta_1 = 0$ (Helsel and Hirsch 2002). Both individual wells with multiple samples and samples on a countywide basis were evaluated. For individual wells, the criteria for calculating β_1 was at least three samples over at least a 5-year period with the most recent sample in the 1980s or later. A total of 239 public supply wells and three private wells meeting these criteria were identified. The number of wells per county was Cook (29), DuPage (43), Kane (42), Lake (49), McHenry (53), and Will (26). For wells that had samples from before 1960, β_1 calculations were performed only on the post-1960 data. This was when significant road salting began in the Chicago area, and no changes in Cl^- concentrations were observed for these wells before 1960 (Kelly 2001).

Spatial Variability Analysis

Geospatial data such as till thickness, depth to aquifer, soil leachability, location of major roads, and so forth were downloaded from the Illinois Natural Resources Geospatial Data Clearinghouse (http://www.isgs.uiuc.edu/nsdihome/ISGSindex.html). The geological data are from Keefer (1995a, 1995b) and Berg and Kempton (1988). Chloride concentrations and trend data were plotted on these maps to observe potential relationships. Relationships were tested using ANOVA on ranks and rank sum tests. For analyses using concentrations, samples from between 1998 and 2004 from the ISWS data base were used. For the wells analyzed for trends that did not have samples from this period, concentrations for the year 2000 were calculated from β_1 values.

Data and Statistical Limitations

There are a number of limitations in evaluating these data that need to be noted. First, these are not random samples, primarily being either public supply wells required to be sampled or private wells sampled at the discretion of the well owner. Second, there is variability in location with time due to changes in population patterns and decisions regarding water sources. For example, before 1970, about 30% of the samples in the Chicago region came from wells in Cook County, but that number has been dropping as users have been going off ground water and using Lake Michigan water; between 1990 and 2005, only 8% of the samples came from Cook County. In contrast, the number of samples from Kane and McHenry Counties has been increasing as residential density has increased; the percentage of samples from these two counties combined has increased from about 25% to 45% over the study period.

An additional limitation is that public supply well sampling has varied over time due to changes in funding and switching to a more statistically random sampling scheme allowing for a decrease in the number of samples. Peak sampling frequency occurred during the late 1970s and early 1980s. The data groupings with the smallest number of samples are from the 1960 to 1969 time period and in the less than 30 m well depth group for the 1990 to 2005 period. Also, the identity of the wells in each group is not necessarily the same. Many of the wells sampled in the 1980s were not sampled in the 1990s. Thus, the analyses are not as rigorous as they would be if the same wells were being compared over the entire period.

Results and Discussion

Bulk Data

When examining all the available data for the Chicago area, the median Cl^- concentration steadily increased from 6 mg/L before 1950 to almost 20 mg/L in samples from 1990 to 2005, and each time period had significantly greater concentrations than the previous time period except for the 1990 to 2005 group compared to the 1980s. When the data are separated based on well depth, the trends for Cl^- were generally the same for both the shallower (<30 m) and deeper (30 to 60 m) wells (Table 1). The median Cl^- concentration increased from 8 to 36 mg/L in the shallower wells and from 5 to 17 mg/L in the deeper wells. The spread in Cl^- concentrations (as indicated by IQR in Table 1) also has been increasing, indicating spatial variability in the sources of contamination. Chloride concentrations were greater in the shallower wells compared to the deeper ones for all date groupings, and the differences were always statistically significant. Chloride also tended to have more spread in the shallower wells (Table 1).

Spatial variability in Cl^- concentrations was observed when the data were separated based on location (county), with the largest increases occurring in the western and southern counties (Figure 3). Chloride concentrations increased significantly with each consecutive data group for DuPage County, increased in McHenry and Will Counties starting in the 1970s, and increased in Kane County starting in the 1980s. The increase in Cl^- concentrations was not significant in Cook County until the last data set, and there were no significant changes in Lake County.

Considered separately, the public supply well data generally showed trends identical to those of the full data

Table 1
Median and IQR Values (mg/L) for Cl^- for Complete Data Set as a Function of Time and Well Depth

Depth (m)	Dates	Cl^- *N*	Median	IQR
<30	<1950	236	8.0	13
	1950–1960s	138	9.0	14
	1970s	223	22.0	37
	1980s	142	36.0	46
	1990–2005	110	35.7	95
30–60	<1950	526	5.0	10
	1950–1960s	451	7.0	12
	1970s	773	9.0	19
	1980s	603	12.0	36
	1990–2005	509	16.9	56

