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The Sources, Distribution, and Trends of Chloride in the Waters of Illinois

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Abstract

Chloride (Cl^-) is a major anion found in all natural waters. It occurs naturally and is also a relatively minor contaminant. Chloride concentrations in Illinois range from less than 0.1 milligrams per liter (mg/L) in precipitation to close to 100,000 mg/L in Paleozoic brines. Chloride is non-toxic to humans, although there is a secondary drinking water standard of 250 mg/L. It is, however, deleterious to some plants and aquatic biota, thus the Illinois Environmental Protection Agency (IEPA) has set an acute standard of 500 mg/L for surface waters in Illinois. Chloride is also a very corrosive agent, and elevated levels pose a threat to infrastructure, such as road beds, bridges, and industrial pipes.

Some streams and aquifers in Illinois have naturally elevated Cl^- concentrations due to surface or near-surface discharge of Paleozoic brines. Of greater concern to water resources in Illinois are anthropogenic sources of Cl^- , including road salt runoff, sewage, water conditioning salts, and fertilizer. Chloride concentrations are elevated in most water bodies in the Chicago region, primarily due to road salt runoff. Concentrations have been increasing since approximately the 1960s, and in general, concentrations continue to increase. These elevated Cl^- concentrations may pose a risk to infrastructure as well as aquatic to ecosystems.

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Introduction

Chloride (Cl^-) is a naturally occurring major anion found in all natural waters. Chloride behaves as a conservative ion in most aqueous environments, meaning its movement is not retarded by the interaction of water with soils, sediments, and rocks. As such, it can be used as an indicator of other types of contamination. Anomalously high concentrations can act as an “advance warning” of the presence of other more toxic contaminants. Concentrations of Cl^- in natural waters can range from less than 1 milligram per liter (mg/L) in rainfall and some freshwater aquifers to greater than 100,000 mg/L for very old groundwaters within deep intracratonic basins (Graf et al., 1966; Psenner, 1989). Its concentration in precipitation in mid-continental regions (far from oceans and other salt sources) is almost always less than 1 mg/L, and often less than 0.1 mg/L (NADP, 2011). Upon contacting land surface, Cl^- concentrations in water increase as a result of interaction with soils, rocks, and biota (waste products), as well as the effects of evaporation. Chloride is the most abundant ion in seawater, with a concentration greater than 19,000 mg/L (Stumm and Morgan, 1996). Extremely elevated levels of Cl^- in surface water are generally due to significant evaporation (e.g., the Dead Sea has a Cl^- concentration $> 230,000$ mg/L).

Chloride is non-toxic to humans, but elevated levels make water unpotable due to the salty taste. In the U.S., there is a secondary (non-enforced) drinking water standard of 250 mg/L, but in areas of the world with water scarcities, drinking water can have considerably greater concentrations of Cl^- . Chloride is corrosive to steel, thus it may corrode pipes in water treatment and industrial plants. Because it imparts a salty taste to water and is corrosive, elevated Cl^- levels in drinking water supplies can lead to increased treatment costs. Elevated Cl^- in surface water has been linked to damage of terrestrial and aquatic plants and aquatic animals at concentrations as low as 210 mg/L (Environment Canada, 2001; Hart et al., 1991; Kaushal et al., 2005; Wilcox, 1986). The U.S. Environmental Protection Agency (USEPA) recommends a chronic criterion for aquatic life of a four-day average Cl^- concentration of 230 mg/L with an occurrence interval of once every three years (USEPA, 1988). The recommended acute criterion is 860 mg/L, which relates to a one-hour average concentration with a recurrence interval of less than once every three years. The Illinois EPA (IEPA) uses an acute criterion of 500 mg/L, but there is no chronic standard. The government of British Columbia has proposed a lower maximum Cl^- concentration of 600 mg/L and a 30-day average concentration of 150 mg/L to protect freshwater life (Nagpal et al., 2003). Increased Cl^- concentrations in some environments have killed off native vegetation and allowed invasive salt-tolerant species to thrive (Panno et al., 1999).

The objective of this report is to characterize the sources, distribution, and trends of Cl^- in the waters of Illinois, including rainwater, lakes, rivers and streams, groundwater, and wetlands.

Acknowledgements

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Natural Sources of Chloride

Precipitation

Chloride in precipitation and dry deposition originates from marine aerosols or volcanic gases. Naturally-occurring Cl^- concentrations in rainwater and snowmelt can be several mg/L near the coastal regions of the U.S. due to the contribution of seawater aerosols (Figure 1). Chloride concentrations in mid-continental regions are much lower. Concentrations in Illinois are typically less than 0.1 mg/L (NADP, 2011).

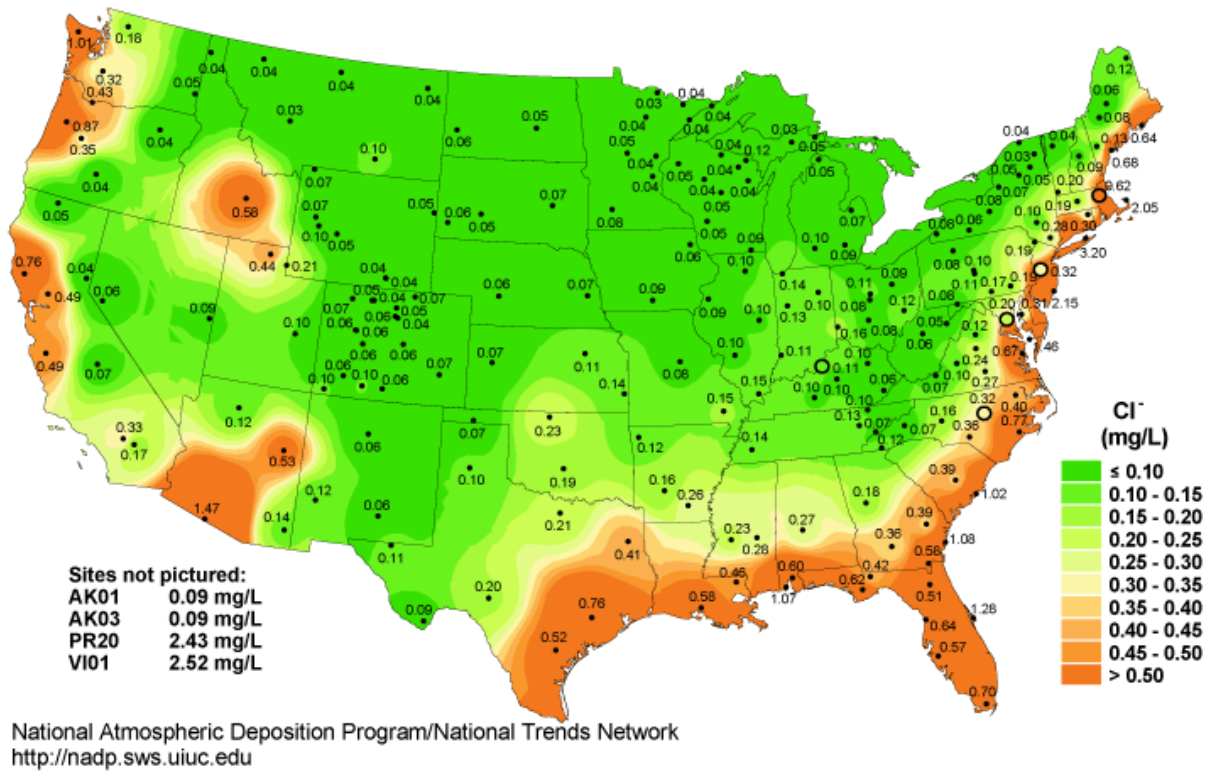


Figure 1. Chloride concentrations in U.S. precipitation for 2009. Map from NADP, 2011.

Rock-Water Interactions

Once rainwater and snow fall to the ground, evaporation and evapotranspiration tend to concentrate the Cl^- in soil water to levels ten or more times their original concentration. Rock-water interactions such as mineral dissolution and desorption within the soil zone and groundwater can further increase Cl^- concentrations.

The largest source of Cl^- in the Earth's crust is the mineral halite (NaCl) in evaporate deposits, which formed over geologic time by the evaporation of seawater. Chloride is also found in other less common salts (e.g., potassium chloride [KCl] and calcium chloride [CaCl_2]) associated with these evaporite deposits. Because halite and other chloride salts are extremely soluble, they are not found in areas where there is active circulation of fresh water. There are no known halite deposits in Illinois, although there is evidence from brecciated limestone that evaporates may have existed in the geologic past (Willman et al., 1975). Chloride is found in small amounts (1000 to 10,000 parts per million [ppm]) in some silicate and phosphate minerals, including biotite, amphibole, apatite, sodalite, and scapolite (Kamineni, 1987), but these are not common minerals in the sedimentary rocks and sediments of Illinois. Chloride is a minor constituent of sedimentary rocks such as limestone, sandstone, and shale (as well as granitic rocks), but typically at low concentrations. Krauskopf (1979) reported typical Cl^- concentrations of 150, 10, and 200 ppm for limestone, sandstone, and shale, respectively. Chloride is also present within some minerals as fluid inclusions and can have very high concentrations comparable to those of a concentrated brine; however, fluid inclusions are typically very small (a few microns in diameter) and impart very little Cl^- to circulating groundwater. Because of the lack of appreciable amounts of Cl^- in rocks and sediments of Illinois, soils, sediments, and rocks in the shallow subsurface in Illinois would not be expected to have appreciable amounts of naturally-occurring Cl^- .

There are, however, natural brines in Paleozoic sedimentary formations of the Illinois Basin that underlie the southern two-thirds of the state (Figure 2). Meents et al. (1952) sampled over 700 oil field brines in the oil-producing regions of Illinois, primarily in the southeastern quadrant of the state; more than 80 percent of the samples had Cl^- concentrations greater than that of seawater, with a high of ~95,000 mg/L. Panno et al. (2006) summarized data from several studies in the Illinois Basin, and calculated a median Cl^- concentration of 64,600 mg/L, about three times the concentration in seawater.

Naturally saline groundwater in Illinois is very old. The chemical and isotopic compositions of brines in the Illinois Basin suggest they were formed as a result of the partial evaporation of seawater short of the precipitation of halite (Walter et al., 1990; Stueber and Walter, 1991; Kesler et al., 1995). Deeper groundwater in Precambrian granitic bedrock is even more saline, intensified by very long-term rock-water interactions at much warmer conditions than those encountered nearer the surface. Groundwater in the deeper parts of the Paleozoic and crystalline basement bedrock of the Illinois Basin is typically a hypersaline, calcium (Ca)-sodium (Na)-Cl-type brine with total dissolved solids (TDS) concentrations greater than 100,000 to over 250,000 mg/L (Horita, 2005).

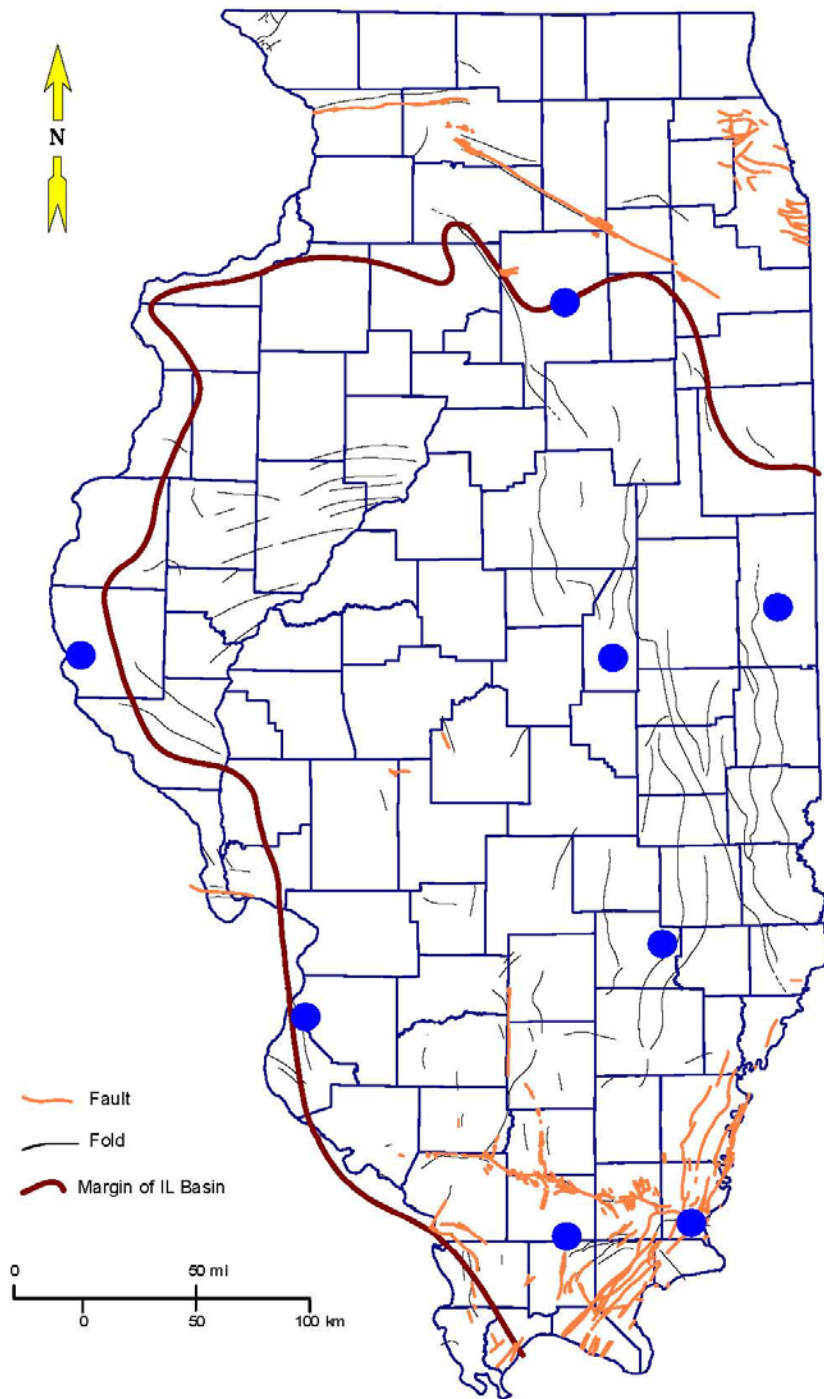


Figure 2. Illinois Basin. Blue circles indicate location of saline springs. Figure from Panno et al. (in preparation).

Saline groundwater in Illinois is under pressure, and at many locations it discharges into shallower aquifers or at the land surface as saline springs (Bartow et al., 1909; Willman et al., 1975; Cartwright, 1970; Panno et al., 1994, 2006). Bedrock discharge into the Mahomet Aquifer in Piatt County in east-central Illinois increases the Cl⁻ concentration from less than 10 mg/L to concentrations as high as 500 mg/L (Hackley et al., 2010). Thirteen samples of brine-affected groundwater collected by Panno et al. (2006), primarily in the southern part of the state, had a median Cl⁻ concentration of 474 mg/L. In some parts of Illinois, especially in the south, these deep brines discharge to surface waters, increasing the natural Cl⁻ concentration. For example, the North Fork of the Saline River in southeastern Illinois, named for its natural saltiness, had a median Cl⁻ concentration of 109 mg/L between 1978 and 1997 (USGS, 2009).

Background Chloride Concentrations

Despite the existence of saline seeps in Illinois, the vast majority of groundwater has relatively low concentrations of Cl⁻, especially in major aquifers. In a study of shallow groundwater (< 100 meters) in northern Illinois, Panno et al. (2006) determined that Cl⁻ concentrations in shallow aquifers ranged from less than 1 to 15 mg/L. They suggested that concentrations greater than 15 mg/L indicated contamination from human sources. This threshold is probably similar (or lower) for aquifers in the rest of Illinois as well, where urbanization is less (Panno et al., 2005). Prior to human alterations to the landscape, almost all water discharging to surface streams in Illinois passed through the subsurface (i.e., groundwater), and a large majority still does. Thus pristine surface waters in Illinois should have Cl⁻ concentrations < 15 mg/L. Lusk Creek, for example, which flows through the undeveloped Shawnee National Forest in southern Illinois, had a median Cl⁻ concentration of 2.3 mg/L between 1978 and 1997 (USGS, 2009).

Anthropogenic Sources

Schlesinger (2004) estimated that more than 140 teragrams (140 trillion kilograms) of Cl⁻ are annually cycled through various reservoirs on Earth, almost all of it due to human activities. Anthropogenic sources include human sewage, livestock waste, water conditioning salt, synthetic fertilizer (primarily KCl), brine disposal pits associated with oil fields, chemical and other industries, and, in snowy climes, road salt runoff. From a volume standpoint, the most important anthropogenic sources of Cl⁻ to waters in Illinois are fertilizer, road salt, water conditioning salt, sewage, and livestock waste (Table 1). Chloride concentrations for potential contamination sources of Cl⁻ in Illinois are shown in Table 2. Once in groundwater, Cl⁻ and other contaminants can persist for many years if travel times are slow. For example, Howard et al. (1993) estimated that if road salting was stopped immediately in the Toronto area, it would be decades before the Cl⁻ concentrations returned to pre-1960 levels in shallow groundwater. In rural areas, agricultural sources of Cl⁻ are of greater importance. Oil field-related contamination problems have occurred primarily in the southern two-thirds of Illinois.

Table 1. Annual Chloride Fluxes in Illinois

<i>Source</i>	<i>Flux (metric tons)</i>
Treated Wastewater	
MWRDGC	175,000
Remainder of state	125,000
Atmospheric	18,000
Road Salt	471,000
Water Conditioning Salt	135,000
Fertilizer (KCl)	373,000
Livestock	139,000
Lake Michigan withdrawals	34,000
Groundwater withdrawals	
Public supply wells	12,500
Industrial/commercial	5,300
Irrigation	10,000
Oil-Field Brines	23,000

Note: The treated wastewater fluxes do not include road salt inputs.

Table 2. Chloride Concentrations (mg/L) for Potential Sources in Illinois

<i>Sample Type</i>	<i>Location</i>	<i>Min</i>	<i>Median</i>	<i>Max</i>	<i>Reference</i>
Tile Drain	Ludlow	10.3	14.5	17.8	Kelly et al. (2010)
	Champaign	23.1	25.4	36.5	Panno et al. (2005)
Treated Wastewater	Stickney (2000-2008)	26.3	145	1,481	MWRDGC
Road Salt Runoff	Willow Springs		8,930		Kelly et al. (2010)
	Pekin		1,572		Kelly et al. (2010)
Agricultural Soil Water	Central Illinois	16.2	17.5	20.8	W. Kelly (unpublished data)
Natural Brine	Central Illinois		6,517		Panno et al. (2006)
	SW Illinois		8,080		Panno et al. (2006)
Illinois Basin Brine		557	64,600	125,000	Panno et al. (2006)
Livestock Manure	Central Illinois	440	847	1,980	Panno et al. (2006)
Septic System Discharge	SW Illinois	20.8	91	5,620	Panno et al. (septic paper)
Landfill Leachate		198	1,284	6,170	Panno et al. (2006)

Human Waste

The median Cl^- concentration in treated wastewater (TWW) discharging from the Stickney wastewater treatment plant (WWTP) in Chicago (the largest in the U.S.) between 2000 and 2008 was 145 mg/L (based on weekly sampling) (MWRDGC, 2010) (Table 2). Kelly et al. (2010) got similar results in samples collected on three dates between 2003 and 2005 from two Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) WWTPs (Stickney and Calumet); they reported a median Cl^- concentration of 141 mg/L. Kelly et al. (2010) also collected samples from the Peoria WWTP, which had Cl^- concentrations that ranged from 113 to 291 mg/L. TWW is generally discharged directly into surface waterways in Illinois.

