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2008-42

Study of Environmental Effects of De-Icing Salt on Water Quality in the Twin Cities Metropolitan Area, Minnesota

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A study was conducted to generate knowledge on the environmental effects of de-icing salt, particularly sodium chloride (NaCl), on water quality in Minnesota, especially the Twin Cities Metropolitan Area (TCMA). The Mississippi River receives substantial sodium chloride inputs from the Minnesota River and waste water treatment plants as it passes through the TCMA. In addition, road salt applications in the TCMA use about 350,000 short tons of NaCl every year. A chloride budget at the scale of the TCMA and on individual sub-watersheds in the TCMA indicates that about 70% of the road salt applied in the TCMA is not carried away by the Mississippi River. Rates of seasonal road salt use are correlated with snowfall, road miles and population. Salinity in TCMA lakes increases in winter and decreases in summer. Ionic composition of dissolved substances in lakes of the TCMA suggests unnaturally high sodium and chloride concentrations compared to lakes and other water bodies in the Midwestern U.S. Data indicate a rising trend in urban lake water salinity over the last 30 years. Shallow groundwater in the TCMA, especially near major roadways, has started to show increasing chloride concentrations. Salinity trends in lakes and shallow aquifers of the TCMA are of concern.

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Study of Environmental Effects of De-Icing Salt on Water Quality in the Twin Cities Metropolitan Area, Minnesota

Final Report

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The technical findings presented in this report were obtained by Eric Novotny, Ph.D. candidate, and Andrew Sander, M.S. graduate student, in the Department of Civil Engineering under the guidance of Heinz Stefan, James L. Record Professor of Civil Engineering and Omid Mohseni, Associate Director for Applied Research, at the St. Anthony Falls Laboratory.

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Executive Summary

Salt has been widely used for ice and snow control on roads in the US, Canada and other parts of the world affected by adverse winter driving conditions. The primary product used in North America for deicing of roads is sodium chloride (NaCl), a readily available and inexpensive material that provides adequate treatment to roadways under winter conditions. In winter and spring, road salt dissolved in the runoff from roadways and parking lots enters ditches, streams or storm sewers, which, in turn, drain into rivers and lakes, estuaries and oceans.

The use of sodium chloride as a road de-icing chemical has increased dramatically in the northern areas of the United States over the last 50 years. The leading states in highway road salt use are Minnesota, Michigan, New York, Ohio, and Pennsylvania. About 23 million tons of salt were spread on road surfaces, parking lots, sidewalks etc. in the United States in 2005. Sodium chloride is a highly soluble substance that easily travels with the water into storm sewers, streams, rivers, lakes, wetlands and groundwater. The final recipients (sinks) of sodium chloride dissolved in water are terminal water bodies such as the oceans, saline terminal lakes, and (deep) groundwater. Chloride has adverse effects on aquatic plants and invertebrates. In Minnesota water quality standards for chloride are 230 mg/L for chronic exposure and 860 mg/L for acute exposure. These standards are intermittently exceeded in a few fresh water bodies in Minnesota.

The overall objective of this project was to create knowledge about the effects of de-icing salt, particularly sodium chloride, on water quality in lakes, rivers, streams and groundwater in Minnesota. To this end, several specific goals were pursued:

(1) Data on the use of sodium chloride in the Twin Cities metropolitan area as road salt, were assembled. The data were correlated with snowfall, road lengths and population.

(2) Data on sodium chloride concentrations in streams, rivers, lakes, and groundwater in Minnesota, especially in the Twin Cities area, were assembled and analyzed for regional differences and trends over time

(3) A chloride budget at the scale of the Twin Cities Metro Area was developed including all major chloride uses and discharges, to establish how much of the imported road salt is exported by the Mississippi River; a similar budget was developed at the scale of several small sub-watersheds for comparison.

(4) Several lakes in the Twin Cities Metro Area were monitored for chloride and temperature on a monthly timescale to see seasonal effects that could be related to road salt applications. Ionic composition of lake waters in the Twin Cities Metro Area were determined and compared to other regional water bodies to determine the prevalence of sodium and chloride. Historical data on lake salinity were assembled to determine lake salinity trends in the Twin Cities metro area.

(5) Data on chloride concentrations in Minnesota's groundwater were assembled and analyzed.

The results of this study provide baseline information on seasonal and long-term effects of road salt applications on water resources at a regional scale (metropolitan area) and a local scale (lake watershed). Information is provided on the geographic distributions of chloride concentrations in surface water bodies and in groundwater, on salt residence times in lakes and and on trends in chloride concentrations of lakes and rivers. Specific preliminary results are:

(1) About 350,000 (short) tons of road salt (NaCl) are applied in the Twin Cities Metro Area every year.