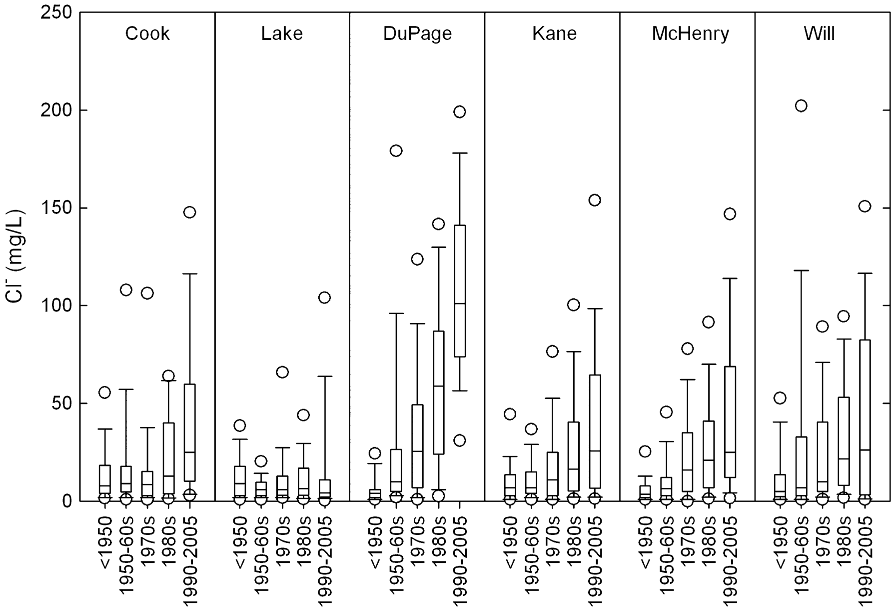

Figure 3. Box-and-whisker plots for Cl^- concentrations in shallow aquifers based on county. The boxes show the median, 25th, and 75th percentile values; the whiskers show the 10th and 90th percentile values; and the points show the 5th and 95th percentile values.

set, although the increase in Cl^- was more rapid. The percentage of samples from public supply wells with elevated Cl^- concentrations has been increasing with time (Table 2). Before 1970, about 80% of the samples (70% for wells less than 30 m) had Cl^- concentrations less than 15 mg/L, which Panno et al. (2006) determined to be the high end for background Cl^- concentrations in shallow ground water in Illinois, and only about 3% and 1% had concentrations greater than 50 and 100 mg/L, respectively. Since then, the number of possible "background" samples has decreased and those with very high concentrations have been increasing. For the 1990 to 2005 data, 37% of the samples had concentrations less than 15 mg/L (16% for wells <30 m) and 38% and 14% had concentrations exceeding 50 and 100 mg/L, respectively. In the shallower wells, the percentages of public supply well samples exceeding 50 and 100 mg/L were 66% and 34%, respectively.

Individual Wells

Graphical representations of Cl^- concentrations as a function of time are presented in Figure 4 for some of

Table 2
Chloride Concentrations in Public Supply Wells as a Function of Time Showing Median and IQR Values (mg/L) and Fractions of Samples Less Than 15 mg/L and Exceeding 50 or 100 mg/L

	N	Median	IQR	<15 mg/L	≥50 mg/L	≥100 mg/L
<30 m						
<1950	52	10	10	0.69	0.02	0.00
1950–1960s	68	10	13	0.71	0.03	0.00
1970s	139	24	37	0.36	0.19	0.04
1980s	127	39	47	0.16	0.39	0.11
1990–2005	44	87	94	0.16	0.66	0.34
30–60 m						
<1950	116	4	5	0.95	0.00	0.00
1950–1960s	188	6	7	0.82	0.03	0.01
1970s	538	8	19	0.66	0.11	0.02
1980s	549	12	35	0.53	0.22	0.05
1990–2005	333	25	56	0.40	0.34	0.12
All						
<1950	168	6	7	0.87	0.01	0.00
1950–1960s	256	7	9	0.79	0.03	0.01
1970s	677	10	24	0.60	0.13	0.03
1980s	684	17	43	0.46	0.25	0.06
1990–2005	377	29	64	0.37	0.38	0.14