Livestock Waste

Animal waste contains elevated concentrations of Cl^- ; Panno et al. (2006) measured levels as high as 1980 mg/L (Table 2). Because of this, even relatively small concentrations of livestock can create a local problem for shallow groundwater. Large confined animal feeding operations, which can concentrate thousands of animals in a relatively small area, have the potential to produce more widespread contamination of shallow groundwater, streams, and rivers (Wing et al., 2002; Showers et al., 2008).

Road Deicers

The chemical industry and governmental departments handling road ice control are the major importers and consumers of halite in the U.S., accounting for about three-fourths of its total use (Kostick, 2008). Road salt has been linked to groundwater degradation in many urban and roadside areas in snowy climates (Amrhein et al., 1992; Bester et al., 2006; Howard and Haynes, 1993; Huling and Hollocher, 1972; Pilon and Howard, 1987; Williams et al., 2000b). Significant application of road salt began after World War II and accelerated rapidly from the 1960s (Figure 3) (Salt Institute, 2009). Chloride concentrations have been increasing in surface waters and groundwater in urban regions of the northern United States and Canada since the 1960s, primarily due to road salt runoff (Godwin et al., 2003; Howard and Haynes, 1993; Kaushal et al., 2005; Kelly, 2008; Novotny et al., 2009; Kelly et al., 2010).

Two road salt runoff samples collected by Kelly et al. (2010) dripping off road bridges in Pekin and Willow Springs, IL, had very high concentrations of Cl^- : 1572 and 8930 mg/L, respectively (Table 2). Chloride concentrations in road salt runoff samples are extremely variable due to variability in application rates, snowfall amounts, melting rates, etc.; the values measured by Kelly et al. (2010) fall within the range of values reported by others (Amrhein et al., 1992; Environment Canada, 2001; Greb et al., 2000; Pilon and Howard, 1987). Road salt also can increase Cl^- concentrations in precipitation. For example, Williams et al. (2000a) characterized road salt aerosol in suburban areas west and south of Chicago, and measured Cl^- concentrations up to 9.4 mg/L in samples collected after snow events. They also found that Cl^- concentrations in snow samples decreased exponentially with distance from major highways.

Road salt runoff that recharges the soil zone and shallow groundwater can produce very high concentrations of Cl^- . Kelly and Roadcap (1994) measured Cl^- concentrations in excess of 1,000 mg/L in several shallow (< 25 ft; 7.6 m) monitoring wells installed along the uncurbed Interstate 94 in south Chicago, including two exceeding 3,500 mg/L.

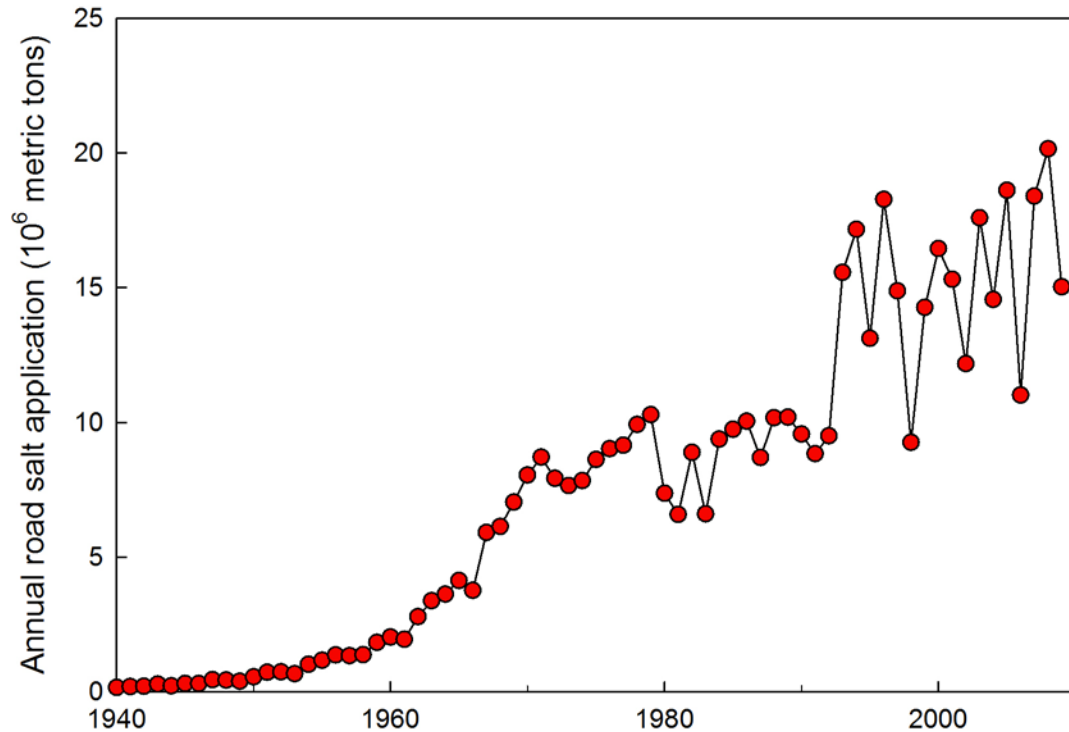


Figure 3. Yearly U.S. highway salt sales. Data from Salt Institute, 2011.

Water Conditioning Salts

In-home water treatment, specifically water softening, typically uses NaCl to recharge ion exchange columns in order to reduce hardness (Ca + Mg) by replacement with Na. For a family of three or four with moderately hard water, the recommended amount of NaCl for water softening is between 1.8 and 2.7 kilograms per day, or 600 to nearly 1000 kg of NaCl per year (Panno et al., 2005, 2007). If a household uses on-site wastewater treatment, the Cl⁻ is discharged to the shallow groundwater system via the leach field. If the household is connected to a community waste treatment facility, the Cl⁻ (which is not removed in the treatment process) is generally discharged to streams or rivers.

KCl Fertilizer

Illinois is a major producer of row crops, primarily corn and soybeans. KCl is the most commonly available potassium (K) fertilizer and usually the cheapest, thus it is widely applied in Illinois. Because it is spread over large areas (i.e., non-point source), its impact on soil water and

groundwater quality is less than more concentrated Cl^- applications, such as road salt. In much of Illinois, agricultural fields are tiled to facilitate drainage of soils, and these drain tiles are the major source of water to many streams in Illinois. Panno et al. (2005) and Kelly et al. (2010) collected samples from several tile drains in east-central Illinois, which represent shallow groundwater beneath row crop areas. Chloride concentrations in these tile drain samples ranged from 10 to 37 mg/L (Table 2). This is also approximately the same concentration range found in soil water in agricultural fields in central Illinois (W. Kelly, unpublished data).

Municipal Landfills

Panno et al. (2006) measured Cl^- concentrations in municipal landfill leachate as high as 6,170 mg/L. Roy (1994) reported the greatest Cl^- concentration recorded in municipal landfill leachate to be 27,100 mg/L. Potential sources of Cl^- in landfills include food scraps and pet wastes. Chloride concentrations in landfills are not static, but decrease with the age of the landfill (McGinley and Kmet, 1984; Ham, 1980; Lu et al., 1985). Farquhar (1989) reported that Cl^- concentrations in municipal landfill leachate tend to decrease asymptotically with time, with concentrations 1,000–3,000 mg/L during the first five years, 500–2,000 mg/L during years 5 to 10, 100–500 mg/L during years 10 to 20, and < 100 mg/L after that.

Oil and Gas Exploitation

Leakage of brine-holding ponds associated with oil wells has locally contaminated groundwater with high TDS waters in southeastern Illinois. Hensel and McKenna (1989) installed shallow monitoring wells around two brine-holding ponds in Clay County and measured Cl^- concentrations over 10,000 mg/L in several samples. They identified 384 holding ponds in their study area (~300 mi^2 in southeastern Clay County), so the potential for widespread groundwater contamination is significant and hundreds of acres of farm land were reported to have been made unsuitable for crops due to brine leakage and spillage. However, Hensel and McKenna (1989) found no widespread degradation of groundwater resources in the area.

Identification of Sources of Chloride

There are various methods for determining the source(s) of Cl^- in individual water samples, one of the best being halide ratios. In a recent investigation, Panno et al. (2006) collected more than 100 samples from various Cl^- sources (primarily in Illinois) and, by plotting Cl^- and bromide (Br^-) data on a Cl^- vs. Cl^-/Br^- diagram, were able to define domains that distinguish among the sources (Figure 4). TWW can plot outside the septic effluent source domain because there are often multiple sources of Cl^- in TWW. Chicago and many of its suburbs have combined sewers (sewage and storm water), and an average of about 30 percent of the water entering the Stickney WWTP is from storm runoff (J. Wasik, MWRDGC, December 1, 2006, personal communication). The highest Cl^-/Br^- ratios in TWW measured by Kelly et al. (2010) were during the winter, which was due to a dominant road salt component.

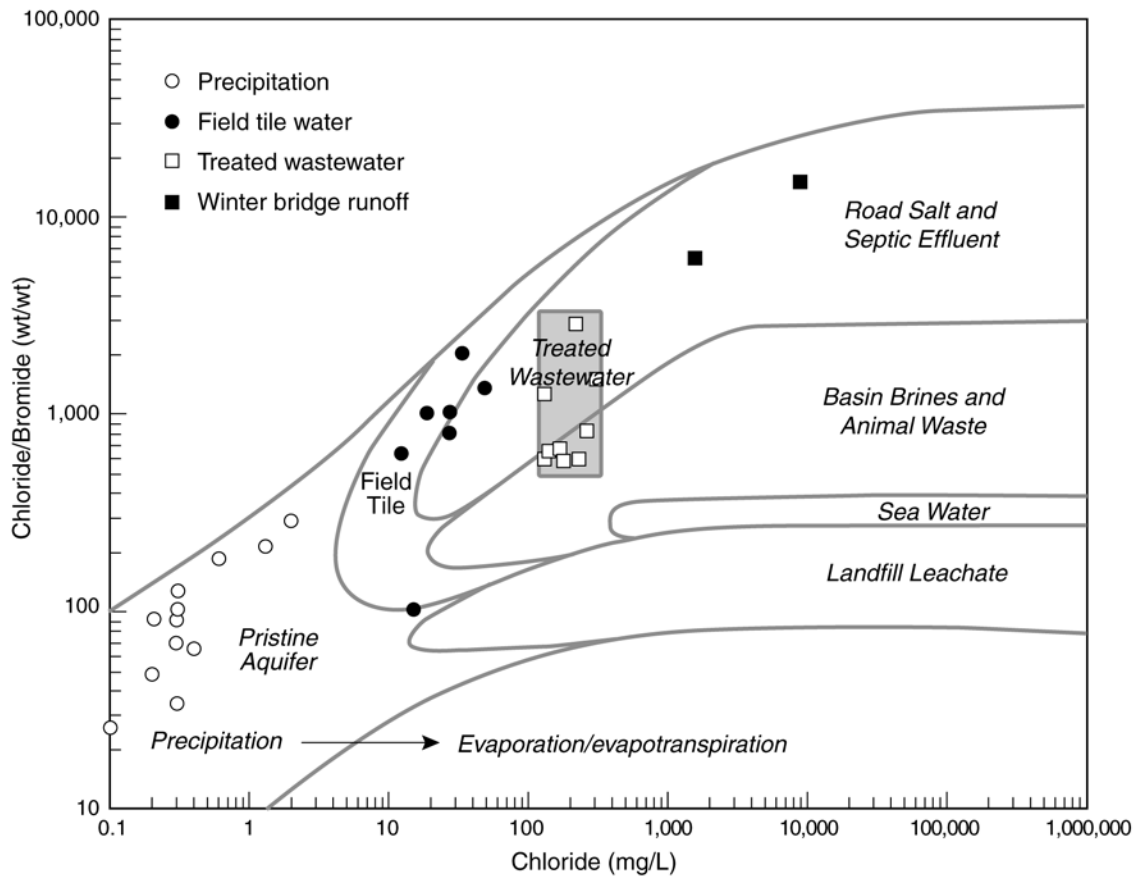


Figure 4. Cl/Br vs. Cl⁻ plot showing source domains (Kelly et al., 2010)

Annual Fluxes of Chloride in Illinois

The estimated annual flux of Cl^- in Illinois from various sources was determined using the methods of Kelly et al. (2010) (Table 2). They found that Cl^- in the Illinois River Basin was predominantly from road salt, TWW, and KCl fertilizer. An accurate estimate of how much road salt is applied in an average winter is difficult, due to the large number of government agencies and private entities that apply salt to roads and parking lots. Friederici (2004) and Keseley (2006) reported more than 250,000 metric tons of road salt is applied annually in the Chicago metropolitan region, but this is almost certainly an underestimate. Probably the best method for estimating road salt applications is to use road salt sales reported by the Salt Institute (Salt Institute, 2009) as a proxy. Using additional state data from Richter and Kreitler (1993) and Panno et al. (2005), Kelly et al. (2010) estimated that an annual average of 471,000 metric tons of road salt (equivalent to ~283,000 metric tons of Cl^-) were used in Illinois for the years 2002 to 2005, mostly in the Chicago region. Average annual road salt sales have increased since 2005, so the amount of road salt applied in Illinois has undoubtedly increased as well. The amount applied in a particular year generally depends on how much snow and ice fall during winter.

The Cl^- flux for TWW from the Chicago region can be calculated from WWTP discharge and Cl^- concentration data reported by MWRDGC (MWRDGC, 2010), but this calculation is complicated by multiple sources in TWW and the potential for “double counting” of sources. In addition to human waste, TWW includes industrial effluent, water conditioning salt, and road salt, as well as Cl^- present in drinking water sources.

Chloride fluxes from the Chicago WWTPs were calculated using Cohn’s equation (Kelly et al., 2010). Road salt contributions were removed from the WWTP loads by assuming that there was no road salt in TWW from May to October. Chloride loads during these months were divided by monthly discharges, and it was assumed that the same load per discharge ratio for non-road salt sources occurred between November and April. The remaining chloride loads between November and April (which varied between 17 percent and 50 percent of the total monthly load) were assumed to come from road salt and were removed from the TWW load calculations.

The seven MWRDGC plants account for almost 60 percent of the TWW discharged to surface water bodies in Illinois. To calculate the Cl^- flux for the remaining TWW, it was assumed that the effluent Cl^- concentration was the same as for the MWRDGC plants, resulting in a flux of 125,000 metric tons.

Human waste actually accounts for a small percentage of Cl^- in TWW. Adult humans excrete between 110 and 250 millimoles of Cl^- per day (3,900–8,860 mg day) (WebMD, 2011). Assuming 5,500 mg of Cl^- per day, a typical value for urine production (1.25 L/day), and a 2010 population of 12.83 million, results in about 32,000 metric tons of Cl^- from human urine annually in Illinois. Another approach taken by Mullaney et al. (2009) is to use per capita salt consumption based on the recommended daily adult sodium intake of 2,300 mg/d, which would include about 3,547 mg of Cl^- . A person on this diet would consume, and release, about 1.3 kg of Cl^- per year, which would be released by wastewater discharge. This would produce almost 17,000 metric tons of Cl^- in Illinois per year. Either estimate represents less than 10 percent of the Cl^- in TWW.

Chloride from water conditioning salt was also estimated from salt sales data. Between 2005 and 2008, approximately 3.2 million metric tons of salt (predominantly NaCl) was sold for water conditioning in the U.S. (Salt Institute, 2009). Assuming that water conditioning salt use was distributed equally across the U.S. based on population, approximately 135,000 metric tons of Cl⁻ is annually consumed in Illinois by water conditioning.

About 80 percent of corn fields and 30 percent of soybean fields in Illinois receive potassium chloride (KCl) annually (USDA, 2008). The amount of KCl applied in Illinois was estimated from state fertilizer sales data (USDA, 2008). Between 2005 and 2007, an average of 373,000 metric tons of Cl⁻ from KCl were purchased per year in Illinois.

Between 2005 and 2008, there were approximately 4.23 million pigs and 1.28 million cattle in Illinois (Illinois Agricultural Statistics Service, 2009). A pig produces about 3 gallons of waste a day and a cow produces 14 gal/day. Using Cl⁻ concentrations of 3,680 mg/L and 3,000 mg/L for pigs and cows, respectively (DeRouchey et al., 2003; Lengemann et al., 1952), an annual total of 139,000 metric tons of Cl⁻ was calculated to come from livestock.

For Cl⁻ from precipitation, a Cl⁻ concentration of 0.12 mg/L and an average annual precipitation of 102 centimeters (cm) were assumed (NAPD, 2011). This gives approximately 18,000 metric tons of Cl⁻.

One source of Cl⁻ that may be overlooked is water extracted from Lake Michigan and groundwater for drinking, industrial, and agricultural purposes. Chicago and many of the inner suburbs obtain drinking water from Lake Michigan, which has a Cl⁻ concentration of approximately 12 mg/L. Because most of the water Illinois takes from Lake Michigan is discharged outside the Great Lakes Basin, Illinois is limited by U.S. Supreme Court decree to 3,200 cubic feet per second (cfs) (~2,900 billion L/yr) of water from the lake. Assuming Illinois diverts all of this each year, approximately 34,000 metric tons of Cl⁻ is removed from the lake. Most of this eventually finds its way into wastewater, which would be included in the TWW Cl⁻ flux, and eventually is discharged down the Illinois River.

Approximately 1,180 million gallons (4,470 million L) of groundwater are withdrawn daily in Illinois (Kenny et al., 2009). About 507 million gallons per day (mgd) (1,920 million L/day) are used for drinking and other household uses, 517 mgd for agriculture (irrigation and livestock), 128 mgd by industrial and commercial applications, 15.5 mgd by mining, and 7.2 mgd for thermoelectric. Most extracted groundwater is not returned to the ground, but eventually finds its way to surface waters. In communities with sewers, most drinking water eventually finds its way into wastewater, which is then discharged to surface streams and rivers, eventually leaving the state. For homes and businesses with private wells and on-site sewage treatment (i.e., septic systems), extracted groundwater is discharged at or just below the ground surface, and most does not recharge underlying aquifers but is either evapotranspired or discharged to nearby streams or other surface waters. The same is true for irrigation water.

Groundwater withdrawal data are available for many public water supply wells and industrial/commercial wells. Of the top 200 pumped public water supply wells, 176 have been sampled sometime in the past 20 years, and the Cl⁻ concentration and withdrawal data from 2008 were used to calculate the mass of Cl⁻ removed. In order to not include potential surface contamination sources in shallow wells, it was assumed that the background Cl⁻ concentration was 15 mg/L in all wells ≤ 250 feet deep. These results were then used to estimate Cl⁻ fluxes

from the other approximately 2,500 public water supply wells for which we have withdrawal data. It was estimated that approximately 12,500 metric tons of Cl^- was extracted from public supply wells.

Sample results were available only for 13 of the top 200 industrial/commercial wells. For 184 of the other 187 wells, samples from a well located near to and at a similar depth to the well in question were found, and the Cl^- concentration from that well was used to calculate Cl^- fluxes. Using these data and the assumption that the background Cl^- concentration was 15 mg/L in all wells \leq 250 feet deep gives an estimate of approximately 5,300 metric tons of Cl^- extracted annually from industrial/commercial wells.