(2) The sodium chloride load of the Mississippi River increases substantially as it passes through the Twin Cities Metro Area. Substantial salt contributions come from the Minnesota River and from waste water treatment plant effluents. Road salt contributions appear in tributary streams and storm sewers, and are highly seasonal.

(3) Many Twin Cities metro area lakes have unnaturally high sodium and chloride concentrations, and these chloride concentrations have a rising trend.

(4) Twin Cities Metro Area lakes have increasing salinity in winter and decreasing salinity in summer, a cycle that corresponds to seasonal road salt applications.

(5) Only about 30% of the road salt applied in the Twin Cities Metro Area is carried away dissolved in the Mississippi River. 70% is not accounted for. Removal by wind in the form of dust or in products that are shipped out of the area, has not been documented, and is currently assumed to be small.

(6) Shallow groundwater aquifers in the Twin Cities Metro Area especially near major roadways have started to show rising chloride concentrations.

(7) Present trends in the chloride concentrations of urban lakes and shallow aquifers are a cause of concern.

The overall conclusion has to be that some deterioration of the water quality of Twin Cities Metro Area lakes due to increasing chloride levels is in progress. No acute problems have been documented yet, but present trends will lead to violations of water quality standards in some urban lakes. Similarly shallow groundwater in the Twin Cities Metro Area appears to receive sufficient salt input annually so that water quality deterioration is likely to be evident in the next decades.

The recommendation is that serious consideration needs to be given to the reversal of current trends. Among the alternatives are changes in road salt use, rerouting of snowmelt water away from lakes and groundwater recharge areas, collection and treatment of saline surface runoff, remediation of shallow groundwater and lake salinity.

Chapter 1

Introduction: Sodium chloride Sources, Uses and Pathways in the Environment

1.1 Sodium chloride (NaCl) sources

The use of sodium chloride as a de-icing chemical has increased dramatically in the northern areas of the United States over the last 50 years (Figure 1.1). The leading states in highway salt use in the United States are Minnesota, Michigan, New York, Ohio and Pennsylvania (Novotny, Smith et al. 1999). Using the estimation done by Marsalek (2003), 9.5 million tons of salt are being added to the runoff in the United States each year. This salt eventually finds its way into lakes, rivers and groundwater.