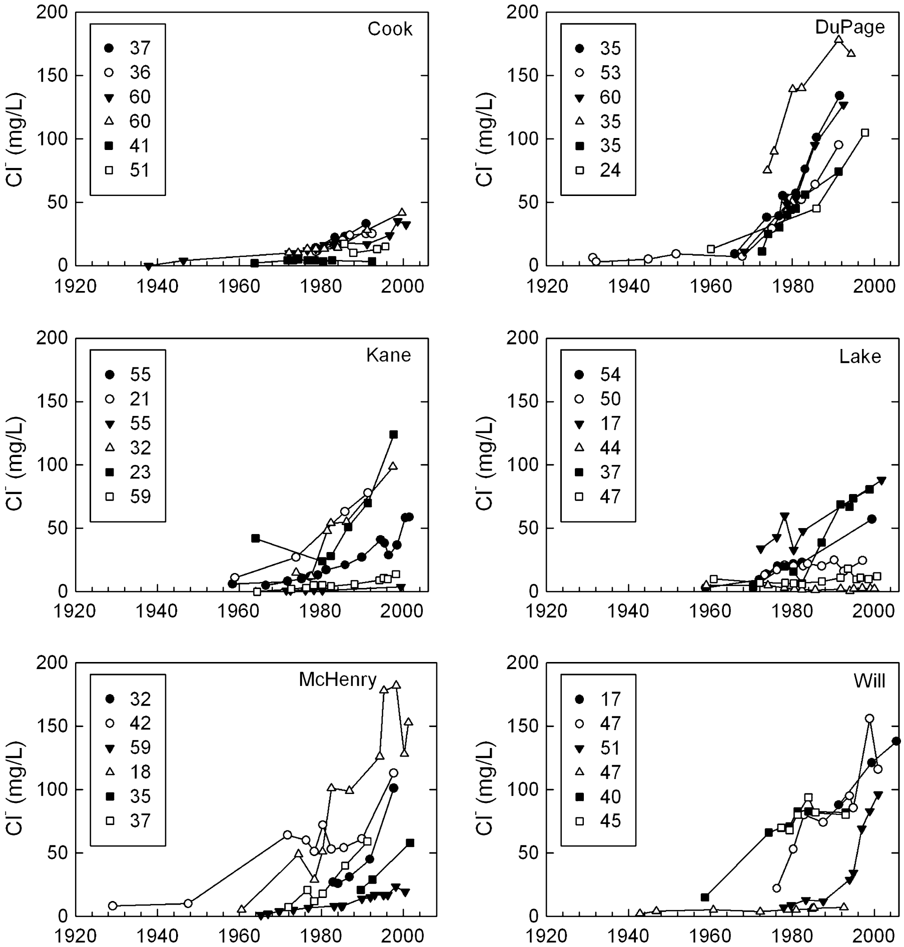

Figure 4. Chloride concentrations as a function of time for some public supply wells in the six counties in the Chicago area. Well depths (m) are given in legends.

the public supply wells having multiple samples. There were significant temporal increases in Cl^- concentrations for the majority of the wells (55%), based on the Kendall's tau statistic (Table 3). Fewer than 3% had decreasing trends. Lake County had the lowest percentage of wells with increasing Cl^- trends (39%) and Kane County had the highest (71%).

Significant positive slope values (β_1) for Cl^- were calculated for 57% of the wells (4% had significant negative slopes), with 37% having values greater than 1 mg/L/year and 12% with values greater than 4 mg/L/year. DuPage, Kane, and McHenry Counties had the highest percentages of wells with positive slope values (62% to 70%) and Lake County had the lowest (39%). DuPage County had by far the largest percentage of wells with slope values greater than 1 and 4 mg/L/year and Lake County had the lowest percentages (Table 3). DuPage County had significantly greater slope values than Lake and Cook Counties, and McHenry had significantly greater values than Lake County. It should be noted that the percentages reported in Table 3 apply only to the data set and cannot be used to draw conclusions for the entire population of wells in each county.

Almost half (113 of 242) of the wells had at least one sample collected in the 1990s or 2000s, with the latest date available in 2005. There was basically no difference between the wells with the most recent data compared to the entire group of wells for Cl^-; 59% had significant positive slopes (vs. 57%), 40% had values greater than 1 mg/L/year (vs. 37%), and 12% had values greater than 4 mg/L/year (vs. 12%). This suggests that there has not been a leveling off in Cl^- concentrations in the 1990s or later.

Changes in Cl^- concentrations for wells with significant slope values were plotted vs. well depth (Figure 5a). The shallowest wells (<30 m) had significantly greater slope values (median 3.0 mg/L/year) compared to deeper wells (median 1.2 mg/L/year), but even some of the deepest wells (60 m) had large increases in Cl^- concentrations. There were no significant differences based on source aquifer (shallow bedrock vs. unconsolidated), although the shallow bedrock wells were significantly deeper (median depth 50 m) than the unconsolidated wells (median depth 38 m). For the 128 wells with significant slopes and information on till thickness, changes in Cl^- concentration vs. overlying till thickness were also plotted (Figure 5b). It was hypothesized that the greater the till thickness overlying the source aquifer, the lower the slope values. There was a significant difference when comparing wells with relatively thin till deposits (<30 m), which had a median slope value of 2.3 mg/L/year, with thick till deposits (>30 m; median 0.83 mg/L/year).

Table 3				
Fractions of Individual Wells with Multiple Samples Having Significant Positive Trends and Slope Values for Cl^-				
County	**Significant Positive Trend**	**Significant Positive Slope**	**>1 mg/L/year**	**>4 mg/L/year**
Cook	0.45	0.48	0.31	0.07
DuPage	0.60	0.70	0.63	0.28
Kane	0.71	0.62	0.36	0.05
Lake	0.39	0.39	0.22	0.04
McHenry	0.55	0.62	0.38	0.15
Will	0.62	0.54	0.31	0.08
Total	0.55	0.57	0.37	0.12

Note: Significant trends are determined by the Kendall tau statistic, and significant slopes are determined by the *t* statistic for samples collected after 1960.