In 2005, the U.S. Geological Survey estimated that approximately 479 million gallons of water were pumped from irrigation wells in Illinois (USGS, 2009). Withdrawal data from individual irrigation wells are lacking in Illinois. Because most irrigation wells are finished in relatively shallow sand and gravel aquifers, it was assumed that the Cl^- concentration was 15 mg/L. This gives a Cl^- flux of approximately 10,000 metric tons from irrigation wells.

It is difficult to get accurate estimates of how much water is withdrawn for oil and gas production. The most recent and most reliable estimates are from the 1980s, when Kirk (1987) reported that 25.5 million gallons per day (~9.3 billion gallons annually) were withdrawn. Almost all of this is reinjected for secondary oil and gas recovery. However, some of this brine was temporarily stored in ponds at the surface, and leakage to surface and shallow subsurface environments has been reported (Hensel and McKenna, 1989). Using the median concentration of 64,600 mg/L reported by Panno et al. (2006), and assuming leakage of 1 percent of the withdrawn brine, gives an annual Cl^- flux of approximately 23,000 metric tons.

Distribution and Trends in Chloride Concentrations in Waters of Illinois

Recent research has suggested that Cl^- concentrations in many water bodies in Illinois are changing (e.g., Kelly [2008] and Kelly et al. [in press]), thus any report on the distribution of Cl^- is a “snapshot in time,” subject to change. This is especially true for rivers and shallow groundwater in urban and urbanizing areas, most notably the Chicago region. In order to fully understand the distribution of Cl^- in the waters of Illinois, a discussion of temporal trends must also be included. Trends in Cl^- concentrations in surface water and groundwater can reveal much about the origin, evolution, character, and movement of its sources. Such information is critical to predicting future changes in Cl^- concentrations.

Lakes

As mentioned previously, Lake Michigan currently has an average Cl^- concentration of 12 mg/L, its highest historical level. Concentrations have been slowly increasing since the late 1800s, due to human inputs to the lake (Chapra et al., 2009), with an increase of about 3 mg/L since the 1980s (USEPA, 2011a) (Figure 5). While the increase seems small, it represents an additional annual load of approximately 600,000 metric tons of Cl^- to Lake Michigan.

Natural lakes in Illinois are primarily found in the northern part of the state, especially Lake and McHenry Counties. Most lakes in downstate Illinois are reservoirs created by the

damming of streams and rivers. Their Cl^- concentrations are similar to those found in their stream or river supplies, potentially increasing in summer if there is significant evaporation.

Many lakes in Lake County have been monitored between April and October for dissolved solids since the late 1980s by the Lake County Health Department (LCHD). Chloride concentrations have been routinely monitored only since 2005, but specific conductance, which is highly correlated with Cl^- concentrations, has been monitored from the beginning. Specific conductance values have been increasing with time in most of these lakes (Figure 6). In 2010, the median Cl^- concentration in the 22 lakes being monitored by LCHD was 112 mg/L, with highest concentrations usually measured in the first sample collected (May). Between 2005 and 2010, Cl^- concentrations have generally dropped in many of these lakes, which has been attributed to dilution during the relatively wet summers in recent years (Figure 7) (M. Adams, LCHD, pers. comm.). There is anecdotal evidence that the increasing TDS levels in lakes at golf courses has forced their abandonment as sources of irrigation water due to the deleterious effects on turf. This in turn has led to drilling of new wells, increasing the amount extracted from aquifers in Lake County.

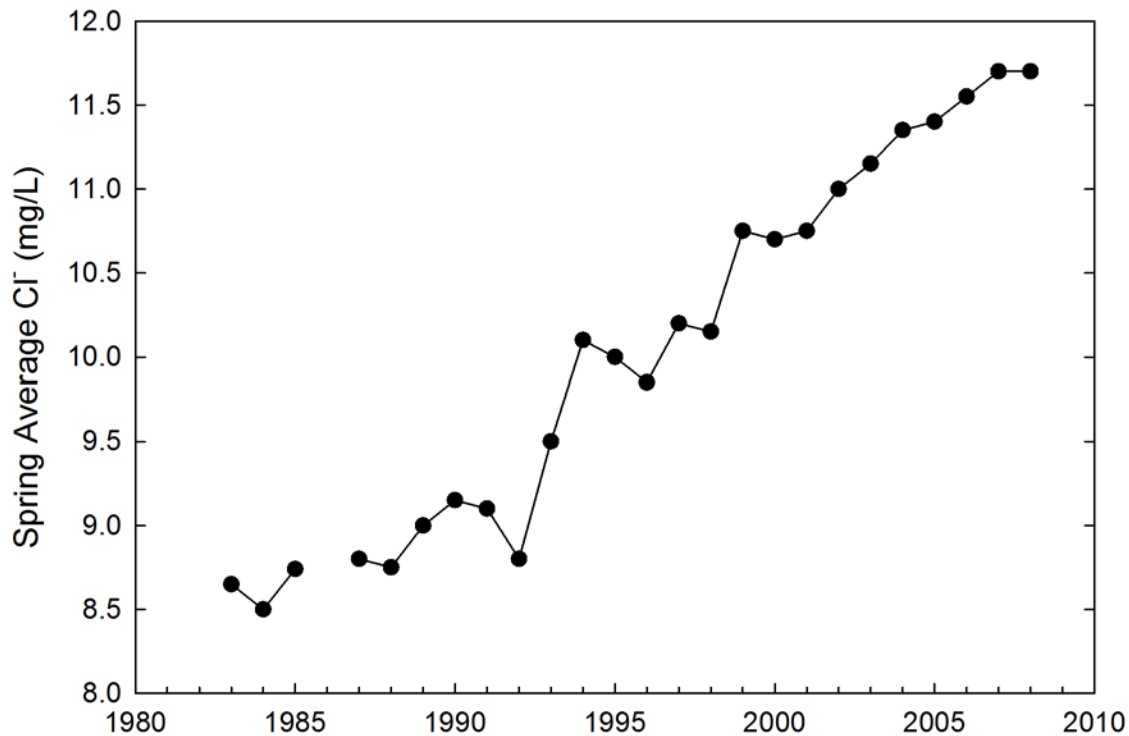


Figure 5. Chloride concentrations in Lake Michigan. Data from USEPA, 2011.

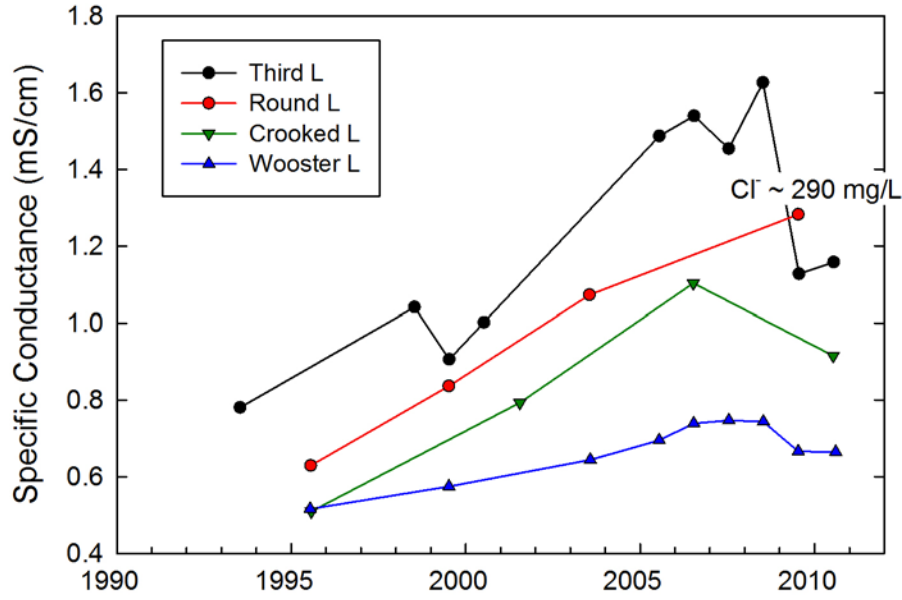


Figure 6. Annual median specific conductance values in selected lakes in Lake County. The chloride concentration for the most recent sample from Crooked Lake is reported. Data from Lake County Health Department.

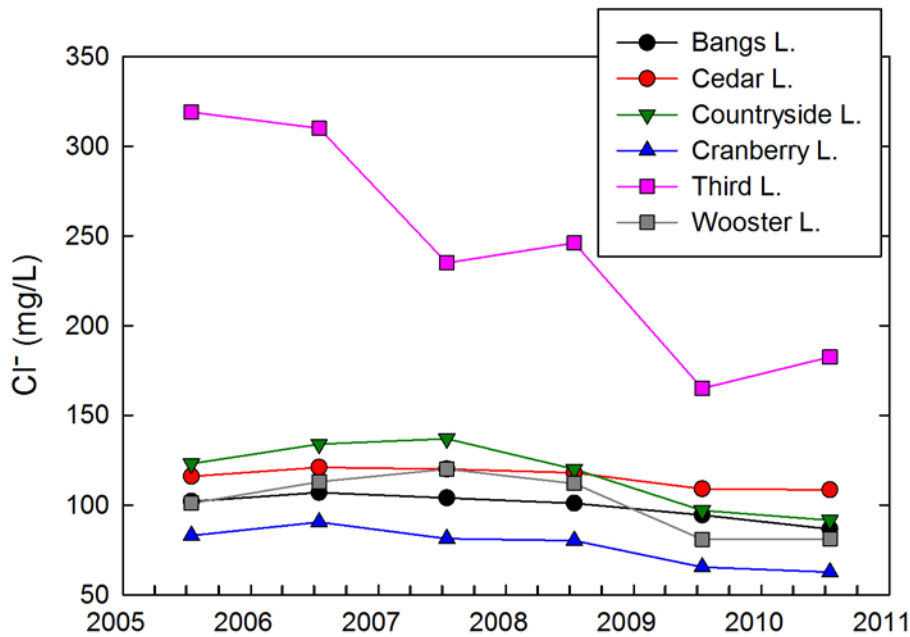


Figure 7. Chloride concentrations in selected lakes in Lake County. Data from Lake County Health Department.

Rivers and Streams

Water quality data for streams and rivers in Illinois are available from several agencies, including the ISWS, USGS, MWRDGC, and IEPA. Chloride concentrations in streams in Illinois are highest in the Chicago region and lowest in streams in forested watersheds in far southern Illinois. The USGS has historical data from a number of streams and rivers throughout Illinois. A comparison of data sets from a time period with the greatest overlap of data (1990–1992) indicates that downstate rivers draining primarily agricultural watersheds (Kankakee, Spoon, La Moine) had median Cl^- concentrations $< 30 \text{ mg/L}$ (Table 3 and Figure 8). Even though the North Fork of the Saline River drains an agricultural watershed, it has natural sources of Cl^- (geological brine discharge) and thus had a significantly higher median Cl^- concentration (86 mg/L). The Sangamon River, which has several large cities in its watershed (Bloomington-Normal, Decatur, Springfield), had a median concentration (34 mg/L at its most downstream station, Oakford) higher than rivers draining primarily agricultural land. The Fox River, which drains some of the western suburbs of the Chicago region and receives TWW, had an even higher median concentration (70 mg/L at its most downstream station, Dayton). Major Chicago waterways, including the Des Plaines River and the Chicago Sanitary & Ship Canal (CSSC), had median values $> 90 \text{ mg/L}$. The median Cl^- concentration in the Illinois River, which receives water from tributaries in the Chicago region as well as down-state, is $> 60 \text{ mg/L}$ at Peoria and upstream, dropping to around 50 mg/L near its discharge to the Mississippi. Figure 9 shows that there are large annual variations in Cl^- concentrations in rivers throughout Illinois.

The MWRDGC has been monitoring water quality monthly at surface water stations in the Chicago region since 1975, primarily in Cook County but also at a few stations in DuPage and Will Counties (Figure 10). Forty-one stations have been monitored relatively continuously since 1975, with more than 30 others having a shorter period of record. Median Cl^- concentrations in 2008 were $> 150 \text{ mg/L}$ at about 80 percent of the stations (Figure 11 and Table 4). The highest values tended to be in the smallest streams in northern Cook County, including Higgins Creek, Salt Creek, and Buffalo Creek, as well as the North Branch of the Chicago River. The stream with the lowest values appears to be the North Shore Channel, which receives significant flow from Lake Michigan.

The presence of trends in Cl^- concentrations were determined using Kendall's tau test at the 95 percent confidence level, and annual rates of change were estimated by calculating slope coefficients (β_1) on 5-point running medians (Helsel and Hirsch, 2002). Rivers draining the Chicago region, including the Illinois River, have increasing trends in Cl^- concentrations. Of the 41 stations monitored by MWRDGC since 1975, 35 had statistically significant positive trends in Cl^- concentrations, with a median increase of $2.7 \text{ mg/L per year}$ (Table 5). Five stations had increases of greater than 5 mg/L/yr ; two of these stations were in the North Branch of the Chicago River. Of a total of 78 USGS stations tested throughout the entire state, 36 had significant positive trends in Cl^- concentrations, and 10 had significant negative trends (Table 6). The positive stations included almost all the Chicago region rivers and canals (Des Plaines River, Fox River, Chicago River, Addison Creek, CSSC), as well as a number of down-state rivers, including the Kankakee, Rock, and Sangamon Rivers. All of the Illinois River stations, as well as those on the Mississippi and Ohio, had positive trends. The stations with negative trends were scattered throughout the state.

Table 3. Median Cl⁻ Values (mg/L) for Rivers in Illinois for Water Years 1991–1992 at USGS stations. For Rivers with More Than One Station (Ordered from Upstream to Downstream)

<i>River</i>	<i>Location</i>	<i>Station</i>	<i>Median</i>	<i>River</i>	<i>Location</i>	<i>Station</i>	<i>Median</i>
Big Muddy	Murphysboro	5599500	31	La Moine	Colmar	5585000	17
Cache	Forman	3612000	10	Little Wabash	Effingham	3378635	30
Cal Sag Channel	Sag Bridge	5536700	105	Little Wabash	Carmi	3381495	34
Casey Fork	Mt Vernon	5595830	67	Lusk Ck	Eddyville	3384450	2.3
CSSC	Romeoville	5536995	109	Md Fk Vermilion	Oakwood	3336645	24
CSSC	Lockport	5537000	91	N Branch Chicago	Deerfield	5534500	131
Crab Orchard Ck	Carbondale	5598245	13	N Branch Chicago	Niles	5536000	146
Des Plaines	Riverside	5532500	158	N Fork Saline	Texas City	3382325	86
Des Plaines	Joliet	5537980	99	Pecatonica	Freeport	5435500	20
Embarras	Camargo	3343395	30	Richland Ck	Hecker	5595200	65
Embarras	Diona	3344000	29	Rock	Rockton	5437500	24
Embarras	Billett	3346550	30	Rock	Como	5443500	38
Fox	Channel Lk	5546700	65	S Fork Saline	Crab Orchard	3382055	32
Fox	S Elgin	5551000	75	S Fork Saline	Carrier Mills	3382100	19
Fox	Montgomery	5551540	85	Saline Branch	Mayview	3337700	51
Fox	Dayton	5552500	70	Salt Fork	St Joseph	3336900	39
Green	Geneseo	5447500	25	Sangamon	Allerton Park	5572125	44
Illinois	Marseilles	5543500	63	Sangamon	Oakford	5583000	34
Illinois	Peoria	5559900	59	Sangamon S Fork	Kincaid	5575500	50
Illinois	Valley City	5586100	52	Spoon	Seville	5570000	31
Iroquois	Chebanse	5526000	40	Sugar Ck (Saline)	Stonefort	3382090	5.9
Kankakee	Wilmington	5527500	27	Sugar Ck (Lk Springfield)	Springfield	5576250	56
Kaskaskia	Cooks Mills	5591200	33	Sugar Ck (Salt Ck)	Hartsburg	5581500	48
Kaskaskia	Venedy Station	5594100	27	Thorn Ck	Thornton	5536275	130
Kishwaukee	Perryville	5440000	43				

Table 4. Median Cl⁻ Values (mg/L) for 2008 at River Stations Monitored by MWRDGC

<i>Station</i>	<i>River</i>	<i>Location</i>	<i>Cl⁻</i>	<i>Station</i>	<i>River</i>	<i>Location</i>	<i>Cl⁻</i>
12	Buffalo Ck	Lake-Cook Rd	286	34	N Br Chicago	Dempster St	231
43	Cal-Sag Channel	Rte 83	186	37	N Br Chicago	Wilson Ave	166
58	Cal-Sag Channel	Ashland Ave	176	46	N Br Chicago	Grand Ave	159
59	Cal-Sag Channel	Cicero Ave	173	73	N Br Chicago	Diversey Ave	159
49	Calumet	Ewing St	33.5	96	N Br Chicago	Albany Ave	236
55	Calumet	130 th St	156	104	N Br Chicago	Glenview Rd	204
74	Calumet	Lake Shore Dr	45.5	31	N Br Chicago (Md Fk)	Lake-Cook Rd	277
100	Chicago	Wells St	105	103	N Br Chicago (W Fk)	Golf Rd	288
40	CSSC	Damen Ave	143	106	N Br Chicago (W Fk)	Dundee Rd	350
41	CSSC	Harlem Ave	175	35	N Shore Channel	Central Ave	21.5
42	CSSC	Rte 83	169	36	N Shore Channel	Touhy Ave	135
48	CSSC	Stephen St	167	101	N Shore Channel	Foster Ave	140
75	CSSC	Cicero	169	102	N Shore Channel	Oakton Ave	72.0
92	CSSC	Lockport	162	39	S Br Chicago	Madison St	134
13	Des Plaines	Lake-Cook Rd	182	108	S Br Chicago	Loomis St	136
17	Des Plaines	Oakton St	196	99	S Br Chicago (S Fk)	Archer Ave	170
19	Des Plaines	Belmont Ave	196	18	Salt Ck	Devon Ave	241
20	Des Plaines	Roosevelt Rd	195	24	Salt Ck	Wolf Rd	252
22	Des Plaines	Ogden Ave	197	79	Salt Ck	Higgins Rd	388
23	Des Plaines	Willow Springs Rd	209	80	Salt Ck	Arlington Hts Rd	235
29	Des Plaines	Stephen St	198	90	Salt Ck	Rte 19	252
91	Des Plaines	Material Service Rd	193	109	Salt Ck	Brookfield Ave	256
86	Grand Calumet	Burnham Ave	138	32	Skokie	Lake-Cook Rd	247
77	Higgins Ck	Elmhurst Rd	452	105	Skokie	W Frontage Rd	181
78	Higgins Ck	Wille Rd	187	54	Thorn Ck	Joe Orr Rd	160
52	Little Calumet	Wentworth Ave	168	97	Thorn Ck	170 th St	182
56	Little Calumet	Indiana Ave	172	64	W Br DuPage	Lake St	168
57	Little Calumet	Ashland Ave	191	89	W Br DuPage	Walnut Ln	151
76	Little Calumet	Halsted Ave	170	110	W Br DuPage	Springinsguth Rd	297
				50	Wolf Lake	127 th St	64.9

Table 5. Trends Determined by Kendall Tau Statistic and β_1 Values (Reported as Yearly Change in CI) for MWRDGC Stations with Monitoring Data from 1975 to 2008. Kendall Tau Significance Determined at 95% Confidence Level. β_1 Values Reported for All Data (total) as Well as Seasonally.