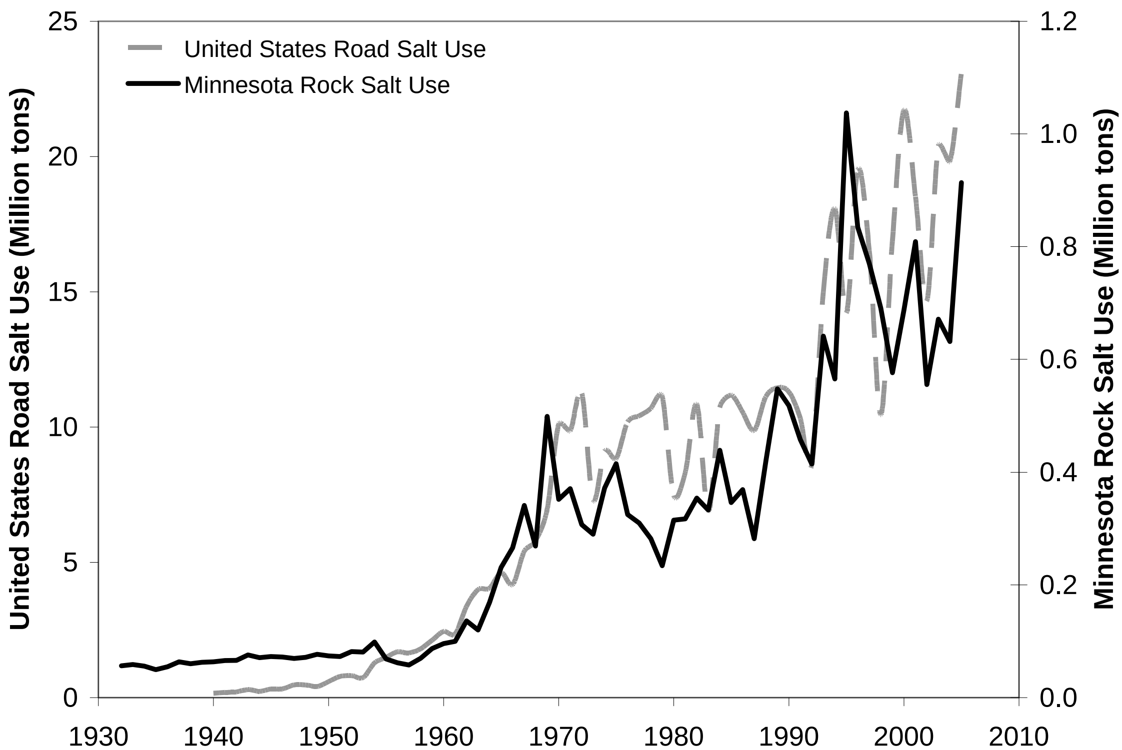

Figure 1.1 Annual road salt purchases for de-icing application in the United States and rock salt purchases for road de-icing by the state of Minnesota.

Sodium and chloride are used for many purposes in the United States including agriculture, chemical production, road de-icing, food processing, metal production, paper production, petroleum, textiles and dying and water softening (Kostick 2004). In 2004 sodium and chloride salts were used in the United States mainly for two purposes: chemical production and road deicing. These two uses accounted for 20.3 Mt (Mt = million tons) and 18.9 Mt, respectively, while all other uses combined totaled 12.3 Mt (Kostick 2004). 37% of the salt use in the United States was used for road de-icing. In the state of Minnesota the ratio is much higher. In 2004 the state of Minnesota used 575,000 tons of rock salt compared to 343,000 tons of evaporated salt (Kostick 2004). In Minnesota rock salt is mainly used for road de-icing, i.e. 62% of the salt use in Minnesota in 2004 was for road salt applications. Sodium and chloride are released to the environment by de-icing applications, industrial wastewater effluents and emissions, landfill leaching, fertilizer applications, and from salt storage facilities and water softeners. Most point or non-point sources of sodium and chloride are anthropogenic, but there are a few natural sources of chloride and sodium in the environment: mineral sodium chloride deposits, weathering of geological formations and wet deposition originating from ocean evaporation (Jackson and Jobbagy 2005).

In many environments the natural source of chloride is very low. For example, in Canada, normal background concentrations of chloride are no more then a few mg/L (ECHC 1999). The same can be said for SE Minnesota where there are no significant natural sources of chloride (Wilson, Crawford et al. 2006). In a sand and gravel aquifer in northeastern Illinois background groundwater concentrations of Cl- were between 1 and 15 mg/L, much lower than concentrations found near roadways (Panno, Hackley et al. 2002). Natural wet deposition of salts also contributes to sodium and chloride concentrations, but compared to de-icing salt applications its effect is minor. Natural wet deposition of Na and Cl over the entire United States was estimated to be 2.2 Mt/year, much lower then the 18.9 Mt of salt added to the environment through road salt applications in 2004 in the United States (Jackson and Jobbagy 2005). Wet deposition is highest next to an ocean. In the Twin Cities Metropolitan area rainwater has been measured to contain 0.1 mg/L of NaCl; typical concentrations in the Midwest were found to be 0.3 mg/L (Panno, Hackley et al. 2002) much lower then the national average of 0.6 (Andrews, Fong et al. 1997).

Salt applied to a road during the winter eventually finds its way into soil, streams, lakes, wetlands and the groundwater. The water bodies that are most effected by road salt application seem to be small ponds draining large urban areas, and streams, wetlands and lakes that receive runoff from major roadways where high salt applications are common (ECHC 1999).The sodium and chloride ions are transported in the snowmelt runoff as well as through the air by splashing and spray from vehicles, and as windborne powder (ECHC 1999).

In snowmelt water the sodium and chloride ions dissociate from one another. Once dissolved in the runoff, the sodium and chloride ions are transported from urban areas to receiving waters in one of three pathways: a rapid runoff pathway corresponding to stormwater overland flow from impervious and pervious surfaces, a shallow subsurface pathway defined as fast soil storage, and a deeper and slower soil storage pathway know as baseflow (Novotny, Smith et al. 1999).

On pathway (1) both chloride and sodium act as a conservative material, i.e. equal ionic equivalents of sodium and chloride are delivered to a lake or river that receives the direct runoff. If snowmelt water follows pathways (2) and (3) more chloride will be present then sodium. The chloride ions are conservative in the soil and will pass readily into the groundwater (ECHC 1999), although retention in the capillary water makes the residence times for Cl- longer than that of water (Mason, Norton et al. 1999). Sodium on the other hand exchanges with other cations adsorbed to soil particles such as calcium, magnesium, potassium and hydrogen ions via cation exchange (Mason, Norton et al. 1999).