Sources of Chloride

It is clear that Cl^- concentrations have been increasing in the shallow ground water in the Chicago area and that the increase started around 1960. From a volume standpoint, road salt is the largest potential source of Cl^- in the Chicago region, and 1960 was when it began being applied in large volumes. Because of the large numbers of counties and municipalities, it is difficult to make a precise determination of the amount of road salt applied annually. In an average winter, the Illinois Department of Transportation uses about 130,000 metric tons of road salt in the six-county region, with counties and municipalities applying approximately the same amount (Keseley 2006). There are more than 55,000 lane miles (88,000 km) in the Chicago region, and because of the high density of roads, most wells are located in the vicinity of major roads; of the 242 individual wells examined, 209 were located within 1 mile (1.6 km) of an interstate highway or major arterial road. There were no statistically significant differences in rates of change of Cl^- or for Cl^- concentrations in 1998 to 2004 between those wells close to (<1.6 km) and those far away (>1.6 km) from major roads. Median rate and concentration values, however, were considerably lower for wells far away from roads in Lake, McHenry, and Will Counties. For example, the median Cl^- concentration in five wells in Will County far away from major roads was 25.0 mg/L compared to 46.9 mg/L in the 21 wells close to major roads. Median Cl^- concentrations were higher in wells far away from roads in Cook County, approximately the same in Kane County, while all the wells in DuPage County were within 1.6 km of major roads.

Septic systems are another potentially important source of Cl^- to shallow ground water. Approximately 95% of households in the Chicago region were on public sewers in 1990, ranging from 57% in McHenry County to 99% in Cook County; the largest number of septic systems were in Lake County (28,855) and the fewest in Kane County (17,505) (U.S. Census Bureau 1993). Assuming that each household with a septic system has a water softener and uses the typical manufacturer's recommended amount of NaCl (~2.3 kg/d), there is a maximum of about 127,000 metric tons of halite potentially available to enter the subsurface environment, less than half of the amount of road salt applied. In practice, the water quality in the shallow aquifers is often sufficiently soft so that softeners are not necessary.

Other potential Cl^- sources are probably minor, at least in a regional sense. Landfill leachates often have elevated levels of Cl^- but are point sources covering relatively small areas. The largest concentration of landfills is found in heavily industrialized South Chicago. Fertilizer (KCl) does not appear to be a significant source of Cl^- to ground water; concentrations in shallow ground water in

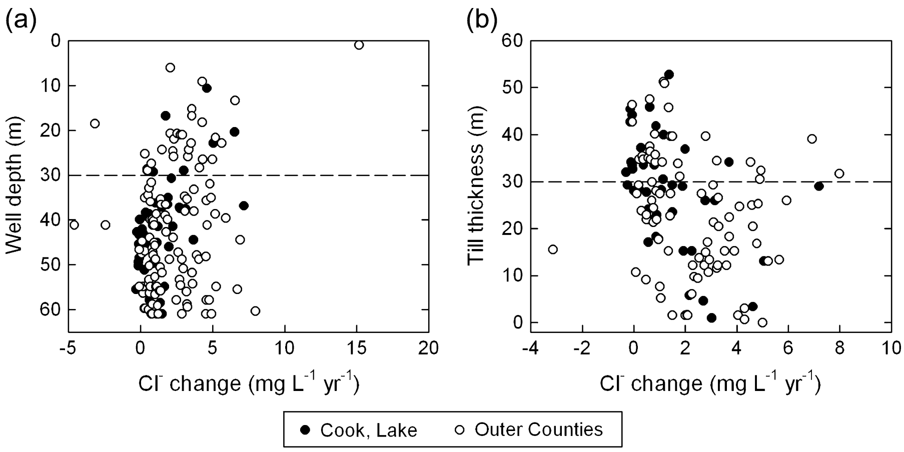

Figure 5. Change in Cl^- concentrations based on β_1 values as a function of (a) well depth and (b) overlying till thickness.

predominantly agricultural areas of Illinois rarely exceed 20 mg/L. Leakage from storm water and sewage pipes is a diminishing issue, because construction of new pipes and tunnels has been increasing. If leaky sewage pipes were a major source of Cl^- to ground water, then one would expect to have seen elevated concentrations in Cook and Lake Counties in the past.