Station	River	Kendall Tau	β_1 (mg/L/yr)				
		Significant?	Total	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec
12	Buffalo Creek	Y	5.8	13.2	6.9	1.4	3.0
13	Des Plaines R	Y	3.4	6.9	3.4	2.1	2.0
17	Des Plaines R	Y	3.8	8.2	3.9	2.6	2.7
18	Salt Creek	Y	2.1	6.7	6.4	-0.1	-1.2
19	Des Plaines R	Y	3.7	8.2	3.4	1.6	2.8
20	Des Plaines R	Y	4.1	8.6	3.7	2.2	3.0
22	Des Plaines R	Y	3.3	2.6	3.8	1.2	1.2
23	Des Plaines R	Y	3.4	8.9	4.0	1.1	2.0
24	Salt Creek	N					
29	Des Plaines R	Y	3.3	8.7	3.8	1.0	1.5
31	N Branch Chicago R (Md Fk)	Y	5.2	7.1	5.9	4.8	3.5
32	Skokie R	Y	4.6	5.5	6.3	4.3	3.5
34	N Branch Chicago R	Y	5.5	9.7	6.3	3.5	3.9
35	N Shore Channel	Y	0.17	5.4	2.0	-0.3	0.3
36	N Shore Channel	Y	1.9	5.2	2.1	0.9	2.7
37	N Branch Chicago R	Y	2.7	6.8	2.9	1.3	3.4
39	S Branch Chicago R	Y	2.6	6.4	2.5	0.5	3.0
40	CSSC	Y	2.7	6.4	2.7	0.4	3.2
41	CSSC	Y	2.5	5.2	2.2	1.0	4.2
42	CSSC	Y	2.7	7.0	2.4	1.1	2.3
43	Cal-Sag Channel	Y	1.4	5.2	1.8	0.1	0.0
46	N Branch Chicago R	Y	2.7	6.8	3.2	1.4	2.7
48	CSSC	Y	2.4	5.2	2.5	0.9	1.9
49	Calumet R	Y	0.76	1.7	0.5	-0.1	0.8
50	Wolf Lake	Y	0.51	0.4	0.7	0.6	0.4
52	Little Calumet R	Y	1.9	3.6	2.5	0.4	0.5
54	Thorn Creek	Y*	-4.8	-1.3	-2.8	-6.1	-7.7
55	Calumet R	N					
56	Little Calumet R	N					
57	Little Calumet R	Y	0.07	5.2	1.8	-2.3	-2.5
58	Cal-Sag Channel	Y	1.2	5.0	0.9	-0.1	1.4
59	Cal-Sag Channel	Y	1.2	4.3	1.8	-0.2	0.2
64	W Branch DuPage R	Y	-0.93	4.4	1.7	-2.2	-3.1
73	N Branch Chicago R	Y	2.5	6.7	2.5	1.0	2.6
74	Chicago R	Y	1.1	6.0	2.7	0.0	1.4
75	CSSC	Y	2.9	7.0	1.5	0.6	3.3
76	Little Calumet R	Y	1.4	4.7	10.1	0.6	1.4
78	Higgins Creek	Y	1.6	3.8	9.9	1.0	1.4
79	Salt Creek	Y	7.3	15.9	6.4	5.8	4.6
80	Salt Creek	Y	2.0	6.6	2.3	0.3	-0.6
90	Salt Creek	Y	6.8	12.8	11.1	4.4	3.7

* Negative trend.

Table 6. Trends Determined by Kendall Tau Statistic and β_1 Values (Reported as Yearly Change in Cl⁻, mg/L/yr) for USGS Stations. Data Start in 1984, and End between 1997 and 2008. Kendall Tau Significance Determined at 95% Confidence.

<i>Station</i>	<i>River</i>	<i>KT sign.</i>	β_1		<i>Station</i>	<i>River</i>	<i>KT sign.</i>	β_1
5532000	Addison Creek	Y	9.33		3384450	Lusk Creek	N	
5599500	Big Muddy	N			3336645	Middle Fork Vermilion	N	
3378000	Bonpas Creek	Y*	-1.08		7022000	Mississippi	Y	0.21
3612000	Cache	Y*	0.07		5587455	Mississippi	Y	0.48
5536700	Cal Sag Channel	N			5534500	N Branch Chicago	Y	7.13
5595830	Casey Fork	N			5536000	N Branch Chicago	Y	5.74
5598245	Crab Orchard Creek	N			3346000	N Fork Embarras	Y*	-2.00
5593520	Crooked Creek	Y*	-3.17		3382325	N Fork Saline	N	
5537000	CSSC	Y	3.84		3338780	N Fork Vermilion	Y*	-0.29
5536995	CSSC	Y	5.64		3612500	Ohio	Y	0.23
5528000	Des Plaines	Y	6.00		5435500	Pecatonica	Y*	-0.15
5529000	Des Plaines	Y	6.03		5550500	Poplar Creek	Y	14.2
5532500	Des Plaines	Y	2.11		5595200	Richland Creek	Y	0.99
5537980	Des Plaines	N			5437500	Rock	Y	1.00
5540500	DuPage	Y*	-2.63		5443500	Rock	Y	0.99
3344000	Embarras	N			5446500	Rock	Y	0.98
3345500	Embarras	Y*	-0.40		3337700	Saline Branch	Y	1.63
3343395	Embarras	N			5531500	Salt Creek	N	
3346550	Embarras	N			3336900	Salt Fork	N	
5551000	Fox	Y	5.89		5576500	Sangamon	N	
5551540	Fox	Y	7.11		5583000	Sangamon	Y	0.58
5552500	Fox	Y	1.76		5572000	Sangamon	N	
5550000	Fox	Y	5.56		5573540	Sangamon	N	
5546700	Fox	Y	2.94		5572125	Sangamon	N	
5447500	Green	N			3382100	S Fork Saline	N	
5539000	Hickory Creek	Y	6.52		3382055	S Fork Saline	N	
5543500	Illinois	Y	1.24		5575500	S Fork Sangamon	N	
5559900	Illinois	Y	2.54		3380500	Skillet Fork	N	
5586100	Illinois	Y	0.90		5594450	Silver Creek	Y	2.04
5526000	Iroquois	Y	0.32		5594800	Silver Creek	N	
5520500	Kankakee	Y	0.36		3382090	Sugar Creek	Y*	-0.59
5527500	Kankakee	Y	0.07		5576250	Sugar Creek	Y	2.53
5594100	Kaskaskia	N			5581500	Sugar Creek	Y	1.18
5592500	Kaskaskia	Y*	-2.08		5536275	Thorn Creek	N	
5591200	Kaskaskia	Y	1.68		3339000	Vermilion	N	
5440000	Kishwaukee	Y	0.98		5539900	W Branch DuPage	Y	4.23
5584500	La Moine	N			5540095	W Branch DuPage	N	
5585000	La Moine	N						
3378635	Little Wabash	N						
3379500	Little Wabash	N						
3381495	Little Wabash	N						

* Negative trend.

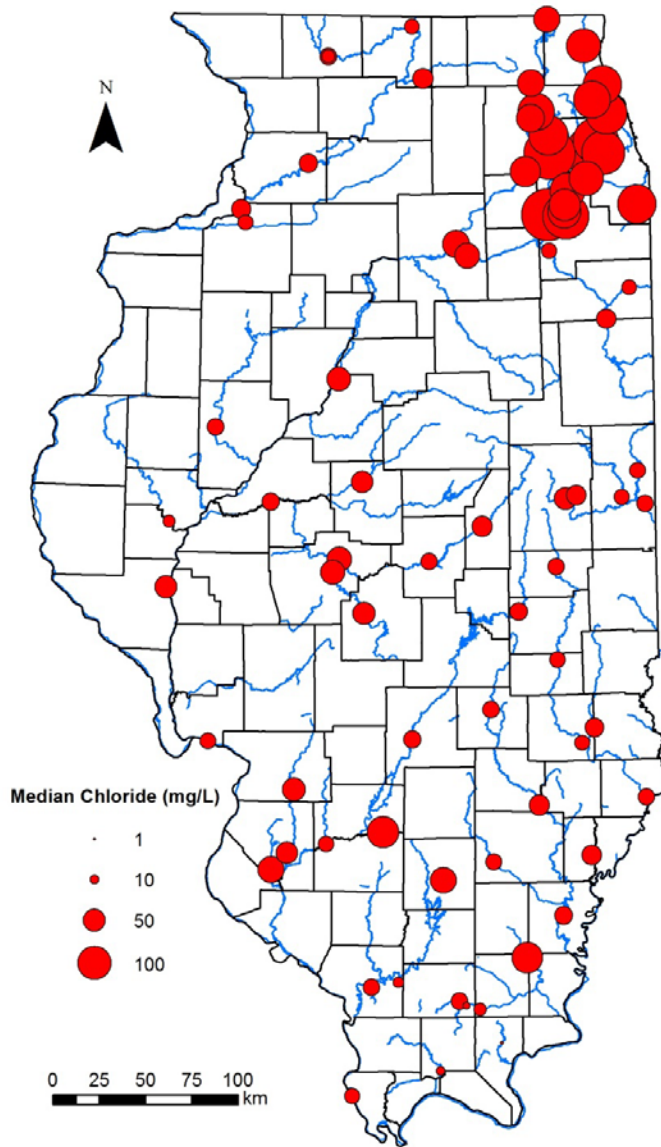


Figure 8. Median Cl⁻ values in streams and rivers of Illinois for the Water Years 1991-1992 for USGS monitoring stations

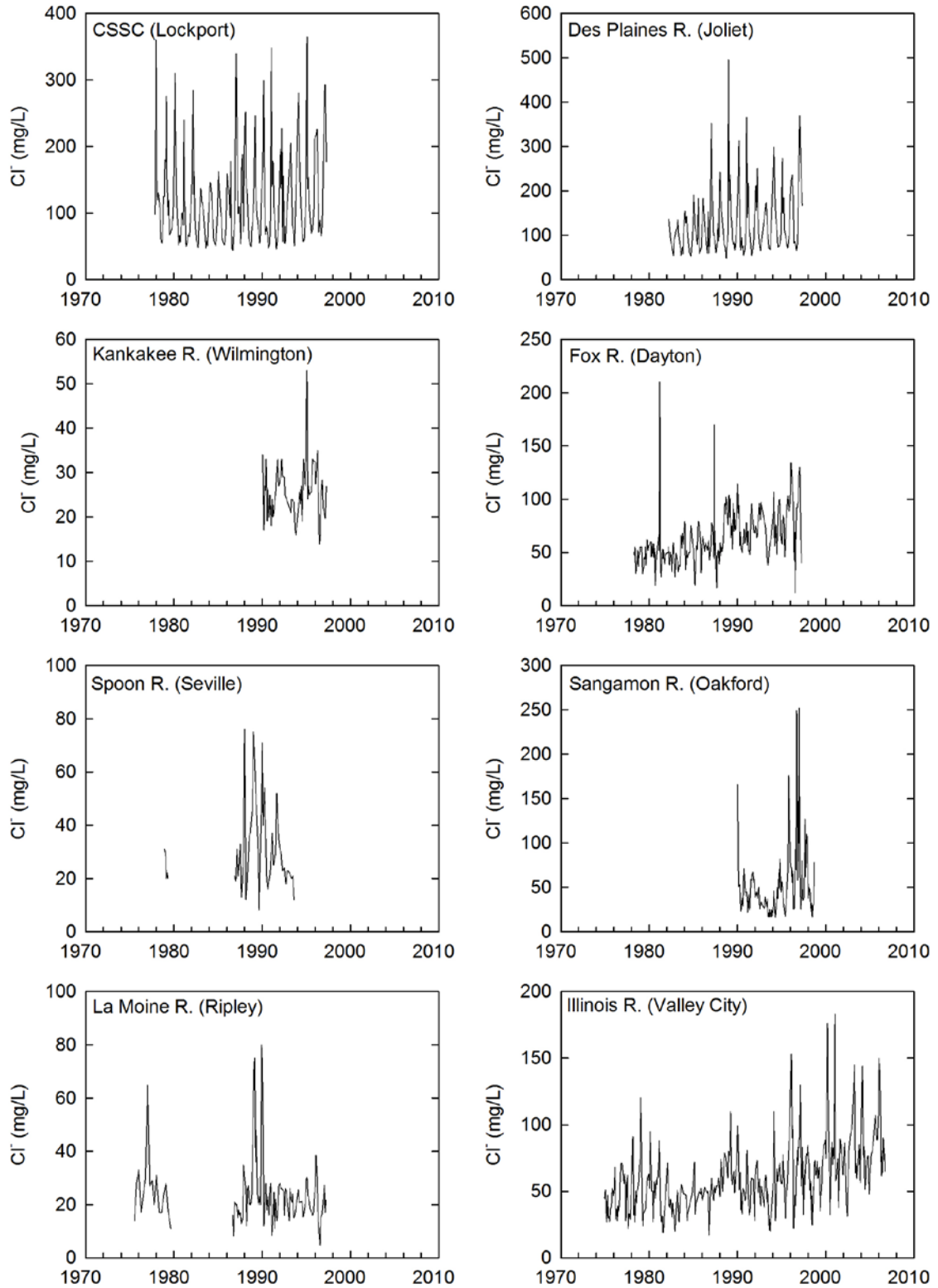


Figure 9. Chloride concentrations at selected USGS monitoring stations in Illinois

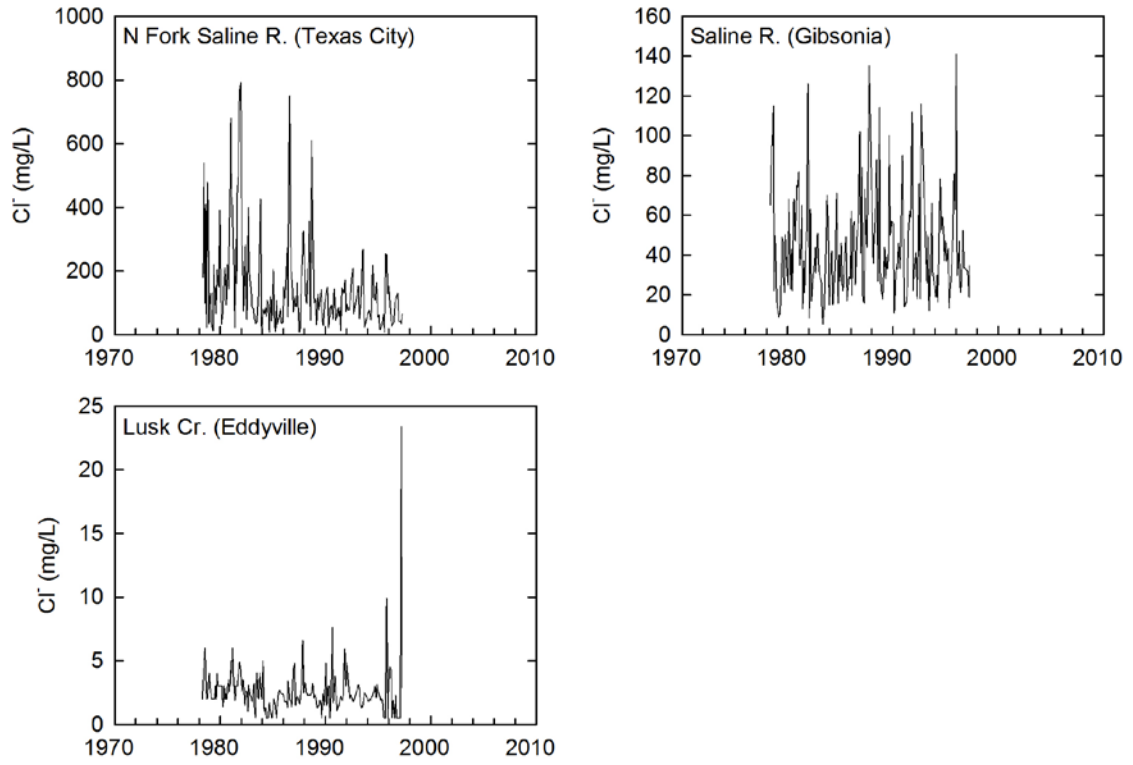


Figure 9. Continued

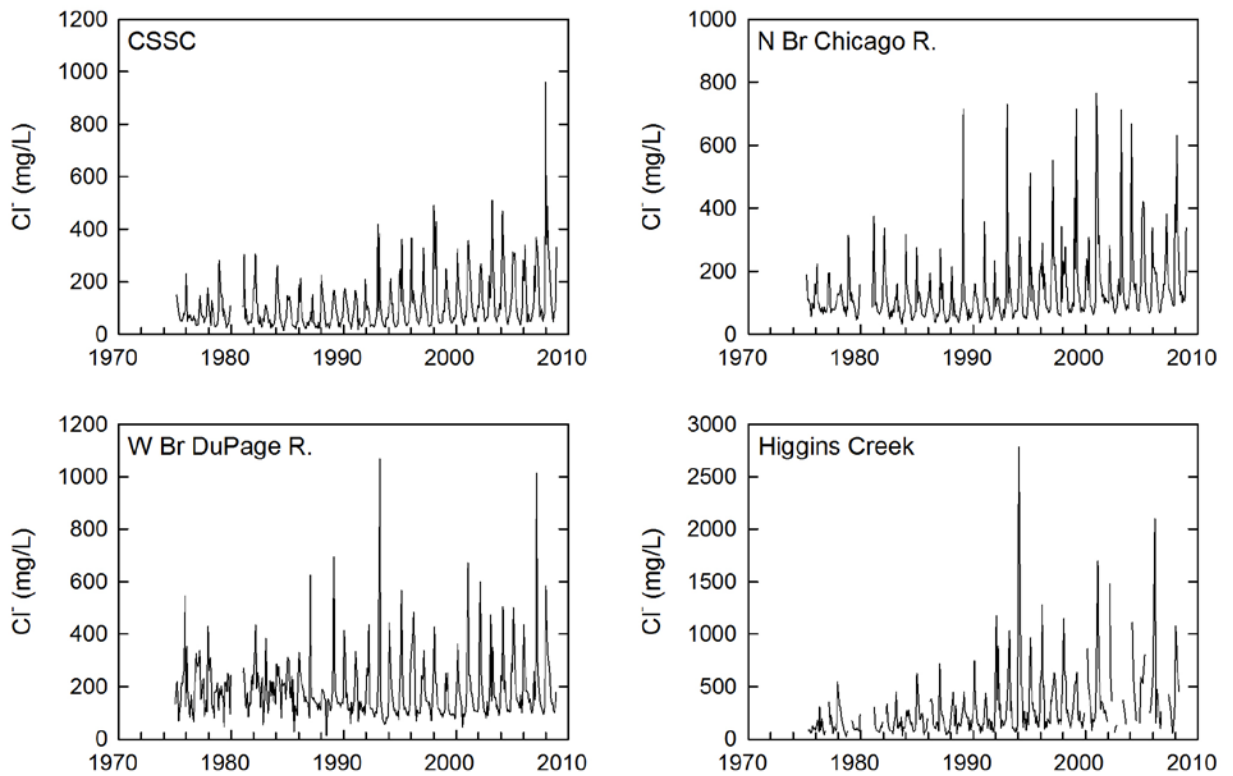


Figure 11. Chloride concentrations at selected MWRDGC monitoring stations in the Chicago region

There are clear seasonal differences in Cl^- concentrations for rivers where concentrations are increasing, with highest values between January and March (Figure 12). At 97 percent of the MWRDGC stations, the largest Cl^- concentrations were in the winter (January–March). At 83 percent of these stations, the winter concentrations were significantly greater (determined by ANOVA on ranks) than each of the other three seasons, and for 16 percent of these stations, concentrations were significantly greater than two of the other seasons. The spring months (April–June) generally had the second highest concentrations (88 percent of the stations), and for 53 percent of these stations spring concentrations were significantly greater than fall or summer. Concentrations were usually lowest in the summer (88 percent of stations). This seasonality is obviously due to road salt runoff. In snowy winters, large applications of NaCl produce Cl^- concentrations and loads in streams and rivers considerably higher than in winters with low snowfalls (Figure 13). It should be noted that during the months when Cl^- concentrations are lowest in the Chicago region (July–October), concentrations still are typically greater than 100 mg/L.

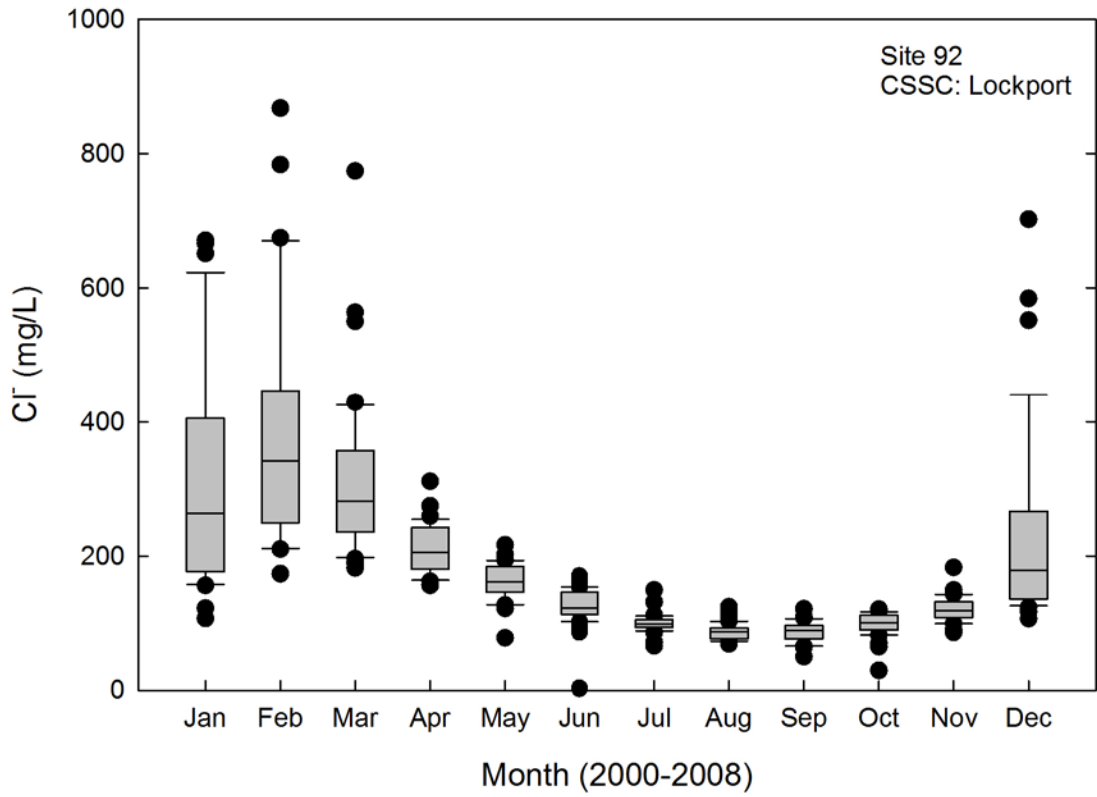


Figure 12. Chloride concentrations by month for MWRDGC station 92 (CSSC at Lockport) between 2000 and 2008. The site was sampled weekly.

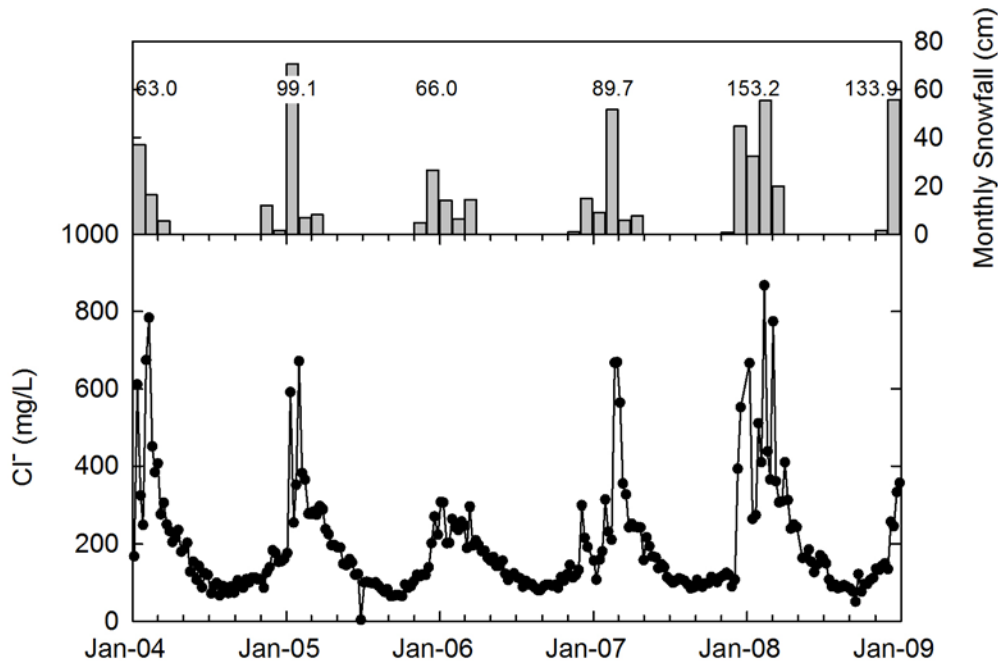


Figure 13. Chloride concentrations at MWRDGC station 92 on the CSSC at Lockport, IL, and monthly snowfall totals in Chicago (winter totals shown above bar). Snowfall data from NOAA, 2010.

Increasing trends in Cl^- concentrations are observed in all seasons at the MWRDGC stations, with the rates of increase following the same seasonal pattern as the concentration data, i.e., greatest increases in the winter and smallest in the summer (Figure 14 and Table 5). This is additional evidence that increases in Cl^- concentrations are the result of road salt runoff.

Rivers outside the Chicago region tended to have different seasonal patterns. Chloride concentrations in the Fox River were significantly lower between April and June than for both autumn and winter samples, and in the Sangamon River, concentrations were significantly lower between April and June than in all other seasons. For both these rivers, the highest Cl^- concentrations were typically measured between October and December. This may be due to leaching of fertilizer, which is typically applied in Illinois in the autumn after harvest. There were no significant seasonal differences for the Kankakee, Spoon, and La Moine Rivers.

Kelly et al. (2010) reported that chloride concentrations were significantly higher when river discharge was low, regardless of season. The USGS data sets showed the influence of discharge on Cl^- concentrations (Figure 15). For every station except CSSC reported by Kelly et al. (2010), Cl^- concentrations at low discharge (bottom 25th percentile) were significantly greater than at high (top 25th percentile) and intermediate (middle 50th percentile) discharges, and concentrations at intermediate discharge were almost always significantly greater than at high discharge. For CSSC, Cl^- concentrations at low discharge were significantly greater than at intermediate discharge.

For the most part, discharge from tributaries to the Illinois River downstream of Chicago dilutes the concentrations of Cl^- and other ions originating from TWW and road salt. Road salt inputs are seasonally variable, with fluxes highest in the winter and early spring; the flux of contaminants from TWW should be less seasonally affected. Thus when the Illinois River discharge is low, there is less dilution of TWW downstream of Chicago. Therefore, Cl^- , which is elevated in TWW, becomes relatively elevated in the river because there is less dilution by downstream tributaries. This relationship can be seen in Figure 16, which shows the fraction of the Cl^- load at Peoria attributable to the load in the CSSC as a function of river discharge at Peoria. When discharge is low, it is not uncommon for more than 60 percent of the Cl^- load at Peoria to be attributable to what is coming out of the CSSC, which is predominantly TWW.

The longest record of data is the Illinois River at Peoria, which indicates that Cl^- concentrations have been steadily increasing since the 1960s (Figure 17). The annual increase since 1960 (from β_1 calculation) is 1.0 mg/L per year (mg/L/yr), and 3.1 mg/L/yr since 1990. Concentrations are highest in the winter and early spring months, and the variability in concentrations during these months has been increasing. The overall temporal increase in Cl^- concentrations is mostly due to increases during January through April; concentrations have increased at rates greater than 4.0 mg/L/yr in all these months since 1990. However, there were positive trends in all months except June, indicating that increases in Cl^- concentrations are due to factors other than just direct road salt runoff. Shallow groundwater in much of the Chicago region has elevated Cl^- due to road salt (Kelly, 2008), and most of this groundwater discharges to tributaries of the Illinois Waterway throughout the year, not just in winter. In addition, the increasing population and concomitant increase in residential acreage and sewage in the Chicago region is likely increasing the Cl^- load to the Illinois Waterway via TWW discharge. The influence of river discharge on Cl^- concentrations can also be seen in Figure 17. Concentrations were relatively low during flood years (e.g., 1972, 1993), and relatively high during droughts (1963–1964, 1977, 1980, 1988–1989).

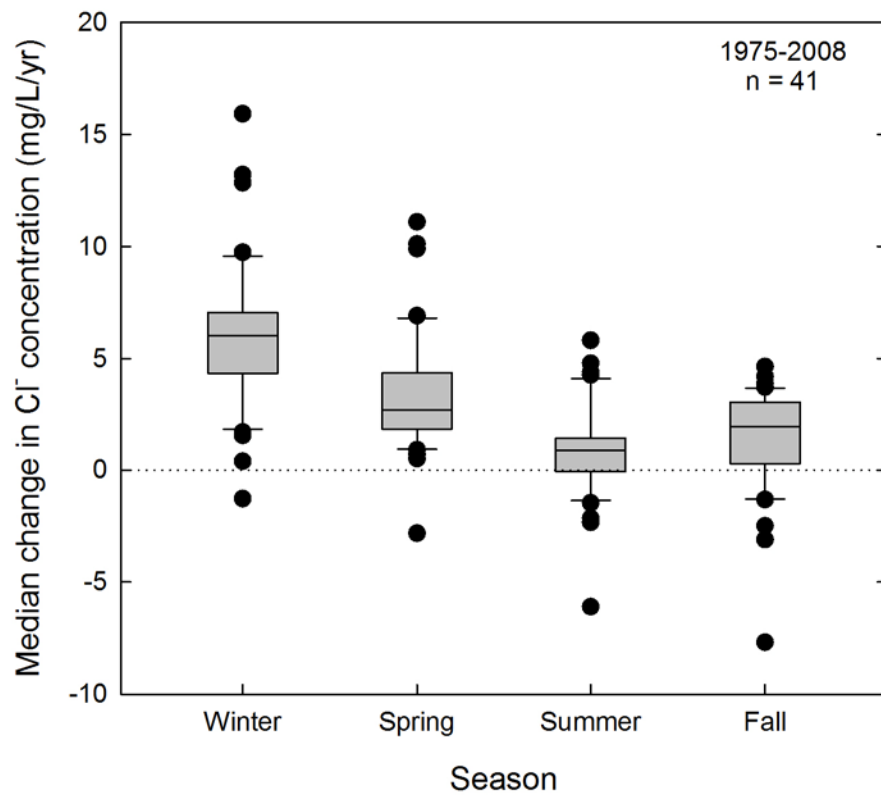


Figure 14. Box and whisker plot of median changes in chloride concentrations for 41 MWRDGC stations monitored between 1975 and 2008, divided by season. Changes calculated from slope statistic ($\hat{\beta}_1$) for linear regressions. Changes were significantly greater for winter compared to all other seasons, and for spring compared to summer and fall (ANOVA on ranks).

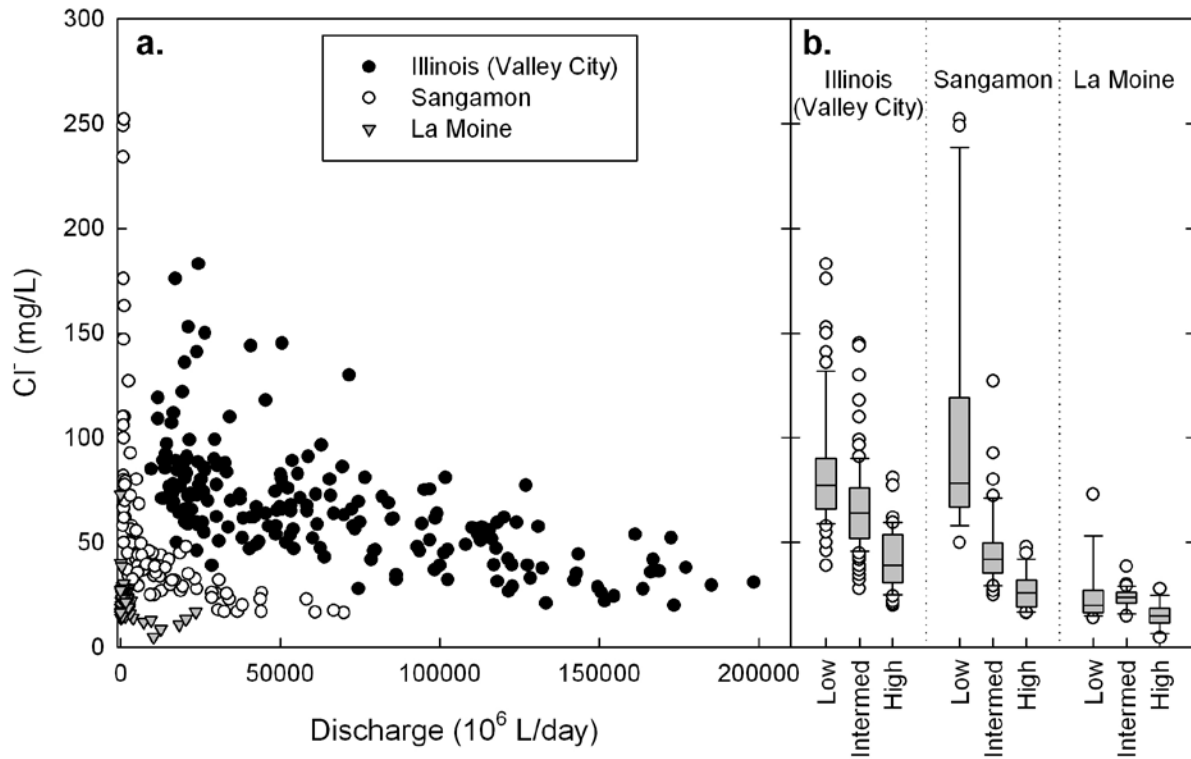


Figure 15. (a) Chloride concentration as a function of discharge for the Illinois River (Valley City), Sangamon River (Oakford), and La Moine River (Ripley). (b) Box plots showing same data as a function of river discharge category; circles are all outliers (< 10%, > 90%). Figure from Kelly et al. (2010), data from USGS (2008).

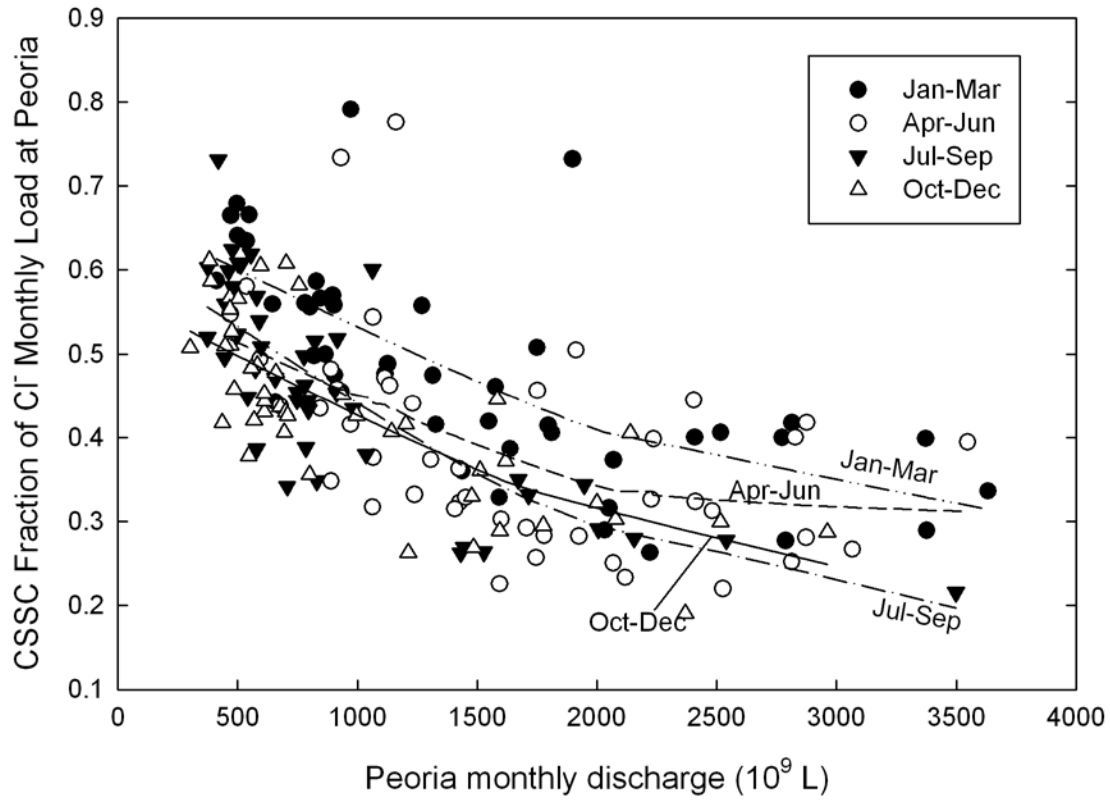


Figure 16. Fractions of the chloride monthly loads in the Illinois River at Peoria that can be attributable to discharge from the CSSC (Romeoville) as a function of monthly discharge at Peoria (1987–2001) Lines are smoothed regressions using LOWESS. Figure from Kelly et al. (2010), data from USGS (2008).