There are additional lines of evidence suggesting that road salt is the major source of Cl^- to ground water in the Chicago region. Roadcap and Kelly (1994) measured Cl^- concentrations in excess of 1000 mg/L in several shallow monitoring wells installed along the uncurbed Interstate 94 in South Chicago, including two exceeding 3500 mg/L. Using various diagnostic techniques, Panno et al. (2006) determined that elevated Cl^- concentrations in 13 shallow wells in McHenry County, the county with the highest percentage of septic systems, were due to road salt runoff. Chloride concentrations have also been increasing in the Illinois River waterway (which includes the Des Plaines River and the Sanitary & Ship Canal in Chicago) since the 1950s. The highest concentrations and most rapid increases have been occurring in the winter and early spring months, suggesting road salt runoff; septic discharge would not be expected to have seasonal variability (Panno et al. unpublished data).

Spatial Variability

There appears to be a geographical influence on Cl^- concentrations and the rate of change, with the western and southern counties generally having the greatest concentrations and increases. This most likely reflects the rapid changes in land use occurring in these outer counties. On the other hand, wells in unincorporated areas or towns in the counties away from the Chicago megalopolis tended to have low Cl^- concentrations and small or insignificant trends. Figure 6a shows Cl^- concentrations from 1998 to 2004 plotted with municipalities. Cook and Lake Counties have been urban and residential areas for much longer than the western and southern counties, and many of the major roads are curbed. Curbing diverts runoff into storm water sewers, which limits the recharge of contaminated surface water to ground water. Chloride concentrations in Lake County tend to be very low, with a median of 4.2 mg/L and a 75th percentile value of 11 mg/L for samples collected from 1990 and later. The median Cl^- value for these most recent samples for DuPage County was 101 mg/L and for the other four counties was between 25 and 26 mg/L. Note that most of the wells analyzed in Cook County were from the extreme northwestern part of the county, which may make them more akin to wells in DuPage County (Figure 6a). There is less curbing in the western and southern counties, and thus more contaminated runoff can recharge the shallow aquifers. About 10% of roadways in Will County and 6.5% of county road miles in Kane County are curbed (P. Killinger and P. Holcomb, personal communication, 2007), while in DuPage County, which is more urbanized, more than 60% of roadways are curbed (M. Cotten, personal communication, 2007). Cook and Lake Counties undoubtedly have curbing percentages higher than DuPage County. To further test this hypothesis, more detailed data on road curbing would be necessary; it is not currently available in geographical information systems (GIS) coverages.

An alternative explanation for the greater increase in Cl^- concentrations in the western and southern counties is that unconsolidated sand and gravel deposits are generally thicker and closer to the surface, especially in McHenry and Kane Counties (Hansel and Johnson 1996). Areas where aquifer material (usually sand and gravel) is within 15 m (50 feet) of the surface in northeastern Illinois are plotted in Figure 6b. Wells with low Cl^- concentrations in

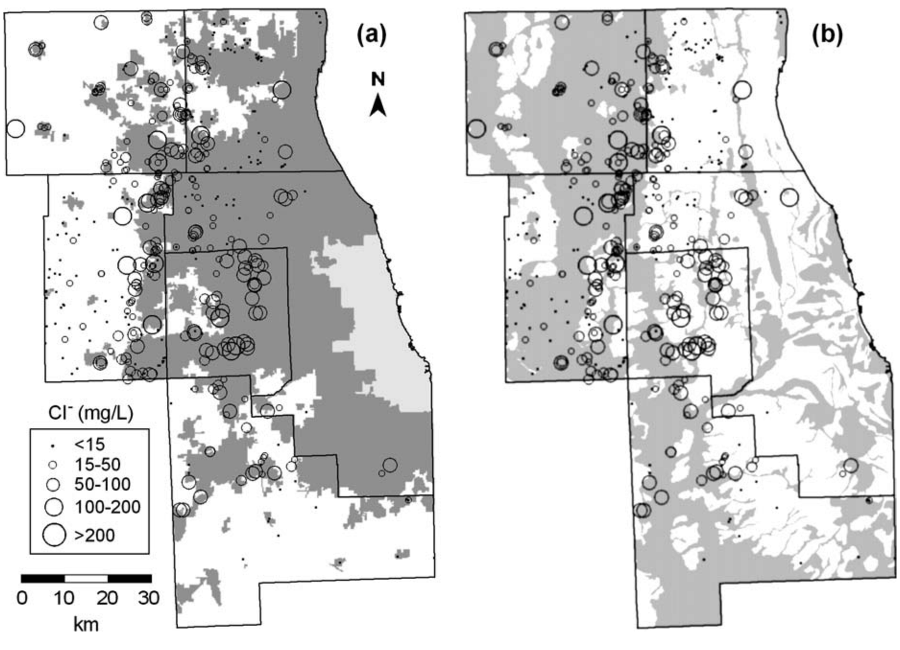

Figure 6. Chloride concentrations for samples from 1998 to 2004. (a) Gray areas show incorporated municipalities, and (b) gray areas show where aquifer material is < 15 m beneath land surface. For wells with no samples from 1998 to 2004, the concentration for the year 2000 was determined using the β_1 value.