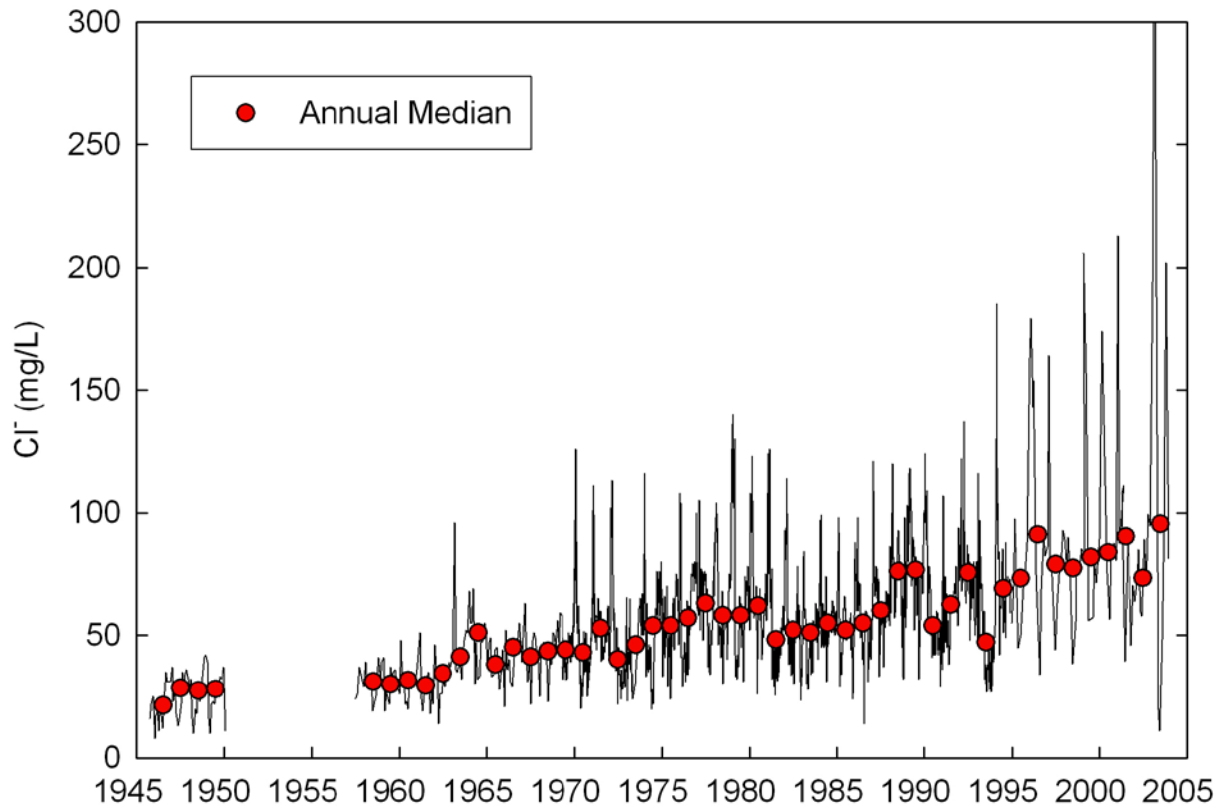


Figure 17. Chloride concentrations in Illinois River at Peoria. Data from ISWS and USGS.

Groundwater

In this report, we use the hydrostratigraphic nomenclature developed by Meyer et al. (2009) to differentiate among aquifers in Illinois. In most of the state, the aquifers closest to the land surface are Quaternary in age. These are composed of unconsolidated sands and gravels deposited by glacial and alluvial processes. Bedrock aquifers in Illinois are all sedimentary rocks (sandstones and carbonates) of Paleozoic age, the youngest being Pennsylvanian and the oldest Cambrian. We divided the bedrock aquifers into three groups (Figure 18), from youngest to oldest: (1) the upper bedrock unit, primarily sandstones of Pennsylvanian and Mississippian age; (2) the Silurian-Devonian carbonate unit, primarily fractured dolomites; and (3) the Cambrian-Ordovician aquifers, which are primarily sandstones. The Cambrian-Ordovician group comprises several aquifers, but because wells are commonly open to more than one of these aquifers, we chose to group them together.

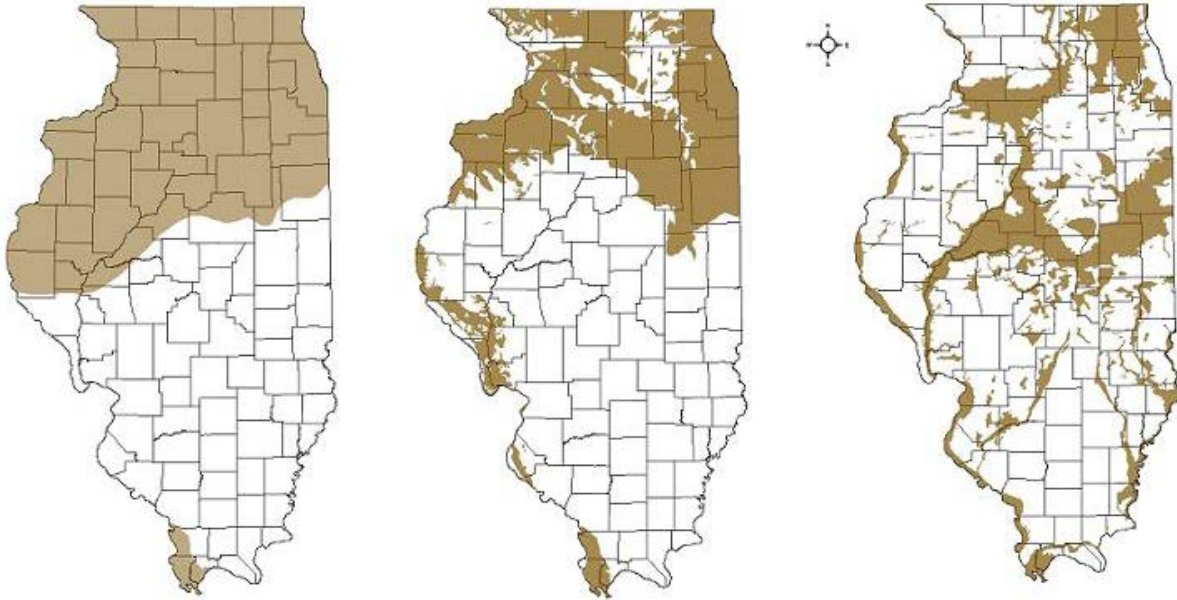


Figure 18. Extents of principal aquifer systems in Illinois (a) Cambrian-Ordovician bedrock; (b) shallow bedrock (Silurian-Pennsylvanian); (c) unconsolidated

Quaternary Aquifers

Sand and gravel Quaternary aquifers are found throughout Illinois (Figure 18c). Alluvial aquifers are found in river valleys; most aquifers in the southern third of Illinois are of this type. Glacial aquifers include buried bedrock valleys filled with sand and gravels and sand and gravel lenses within till deposits. The largest buried bedrock valley aquifer is the Mahomet Aquifer in central Illinois, and other major glacial aquifers are found in the northern half of the state. Chloride concentrations vary greatly in these aquifers (Figure 19).

In the Mahomet Aquifer (Figure 20), chloride concentrations are extremely low in the eastern part of the aquifer, and are < 1 mg/L in parts of Champaign County. Hackley et al. (2010) suggested that recharge from glacial meltwaters recharging the Mahomet aquifer in Champaign County near the end of the Wisconsin Glacial Episode (about 11,500 years BP) leached the fine sediments and sand and gravel of the recharge zone and the aquifer. This resulted in the anomalously low Cl^- concentrations. Near the border between Champaign and Piatt Counties, Cl^- concentrations abruptly increase, due to discharge of brine from Pennsylvanian bedrock. Concentrations then decrease gradually to the west due to dilution. In the western region of the Mahomet aquifer (Piatt, Macon, and DeWitt Counties) where Cl^- concentrations are highest, concentrations along the bedrock valley walls tend to be higher than in the central, thalweg part of the valley. This is likely due to proximity to bedrock discharge along the valley walls and greater dilution in the thalweg. The Mahomet is confined through most of its central and eastern extent, thus surface activities generally do not impact its water quality. In the Sankoty-Mahomet section (Mason and western Tazewell Counties), the Sankoty-Mahomet is unconfined and

surface activities can impact water quality. Elevated Cl^- concentrations in the East Peoria and Pekin regions are probably due to road salt runoff in those urban areas.

Other buried bedrock valley aquifers in Illinois include the Mackinaw and Princeton bedrock valleys northwest of the Mahomet Aquifer. Chloride concentrations are generally low in these aquifers. Burch (2004) reported a median Cl^- concentration of 10.8 mg/L ($N = 30$) in samples from the Princeton bedrock valley, which included several samples impacted by road salt runoff.

Chloride concentrations in glacial aquifers within till deposits vary greatly. For example, the Glasford Aquifer in central Illinois has Cl^- concentrations ranging from < 1 to about 100 mg/L. Sand and gravel aquifers in northeastern Illinois have been heavily impacted by human activities, with the most obvious sign being increasing Cl^- concentrations. Kelly (2008) showed that Cl^- concentrations in shallow groundwater in the Chicago region have been increasing since the 1960s when road salt began being used in earnest. Over half of the public supply wells finished in sand and gravel aquifers have statistically significant increasing trends in Cl^- concentrations. Widespread sampling of shallow aquifers (< 250 feet deep) in Kane County in 2003 indicated the role of urbanization on shallow groundwater quality (Kelly, 2005). Chloride concentrations were significantly higher in the eastern urban corridor compared with the remainder of the county, which was primarily rural (Figure 21). Figure 21 clearly shows that urban land use increases Cl^- concentrations but rural land uses do not.

Mullaney et al. (2009) reported on Cl^- in unconsolidated glacial aquifers of the U.S. and found that land use significantly affected Cl^- concentrations. Shallow monitoring wells in urban areas had significantly greater Cl^- concentrations (median = 46 mg/L, $n = 317$) than in agricultural areas (median = 12 mg/L, $n = 430$), and both were significantly higher than wells in forested areas (median = 2.9 mg/L, $n = 50$). Their source analysis suggested that Cl^- in urban settings was dominated by deicing and/or water softening salt.

Chloride concentrations in alluvial aquifers in southern Illinois are generally low (< 30 mg/L), with a few exceptions. The Rock River valley in Rockford has higher Cl^- concentrations (generally > 50 mg/L), reflecting greater urbanization and heavier amounts of snow and thus road salt runoff. Chloride concentrations also are higher in the American Bottoms area across the Mississippi River from St. Louis, again reflecting the large degree of urbanization. In areas where there are no aquifers, primarily the southern half of Illinois, large-diameter dug and bored wells are used. These wells are vulnerable to surface contamination. Chloride concentrations in these areas vary widely, probably reflecting the local land use activities that impact the wells.

An important control on Cl^- concentrations in Quaternary aquifers is depth. In general, the shallower the aquifer, the more vulnerable it is to surface-derived contamination. Figure 22 shows Cl^- concentrations for wells 50 feet or less. In contrast, Figure 23 shows Cl^- concentrations for wells greater than 250 feet. Figure 24 shows a box-and-whisker diagram of Cl^- concentrations as a function of depth. Results from ANOVA testing indicated that Cl^- concentrations in each depth range were significantly greater than all deeper groups.

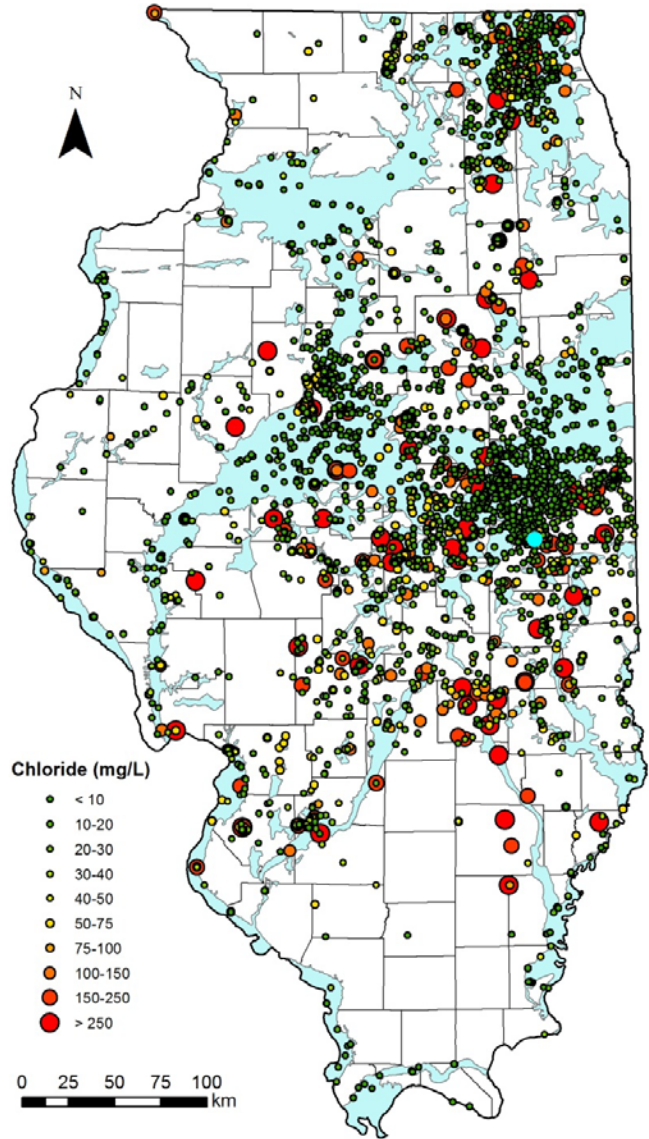


Figure 19. Chloride concentrations in wells open to Quaternary sand-and-gravel aquifers. Locations of significant Quaternary sand-and-gravel aquifers indicated by light blue.

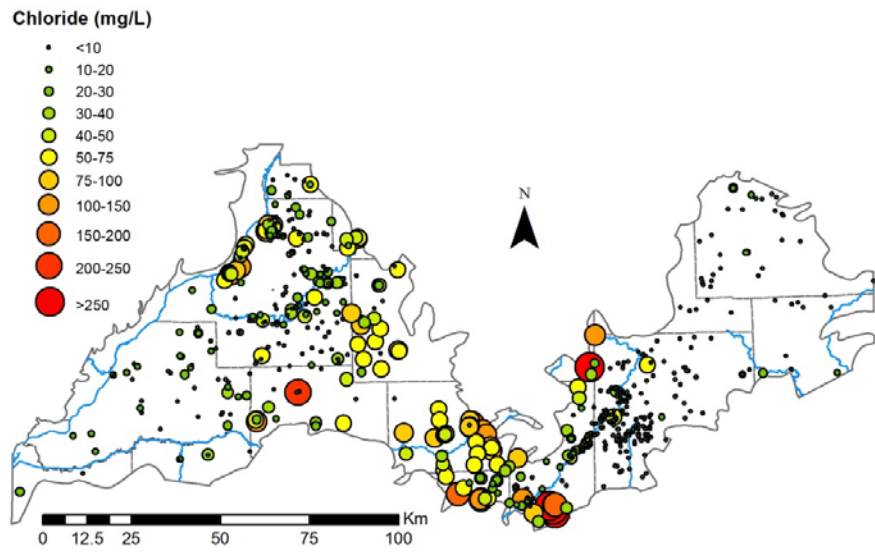


Figure 20. Chloride concentrations in the Mahomet Aquifer

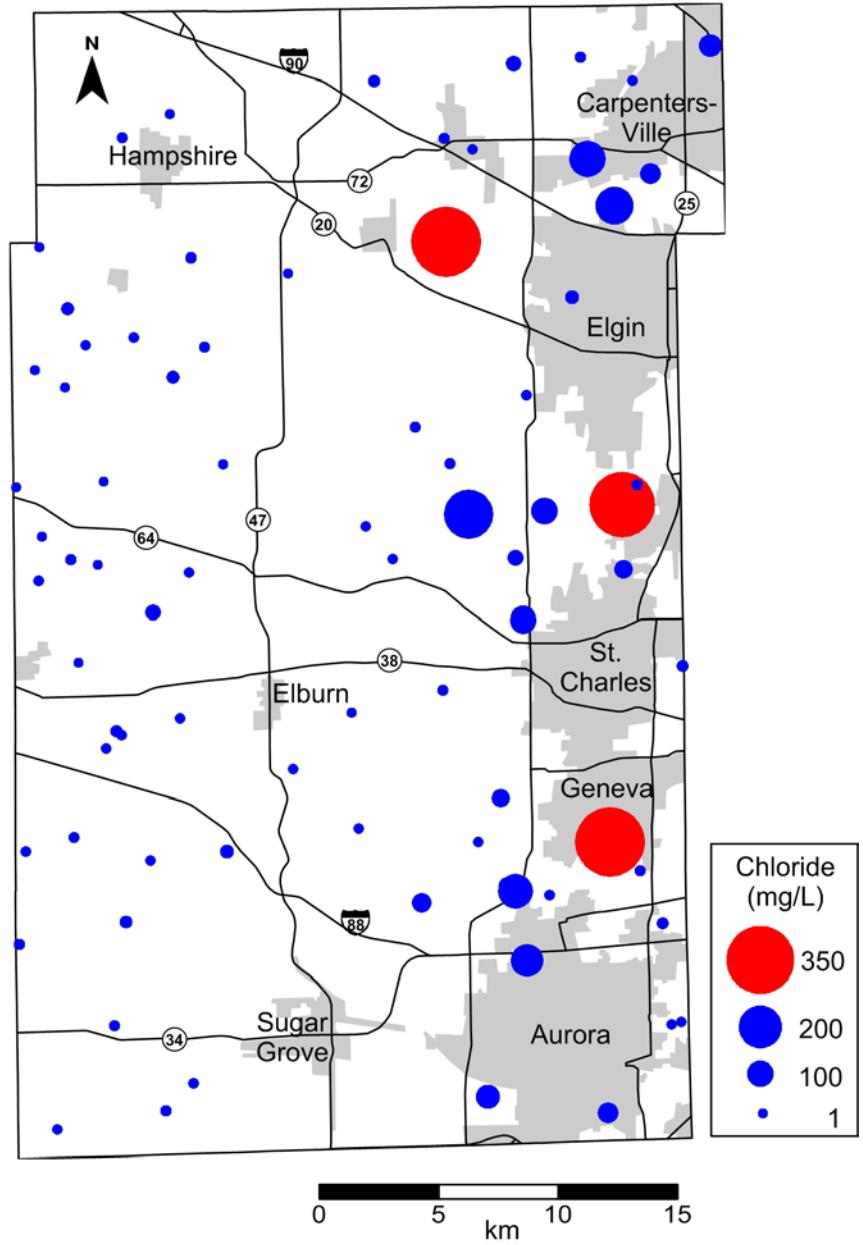


Figure 21. Chloride concentrations in samples collected from shallow wells (< 250 feet) in Kane County in 2003. Size of circle represents Cl⁻ concentration, with red circles indicating values > 250 mg/L. Gray areas represent municipalities. Major roads shown. Figure from Kelly, 2005.

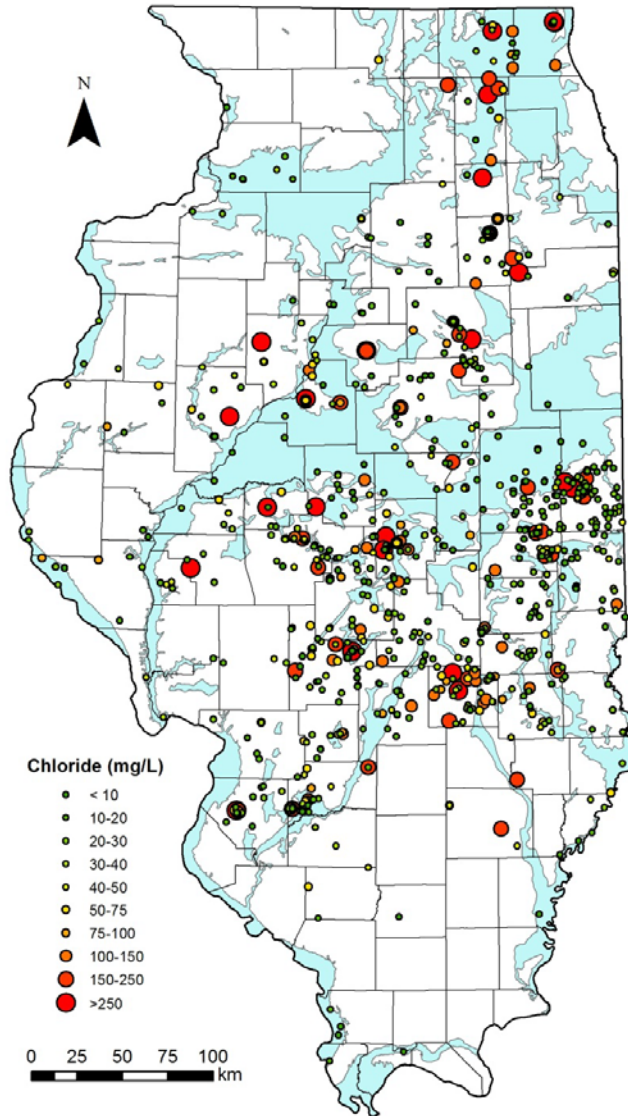


Figure 22. Chloride concentrations in wells 50 feet deep or less open to Quaternary sand-and-gravel aquifers. Locations of significant Quaternary sand-and-gravel aquifers indicated by light blue.