Cook and Lake Counties are usually located where shallow aquifer material is not present within 15 m of the surface. Wells with the greatest Cl^- concentrations (and rates of change) are often found in areas where aquifers are within 15 m of the surface, although there were no consistent statistically significant differences (there were also no significant differences based on soil leachability). In fact, when looking at the data from the four western and southern counties together, there were actually significantly greater Cl^- concentrations and rates of change in areas where there was no aquifer material within 15 m of the surface. This is probably due to DuPage County, which has a relatively small area with shallow aquifers and many wells with elevated Cl^- concentrations, and Kane County, which has shallow aquifers throughout most of the county but many wells with low Cl^- concentrations. It thus appears that the presence or absence of shallow aquifer material is not the sole control of Cl^- concentrations. In Kane and Will Counties, most of the wells with low Cl^- concentrations are in the western and southern sections, respectively, where there is less urban and suburban development (Figure 6a).

Conclusions

Urbanization can seriously degrade the ground water quality of shallow aquifers, particularly in snowy climes where deicers are heavily used. For these areas, patterns and trends in Cl^- concentrations are a useful way to evaluate shallow ground water quality in urban settings. Shallow ground water quality in the Chicago metropolitan area has degraded at least since the 1960s, as indicated by increasing levels of Cl^-. This is especially true in the western and southern counties (DuPage, Kane, McHenry, and Will), where there has been an increase in Cl^- concentrations in the majority of public supply wells since the 1960s. About 43% of the wells in these four counties have rate increases greater than 1 mg/L/year and 15% have increases greater than 4 mg/L/year. Approximately 24% of the samples collected from public supply wells in the Chicago area in the 1990s had Cl^- concentrations greater than 100 mg/L (35% in the western and southern counties); median values were less than 10 mg/L before 1960. Although there is the potential for septic discharge to cause increases in Cl^- concentrations in some parts of the study area, road salt is the dominant source of Cl^- to the shallow aquifers.

Based on trends in Cl^- concentrations, many areas in this region have not yet seen maximum concentrations. With recharge rates giving average ground water travel times of 0.2 to 1.0 m/year, the maximum distance traveled since 1960 for the bulk of recharge from the surface is less than 50 m. Clearly, there are areas where there have been significantly more rapid travel times, as evidenced by elevated concentrations in wells deeper than 50 m. However, even if all sources of pollution were stopped immediately, peak concentrations of surface-derived dissolved contaminants will almost surely be considerably higher in the future than they are now (e.g., Howard et al. 1993). A more detailed evaluation of the Cl^- data may help in estimating recharge rates to shallow aquifers.

There is an interplay between natural hydrogeology and human activities affecting the ground water quality in the Chicago region. There are more significant and shallower sand and gravel deposits in the western and southern counties, where a relatively greater increase in Cl^- concentrations is occurring, but shallow aquifers tend to have good quality in rural parts of these counties (Kelly 2005). Thus, land use, primarily in the form of road salting, is the major control on Cl^- concentrations in the western and southern counties. In Cook and Lake Counties, however, lower Cl^- concentrations and rates of change cannot be attributed to lower rates of road salt application. The hydrogeological conditions (i.e., generally thicker till deposits and deeper aquifers) would be expected to offer better aquifer protection, but similar hydrogeologic conditions in DuPage County have not protected shallow aquifers there. It appears that because most roadways in Cook and Lake Counties are curbed, saline runoff is being channeled to storm water retention and not recharging aquifers. Results from Roadcap and Kelly (1994) indicate that where curbing is absent in the city of Chicago, Cl^- concentrations in shallow ground water can reach extremely high levels (>3500 mg/L). This is an important point, because recently there has developed a consensus among water resource managers that a goal of storm water management should be to maximize infiltration vis-a-vis runoff. If the quality of the recharge to ground water is poor, then fixing one problem (storm water runoff) may produce another (decreasing ground water quality).

Acknowledgments

Thanks to Steve Wilson, Jon Foote, Susan Chi, and Katie Askren for updating and improving the data bases and to Rick Cobb at Illinois Environmental Protection Agency (IEPA). Reviews by Steve Wilson, Doug Walker, Sam Panno, Adam Martinsek, Al Wehrmann, Derek Winstanley, Margaret Townsend, and Kristine Uhlman greatly improved the manuscript. This research was supported with funds from the Illinois Groundwater Consortium. Publication of this article has been authorized by the Chief of the ISWS.

References

Amrhein, C., J.E. Strong, and P.A. Mosher. 1992. Effect of deicing salts on metal and organic matter mobilization in roadside soils. *Environmental Science & Technology* 26, no. 4: 703–709.

Arnold, J.G., R.S. Muttiah, R. Srinivasan, and P.M. Allen. 2000. Regional estimation of base flow and groundwater recharge in the Upper Mississippi river basin. *Journal of Hydrology* 227, no. 1–4: 21–40.

Avery, C. 1999. Estimated water withdrawals and use in Illinois, 1992. USGS Open-File Report 99-97. Reston, Virginia: USGS.

Berg, R.C., and J.P. Kempton. 1988. Stack-unit mapping of geologic materials in Illinois to a depth of 15 meters. Illinois State Geological Survey Circular 542. Champaign, Illinois: Illinois State Geological Survey.

Bester, M.L., E.O. Frind, J.W. Molson, and D.L. Rudolph. 2006. Numerical investigation of road salt impact on an urban wellfield. *Ground Water* 44, no. 2: 165–175.

Broers, H.P., and B. van der Grift. 2004. Regional monitoring of temporal changes in groundwater quality. *Journal of Hydrology* 296, no. 1–4: 192–220.

Bruce, B.W., and P.B. McMahon. 1996. Shallow ground-water quality beneath a major urban center: Denver, Colorado, USA. *Journal of Hydrology* 186, no. 1–4: 129–151.

City of Chicago. 2003. Chicago's Water Agenda 2003. http://egov.cityofchicago.org/webportal/COCWebPortal/COC_ATTACH/wateragenda.pdf (accessed April 9, 2008).

Cotten, M. 2007. E-mail response, March 6, Wheaton, Illinois.

Drake, V.M., and J.W. Bauder. 2005. Ground water nitrate-nitrogen trends in relation to urban development, Helena, Montana, 1971-2003. *Ground Water Monitoring Review* 25, no. 2: 118–130.

Eckhardt, D.A.V., and P.E. Stackelberg. 1995. Relation of groundwater quality to land-use on Long Island, New York. *Ground Water* 33, no. 6: 1019–1033.

Eisen, C., and M.P. Anderson. 1979. The effects of urbanization on ground-water quality—A case study. *Ground Water* 17, no. 5: 456–462.

Gibb, J.P., and M. O'Hearn. 1980. Illinois groundwater quality data summary. Illinois State Water Survey Contract Report 230. Urbana, Illinois: Illinois State Water Survey.

Hansel, A.K., and W.H. Johnson. 1996. Wedron and Mason Groups: Lithostratigraphic reclassification of deposits of the Wisconsin Episode, Lake Michigan lobe area. Illinois State Geological Survey Bulletin 104. Champaign, Illinois: Illinois State Geological Survey.

Helsel, D.R., and R.M. Hirsch. 2002. *Techniques of Water-Resources Investigations of the United States Geological Survey. Book 4, Hydrologic Analysis and Interpretation, Chapter A3: Statistical Methods in Water Resources*. Reston, Virginia: USGS. http://water.usgs.gov/pubs/twri/twri4a3/ (accessed April 9, 2008).

Holcomb, P. 2007. E-mail response, March 8, St. Charles, Illinois.

Howard, K.W.F., J.I. Boyce, S.J. Livingstone, and S.L. Salvatori. 1993. Road salt impacts on ground-water quality—The worst is still to come! *GSA Today* 3, no. 12: 301–321.

Howard, K.W.F., and J. Haynes. 1993. Groundwater contamination due to road de-icing chemicals—Salt balance implications. *Geoscience Canada* 20, no. 1: 1–8.

Huling, E.E., and T.C. Hollocher. 1972. Groundwater contamination by road salt: Steady-state concentrations in East Central Massachusetts. *Science* 176, no. 4032: 288–290.

Hull, L.C. 1984. Geochemistry of ground water in the Sacramento Valley, California. USGS Professional Paper 1401-B. Reston, Virginia: USGS.

Hutson, S.S., N.L. Barber, J.F. Kenny, K.S. Linsey, D.S. Lumia, and M.A. Maupin. 2004. Estimated use of water in the United States in 2000. USGS Circular 1268. Reston, Virginia: USGS.

Jenerette, G.D., and L. Larsen. 2006. A global perspective on changing sustainable urban water supplies. *Global Planetary Change* 50, no. 3–4: 202–211.

Keefer, D.A. 1995a. Potential for agricultural chemical contamination of aquifers in Illinois: 1995 revision. Illinois State Geological Survey Environmental Geology 148. Champaign, Illinois: Illinois State Geological Survey.

Keefer, D.A. 1995b. Nitrate leaching classes for Illinois soils. Statewide map, 1:500,000. Illinois State Geological Survey Open File Series 1995-2. Champaign, Illinois: Illinois State Geological Survey.

Kelly, W.R. 2005. Shallow groundwater quality sampling in Kane County: October 2003. Illinois State Water Survey Contract Report 2005-07. Champaign, Illinois: Illinois State Water Survey.