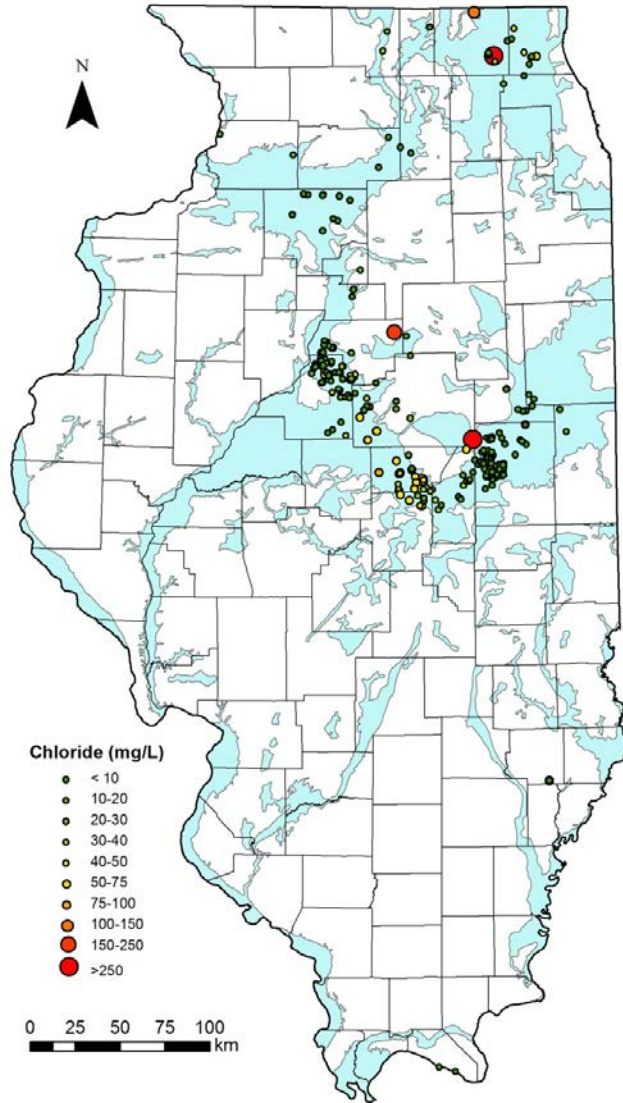


Figure 23. Chloride concentrations in wells equal to or greater than 250 feet open to Quaternary sand-and-gravel aquifers. Locations of significant Quaternary sand-and-gravel aquifers indicated by light blue.

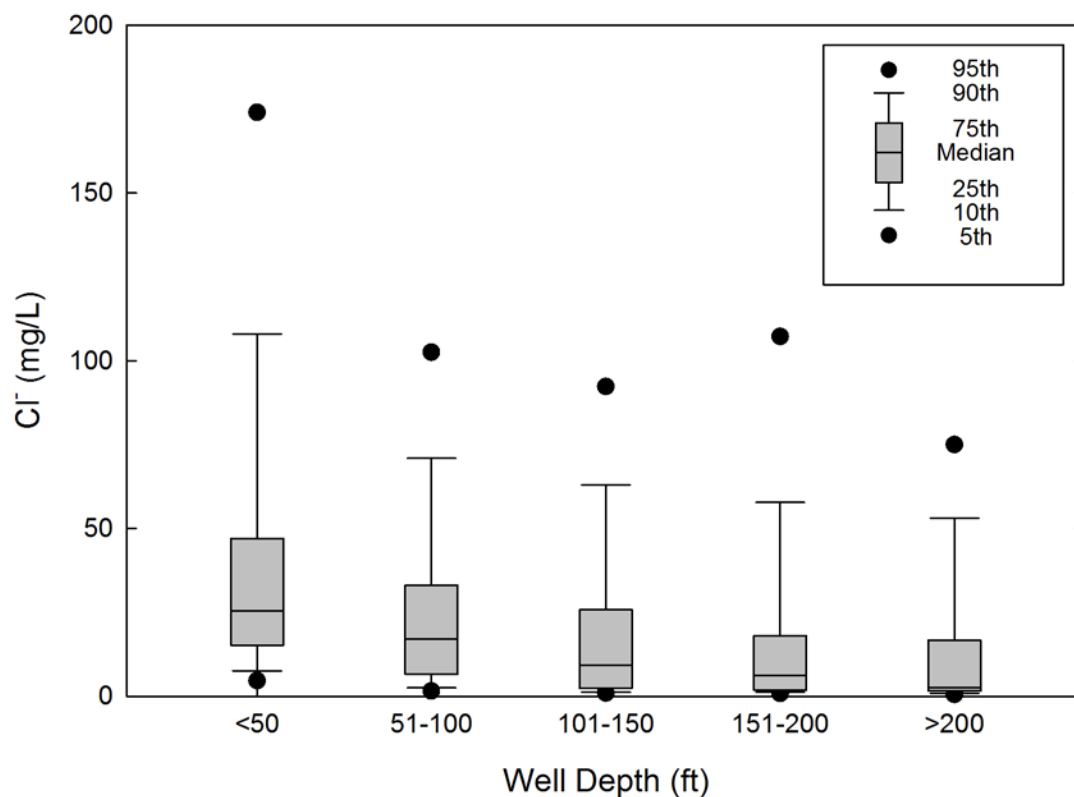


Figure 24. Box-and-whisker diagram for Cl⁻ concentrations in Quaternary aquifers in Illinois as a function of well depth. Concentrations are significantly greater for each depth group compared to all deeper groups.

Bedrock Aquifers

Bedrock aquifers in Illinois are found in the northern third of the state and along the Mississippi River (Figure 18). Aquifers in the upper bedrock unit are used in the southern two-thirds of Illinois. Chloride concentrations vary widely (Figures 25 and 26), and primarily appear to be a function of depth, i.e., the deeper the well, the higher the concentration (Figure 27). Very high concentrations are likely primarily due to natural sources, i.e., recharge from brines; Pennsylvanian formations are the primary oil producing units in Illinois. Some of these wells may also be exhibiting contamination from leaky brine holding ponds commonly associated with oil drilling activities (Hensel and McKenna, 1989). In the sinkhole plain of southwestern Illinois (Monroe, Randolph, and St. Clair Counties), Mississippian limestones exhibit karst features (sinkholes, caves). These aquifers are extremely vulnerable to surface contamination, but Cl⁻ is not an important contaminant in this primarily rural region.

Devonian and Silurian Age aquifers are important aquifers in Illinois, heavily used in northeastern and northwestern Illinois (Figure 26). They are primarily of carbonate lithology, the most productive being fractured dolomites. The heaviest use of these aquifers is in the Chicago

region, in DuPage, northern Will, southern and western Cook, and western Lake Counties. These bedrock units dip towards the south, and Cl⁻ concentrations are significantly greater in areas where the Devonian-Silurian aquifers are deeper (Figures 26 and 27). In northeastern Illinois, the tops of the bedrock aquifers are often in contact with sand and gravel glacial units. Wells are often screened in this interval due to its large hydraulic conductivity. These Silurian bedrock aquifers also show the increasing trend in Cl⁻ concentrations seen in the sand and gravel aquifers due to road salt runoff (Kelly, 2008). More than half of public supply wells finished in these aquifers tested by Kelly (2008) have statistically significant increasing trends in Cl⁻ concentrations.

The oldest aquifers in Illinois are found in the northern third of the state and are Cambrian and Ordovician aged. These aquifers are primarily sandstones and are heavily used in the northern part of Illinois, especially centered around Joliet and Aurora south and west of Chicago, respectively. In general, the salinity of water in the Cambrian-Ordovician aquifers is lowest in north-central and northwestern Illinois where the Ancell Aquifer outcrops at the surface and recharge is occurring (Figure 28). Salinity generally increases to the east and south in the direction of flow and stratigraphic dip. Below a latitude of about 40° the water in these aquifers is unpotable due to high TDS levels. Chloride concentrations tend to increase with well depth (Figure 29).

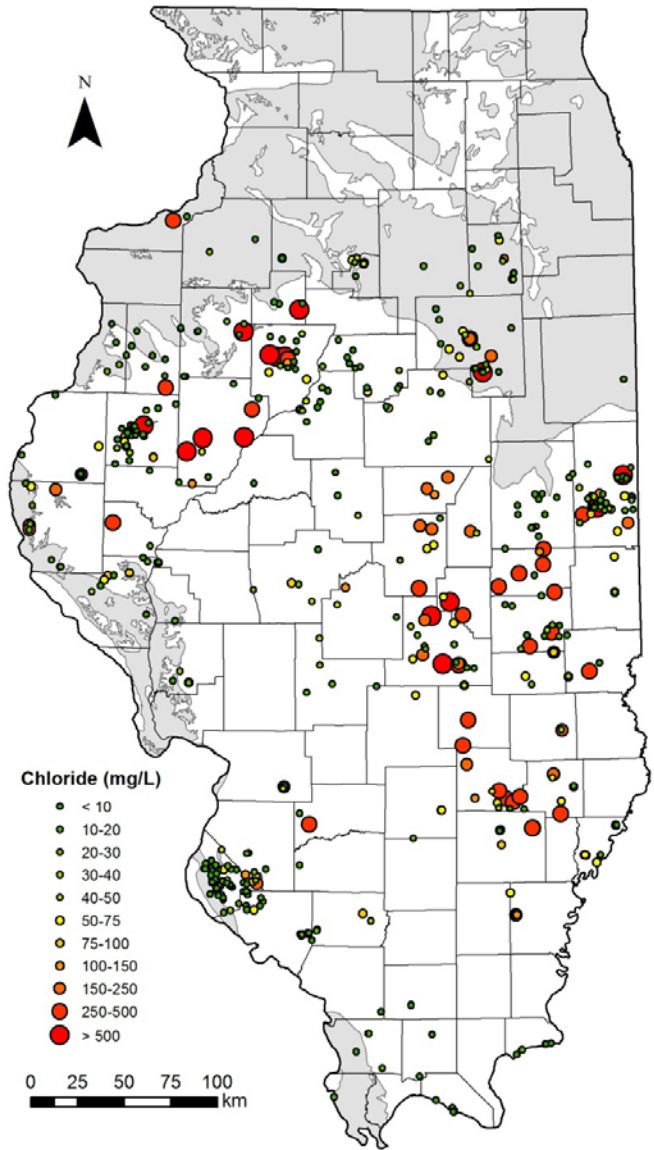


Figure 25. Chloride concentrations in wells open to upper bedrock aquifers (Pennsylvanian-Mississippian). Extent of Silurian-Pennsylvanian aquifers indicated by gray.

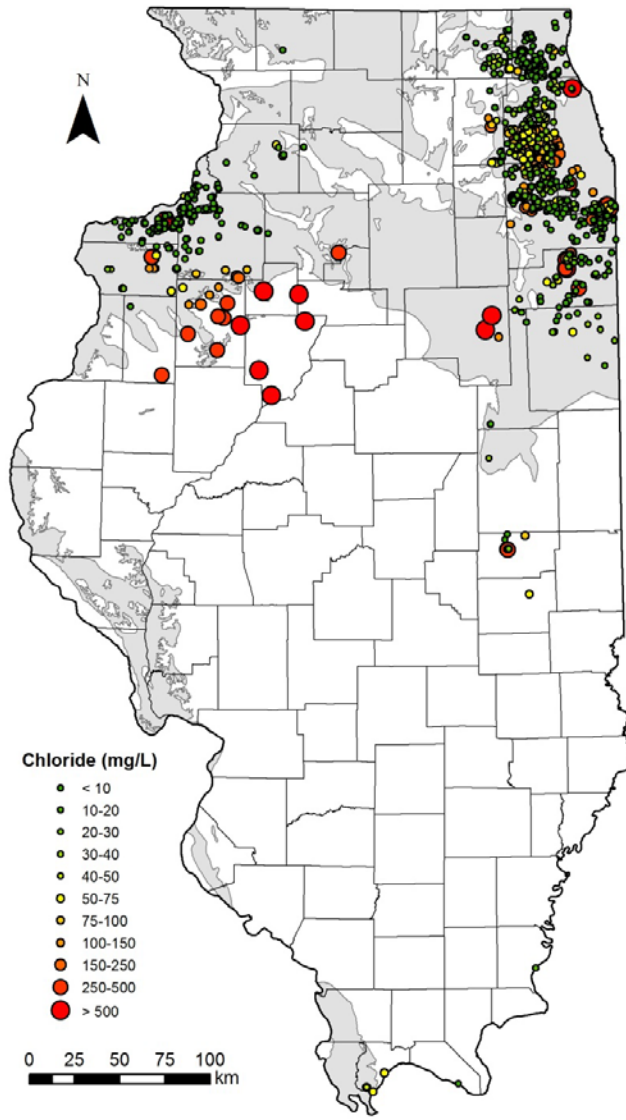


Figure 26. Chloride concentrations in wells open to Devonian-Silurian bedrock aquifers. Extent of Silurian-Pennsylvanian aquifers indicated by gray.

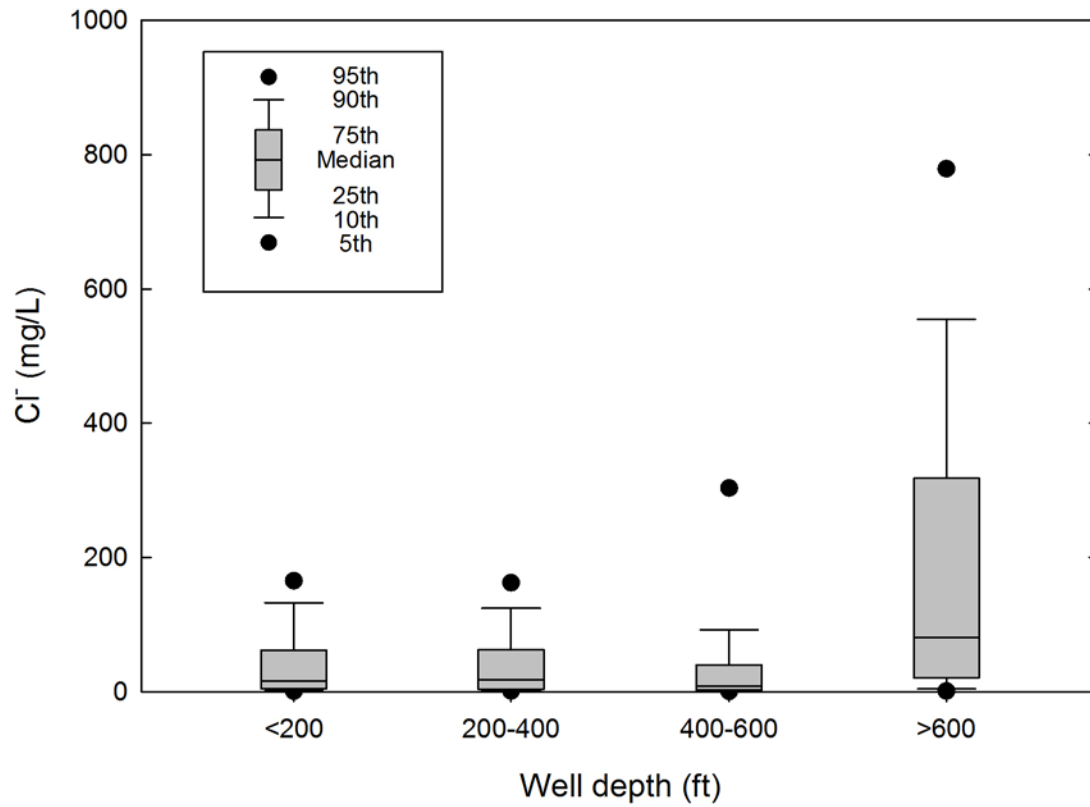


Figure 27. Chloride concentrations as a function of depth for wells completed in Silurian-Devonian bedrock aquifers. The deepest group has significantly greater concentrations than all three shallower groups (ANOVA on ranks).

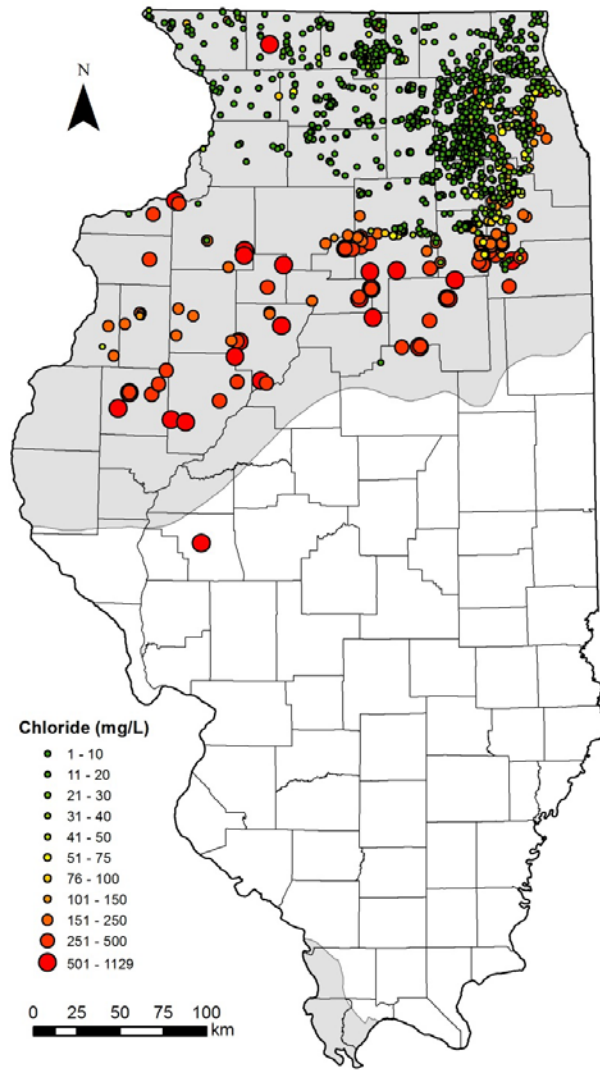


Figure 28. Chloride concentrations in wells open to Cambrian-Ordovician aquifers. Extent of Cambrian-Ordovician aquifers indicated by gray.