Kelly, W.R. 2001. Temporal changes in shallow ground-water quality in Northeastern Illinois: Preliminary results. In *Research on Agricultural Chemicals in Illinois Groundwater: Status and Future Directions XI, Proceedings of the Eighth Annual Illinois Groundwater Consortium Conference, Makanda, IL, April 9, 2001*. http://www.siu.edu/worda/igc/proceedings/ (accessed April 9, 2008).

Kelly, W.R., and S.D. Wilson. 2008. Temporal changes in shallow groundwater quality in northeastern Illinois. Illinois State Survey Scientific Report 2008-01. Champaign, Illinois: Illinois State Water Survey.

Keseley, S. 2006. Road salt is a slippery subject. *Lake County Health Department and Community Health Center Cattail Chronicles* 16, no. 1: 4–5. http://www.co.lake.il.us/elibrary/newsletters/cattail/2007/fall2006.pdf (accessed April 9, 2008).

Killinger, P. 2007. E-mail response, March 8, Joliet, Illinois.

Kirk, J.R., J. Jarboe, E.W. Sanderson, R.T. Sasman, and C. Lonnquist. 1982. Water withdrawals in Illinois, 1980. Illinois State Water Survey Circular 152. Champaign, Illinois: Illinois State Water Survey.

Long, D.T., and Z.A. Saleem. 1974. Hydrogeochemistry of carbonate groundwaters of an urban area. *Water Resources Research* 10, no. 6: 1229–1238.

Montgomery, R.H., J.C. Loftis, and J. Harris. 1987. Statistical characteristics of ground-water quality variables. *Ground Water* 25, no. 2: 176–184.

Murray, K.S., D.T. Rogers, and M.M. Kaufman. 2004. Heavy metals in an urban watershed in southeastern Michigan. *Journal of Environmental Quality* 33, no. 1: 163–172.

NIPC. 1999. NIPC identifies critical water resource issues facing the region. NIPC Bulletin, September. Chicago, Illinois: Northeastern Illinois Planning Commission.

NIPC. 1996. Strategic Plan for Land Resource Management (adopted June 18, 1992). Chicago, Illinois: Northeastern Illinois Planning Commission.

Panno, S.V., K.C. Hackley, H.H. Hwang, S.E. Greenberg, I.G. Krapac, S. Landsberger, and D.J. O'Kelly. 2006. Source identification of sodium and chloride in natural waters: Preliminary results. *Ground Water* 44, no. 2: 176–187.

Pilon, P.E., and K.W.F. Howard. 1987. Contamination of subsurface waters by road de-icing chemicals. *Water Pollution Research Journal of Canada* 22, no. 1: 157–171.

Roadcap, G.S., S.J. Cravens, and E.C. Smith. 1993. Meeting the growing demand for water: An evaluation of the shallow ground-water resources in Will and Southern Cook Counties, Illinois. Illinois State Water Survey Research Report 123. Champaign, Illinois: Illinois State Water Survey.

Roadcap, G.S., and W.R. Kelly. 1994. Shallow ground-water quality and hydrogeology of the Lake Calumet area, Chicago, Illinois. Illinois State Water Survey Interim Report. Champaign, Illinois: Illinois State Water Survey.

Salt Institute. 2006. Salt Institute Web site. http://www.saltinstitute.org/ (accessed April 9, 2008).

Sharp, J.M. Jr., J. Krothe, J.D. Mather, B. Garcia-Fresca, and C.A. Stewart. 2003. Effects of urbanization on groundwater systems. In *Earth Sciences in the City*, ed. G. Heiken, R. Fakundiny, and J. Suter, 257–278. Washington, D.C.: American Geophysical Union.

Spruill, T.B. 1990. Monitoring regional ground-water quality—Statistical considerations and description of a monitoring network in Kansas. USGS Water-Resources Investigations Report 90-4159. Reston, Virginia: USGS.

U.S. Census Bureau. 1993. 1990 census of housing, detailed housing characteristics, Illinois, 1990 CH-2-15. http://www.census.gov/prod/cen1990/ch2/ch-2-15.pdf (accessed February 6, 2008).

USGS. 1999. *Ground Water Atlas of the United States. USGS Hydrologic Atlas 730*. http://capp.water.usgs.gov/gwa/gwa.html (accessed April 9, 2008).

Villholth, K. 2007. Groundwater assessment and management: Implications and opportunities of globalization. *Hydrogeology Journal* 14, no. 3: 330–339.

Williams, D.D., N.E. Williams, and Y. Cao. 2000. Road salt contamination of groundwater in a major metropolitan area and development of a biological index to monitor its impact. *Water Research* 34, no. 1: 127–138.

Willman, H.B., and J.C. Frye. 1970. Pleistocene stratigraphy of Illinois. Illinois State Geological Survey Bulletin 94. Urbana, Illinois: Illinois State Geological Survey.

Yee, J.J.S., and W.R. Souza. 1987. Quality of ground water in Idaho. USGS Water-Supply Paper 2272. Reston, Virginia: USGS.