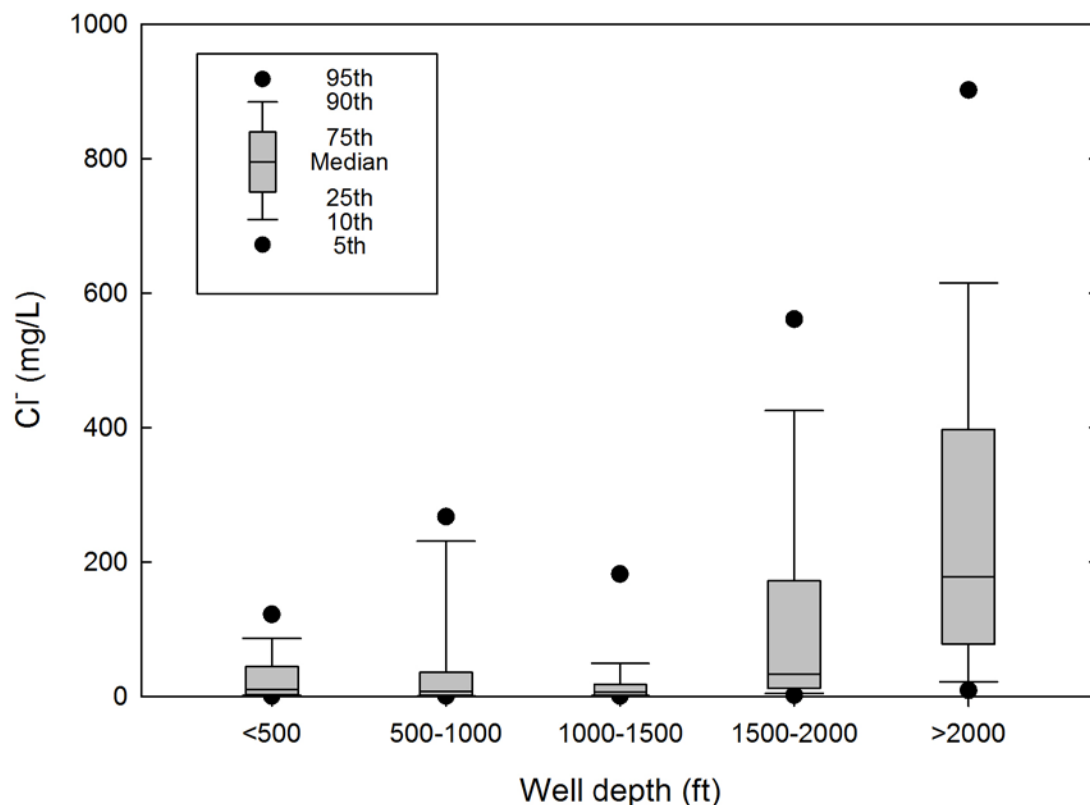


Figure 29. Chloride concentrations as a function of depth for wells completed in Cambrian-Ordovician bedrock aquifers. The two deepest groups have significantly greater concentrations than all three shallower groups (ANOVA on ranks).

Saline Springs

Panno et al. (2010) reported that there are about 30 saline springs throughout the Illinois Basin (most of which are in Illinois) that are coincident with geologic structures within and at the margins of the basin (Figure 2). Saline springs in Illinois have been identified by others (i.e., Bartow et al., 1909; Willman and Payne 1941; Panno et al., 1994, 2006, 2011). Discharge of saline groundwater may be found along the LaSalle Anticlinorium in the form of shallow wells, salt marshes, and springs at Starved Rock, Matheson, and Kickapoo Creek State Parks, and as bedrock seeps into the Mahomet aquifer in east central Illinois (Panno et al., 1994, 2006). Similar saline springs are found in southern Illinois along the Rough Creek-Shawneetown Fault Zone near Equality, and many of these sites are historic in that they were used by Native Americans and early settlers as a source of salt for meat preservation and other uses (Panno et al., 2006, 2010). Chloride concentrations in these springs can range from several hundred to greater than 30,000 mg/L in the case of the Vermilion Salines in Kickapoo Creek State Park (Panno et al., ISGS, unpublished data). The sources of these saline springs range from Cambrian- to Pennsylvanian-age formations (Panno et al., 2010).

Trend Analysis

Shallow aquifers in northeastern Illinois have been heavily impacted by human activities, with the most obvious sign being increasing Cl^- concentrations. Kelly (2008) showed that Cl^- concentrations in shallow groundwater in the Chicago region have been increasing since the 1960s. Over half of the shallow (< 200 ft; 60 m) public supply wells evaluated ($N = 239$) had statistically significant increasing trends in Cl^- concentrations, and there did not appear to be a leveling off of trends for the most recent samples (1990–2005).

Chloride concentrations have been increasing in shallow aquifers since the 1950s–1960s (Figure 30). The median Cl^- concentration steadily increased from 6 mg/L prior to 1950 to nearly 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 1990–2005 group compared to the 1980s. The spread in concentrations has also been increasing, indicating spatial variability in sources of Cl^- contamination. Chloride had greater concentrations in the shallower (< 100 ft) wells than the deeper (100–200 ft) ones for all date groupings (Figure 31). These differences were statistically significant at most time periods for Cl^- . Concentration trends were generally the same for both the shallower and deeper wells. There were increasing trends for Cl^- concentrations for both shallower and deeper wells, with the median concentration increasing from 8 to 36 mg/L in the shallower wells and from 5 to 17 mg/L in the deeper wells from prior to 1950s–1960s to 1990–2005.

For individual counties, the greatest temporal changes for Cl^- were generally found in the western counties, DuPage, Kane, McHenry, and, to a lesser extent, Will County to the south (Figure 31) (Kelly, 2008). In DuPage County, the median values of all major ions tended to increase, especially Cl^- , which increased from 4 mg/L prior to 1950 to 101 mg/L in the 1990s and later, an increase of more than 2500 percent. Chloride in Cook County was highest in the 1990–2005 data group, but there was little change in the previous groups. No significant change occurred in Cl^- concentrations in Lake County during the entire time span.

Kelly (2008) reported there were significant temporal increases in Cl^- concentrations for the majority of the municipal wells tested (55 percent), and significant positive slope values were calculated for 57 percent of the wells (Figure 32). Chloride trends varied spatially; Lake and Cook Counties had relatively low percentages of wells with increasing Cl^- trends (39 to 45 percent) and slope values, while DuPage, Kane, and McHenry Counties had much higher percentages of wells with positive trends (55 to 71 percent) and slope values. Almost half (112 of 239) of the individual public supply wells tested had at least one sample collected between 1990 and 2005. The same trends for Cl^- were observed for the wells with the most recent data compared to the entire group of wells, suggesting that there has not been a leveling off in Cl^- concentrations in the 1990s or later (Kelly, 2008).

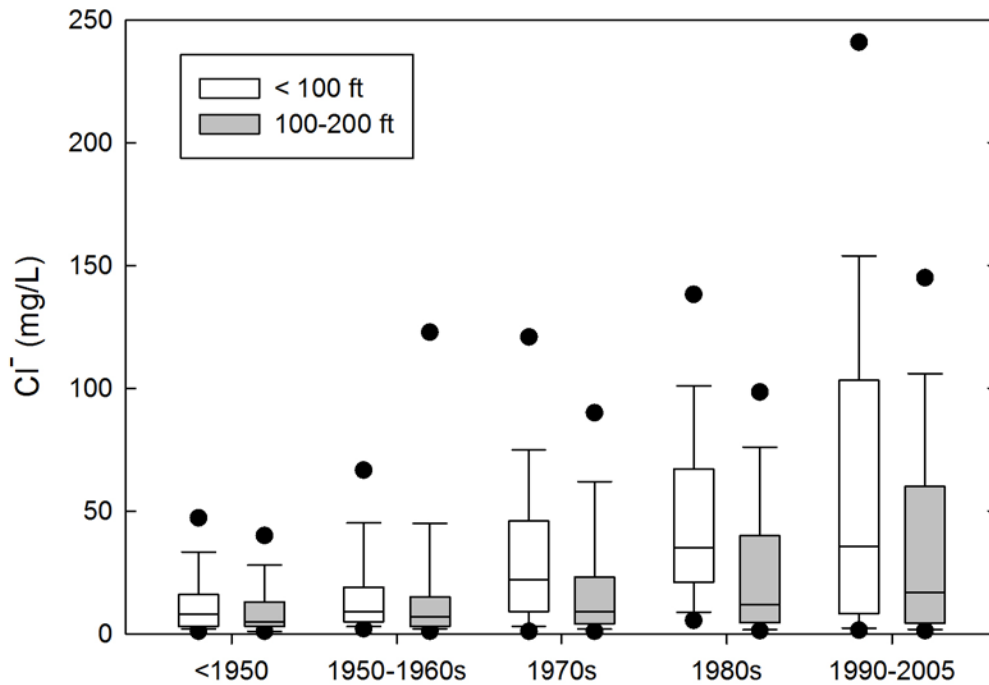


Figure 30. Box plots of Cl^- concentrations in shallow aquifers in the Chicago region. Circles show 5th and 95th percentile data. Figure from Kelly (2008).

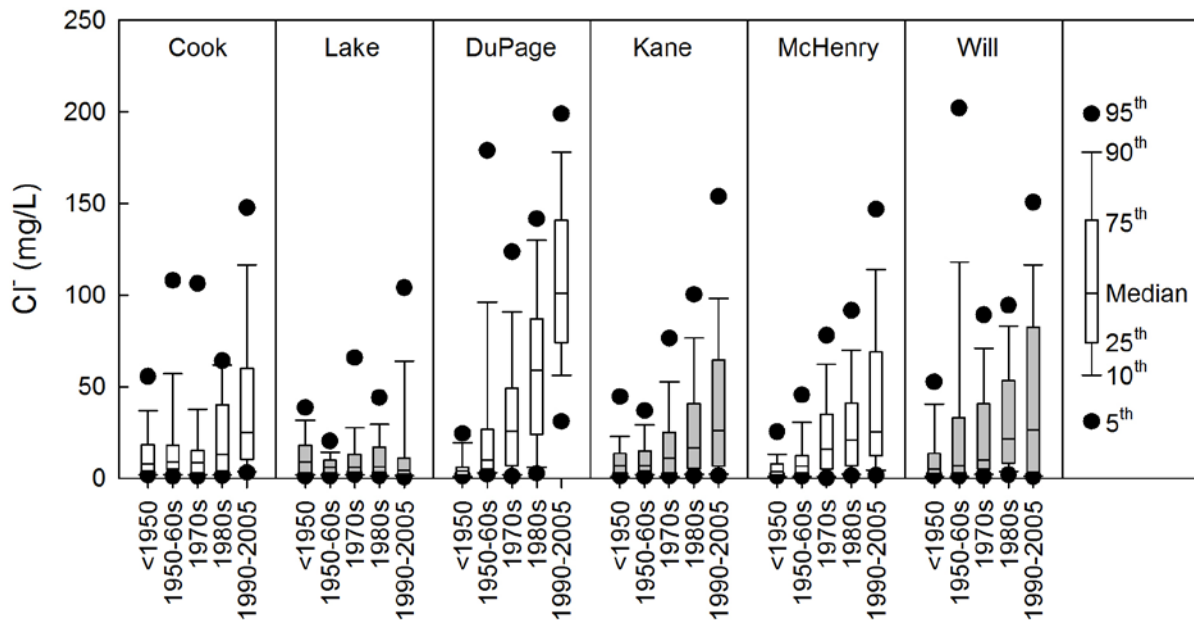


Figure 31. Box plots of Cl^- concentrations in shallow aquifers in the Chicago region by county. Figure from Kelly, 2008.

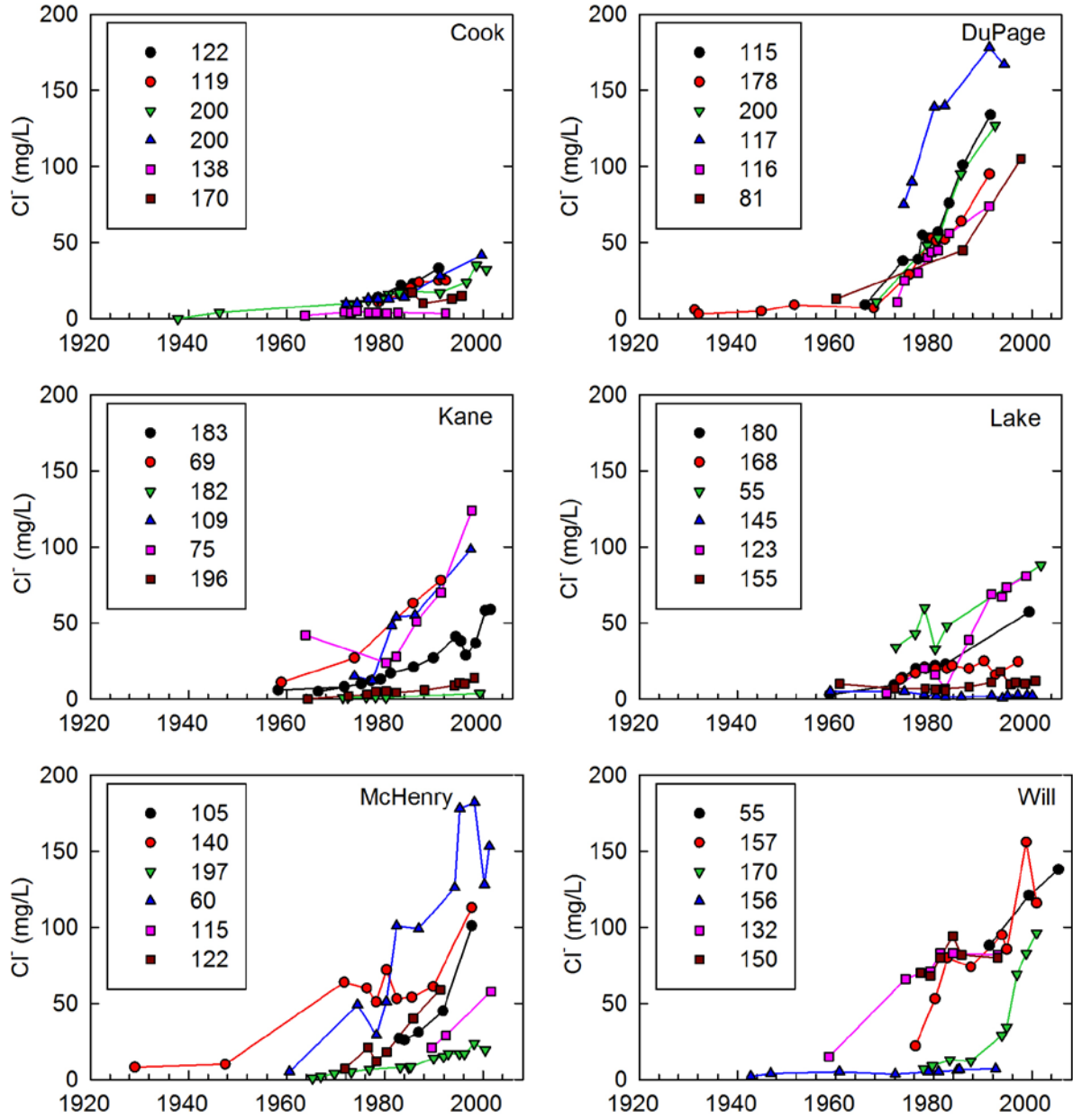


Figure 32. Chloride concentrations as a function of time for selected public supply wells in the Chicago region. Well depths (feet) in legends. Figure from Kelly, 2008.

Wetlands

Wetlands are defined as lands that transition between terrestrial and aquatic systems where the water table is usually at or near the surface or the land is covered by shallow water (U.S. Fish and Wildlife, 2011). Wetland substrates can be either predominantly undrained hydric soils or nonsoils that are saturated or covered by shallow water at some time during the growing season. Wetland types found in Illinois include marshes, swamps, bogs, and fens (USEPA, 2011b). Water quality in wetlands should generally reflect their source water, whether it is shallow groundwater or surface runoff, but land use activities adjacent to wetlands can strongly influence concentrations of Cl^- and other aqueous species within the wetlands.

There have been few published studies that include water quality data, and specifically Cl^- , for wetlands in Illinois. There are some published data for fens and bogs in northeastern Illinois. Fens are essentially springs that receive a very hard Ca-HCO_3 -type groundwater, while bogs receive surface water from more dilute runoff. Both types of wetlands are common in northeastern Illinois. Fens at Sterne's Woods State Natural Area near Crystal Lake and South Elgin Fen near South Elgin were found to be contaminated with road salt and septic effluent (Panno et al., 1999, 2006). One part of a fen at Sterne's Woods that was reported to be in near pristine condition had Cl^- concentrations between 8.8 and 44 mg/L. Two other fens affected by septic effluent and road salt had Cl^- concentrations as high as 339 mg/L and 283 mg/L, respectively. Septic effluent and road salt discharged into South Elgin Fen increased the Cl^- concentration to 116 mg/L (Panno et al., 2005). In cases where septic effluent discharged into fens, the diverse fen-wetland vegetation was replaced by a more salt-tolerant monoculture of cattails (*Typhaangustifolia*). Panno et al. (1999) reported that fen vegetation diversity was profoundly reduced when Cl^- concentrations exceeded 45 mg/L. Road salt runoff has reduced plant diversity in wetlands of northern Illinois, where very high Cl^- concentrations have produced wetlands that can only support cattails and other halophilic vegetation (e.g., *Phragmitesaustralis*).

Discussion and Conclusions

Prior to major settlements in Illinois, Cl^- concentrations in most shallow groundwater and rivers and streams were very low, probably < 10 mg/L, and in many cases much lower. The exceptions were areas where natural brines in Paleozoic sedimentary rocks discharged at or near the land surface. There were numerous saline springs that were exploited by Native Americans and early settlers for making salt. There are numerous streams and rivers in Illinois with names such as Salt Creek or Saline Branch, named because of the discharge of saline water in or near these streams.

Once Illinois became settled as the population grew, contamination of water began. Chloride was not an important component of contamination sources in the 19th century, with the possible exception of livestock waste. It wasn't until around the middle of the 20th century that the important sources of Cl^- contamination, i.e., water conditioning salt, KCl fertilizer, and road deicers, began to be used in large amounts in Illinois. Since that time, there has been an increase

in Cl⁻ concentrations in many water bodies in Illinois, and there does not yet appear to be any slackening in its increase in groundwater or surface waters (Kelly, 2008; Kelly et al., in press).

One of the most likely results of increasing Cl⁻ concentrations in surface waters is degradation of aquatic biota. We are unaware of any systematic studies of the effects of elevated levels of Cl⁻ on aquatic biota in the Chicago area, but it seems certain that there would be negative effects. Corsi et al. (2010) reported that seven of 13 streams in the Milwaukee, WI, area exhibited toxicity to water fleas (*Ceriodaphnia dubia*) and fathead minnows (*Pimephales promelas*) due to road salt runoff. They measured very high Cl⁻ concentrations in some of the streams (commonly > 1,000 mg/L and up to 7,730 mg/L). While these are higher than typically found in stations monitored in Chicago, some of the smaller streams occasionally had Cl⁻ concentrations > 1,000 mg/L, and smaller streams that are unmonitored undoubtedly experience even higher concentrations.

Chicago, many of its suburbs, and many other cities in Illinois have combined sewer systems, with storm water runoff being collected and treated at WWTPs. A large percentage of road salt runoff in the most urban parts of the Chicago region thus does not enter shallow groundwater but is diverted to streams and rivers in discharge from WWTPs. The rapid transfer of saline snow melt to streams and rivers in Chicago produces very high Cl⁻ concentrations in the winter. However, some road salt runoff ends up in the soil zone and shallow groundwater, and this could represent a relatively long-term source of Cl⁻ and other ions to surface water.

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