1.2 Ultimate fate (sinks) of road salt

Road salt can be transported dissolved in water or as powder by air to several 'final' destinations: atmospheric deposition on plants, soils or infrastructure; accumulation in surface water bodies (lakes, wetlands, estuaries and oceans), accumulation in soils and rocks, and groundwater.

Road salt that was dissolved, but is left behind on dry road and land surfaces after the water has evaporated is re-suspended and carried away by the wind as can be observed on windy days after road salt was applied e.g. on black ice. The particles that enter the atmosphere are believed to be very small, and have been found on leaves of plants several hundred meters away from the nearest road. No studies could be found on salt transport away from an entire city or metropolitan area. Studies on roadways have found that almost all of the salt transported by air can be found within 40 m from the road it was applied on with 90% found within 20 m (Bloomqvist and Johansson 1999).

Salt (NaCl) dissolves readily in water and is easily transported over long distances as a solute in water. Saline snowmelt water enters the soil through infiltration or flows through storm sewers or ditches into detention ponds, wetlands, lakes and rivers. In urban settings, the amount of runoff through storm sewers is increased by impervious areas. In the TCMA, there are many natural lakes, creeks and two main rivers that receive snowmelt runoff. The Mississippi River is the largest waterway that transports surface and groundwater from the TCMA.

Snowmelt water that infiltrates into the soil or seeps from streams, ditches, ponds, wetlands and lakes is likely to flow into the groundwater. The salt in the snowmelt water will then become part of the groundwater.

1.3 Adverse effects of road salt applications on the environment

Road salt applications keep roads free of ice for safe winter travel in northern climate regions where air temperatures fall below 0°C. However, road salt can affect the chemistry and biota in the soil and water (Thunquist 2004). Organisms in streams and shallow, small lakes and ponds are particularly vulnerable to road salt application and chloride pollution (ECHC, 1999). Chloride concentrations of 30 mg/L in soils have been found to be lethal to land plants. Salinity levels of 1000 mg/L can have lethal and sub-lethal affects on aquatic plants and invertebrates (ECHC 1999). Continuous levels of as low as 250 mg/L have been shown to be harmful to aquatic life and to render water non-potable for human consumption (ECHC 1999). That is why chloride standards of 860 mg/L for acute events and 230 mg/L for chronic pollution have been established by the Minnesota Pollution Control Agency (MPCA) for surface waters in Minnesota designated as important for aquatic life and recreation (Minnesota R. Ch. 7050 and 7052). The groundwater standard for chloride has been set at 250 mg/L by the USEPA (USEPA, 1992). Increases in sodium and chloride concentrations have been shown to decrease the biodiversity in wetland areas and waterways (Richburg and Lowenstein 2001, Panno , Hackley et al. 2002). Wood frog species richness in wetlands in northwestern and southwestern Ontario have been negatively impacted with increased stress, increased mortality, and altered development resulting from acute and chronic exposure to road salts (Sanzo and Hecnar 2006). Fish diversity and richness were also shown to decrease with the increase in impervious surfaces in river watersheds in the Twin Cities area while chloride and sodium increased (Talmage et al. 1999). Macroinvertebrates on the other hand have not been shown to be affected by levels of chloride found in wetlands (Blasius and Merritt 2002, Bendow and Merritt 2004). Chloride ranks third among chemical ion species for the regulation of diatom species, and is therefore used by paleo-limnologists to reconstruct chloride levels in lakes from sediment cores (Ramstack, Fritz et al. 2003, 2004).

Increases in sodium and chloride can also increase the mobility of metals located in the soils along major highways (Amrheln et al. 1992, Oberts 2003, Backstrom et al. 2004, Norrstrom 2005). In Sweden a strong relationship was seen between trace metal (Cd, Cu, Pd, Zn) mobilization and application of deicing salts. The mobilization was found to take place in the winter months contrary to natural processes in boreal regions and caused by ion exchange, a lowered pH, chloride complexation and colloidal dispersion (Backstrom et al. 2004). Consequently, colloidal assisted transport caused by NaCl from deicing chemicals has been seen to contribute to Pb contamination of groundwater (Norrstrom 2005). The impact to soil chemistry has was restricted to within 10 meters of the road with the most significant soil exchange processes happening within 6 meters of the salt applications (Norrstrom and Bergstedt 2001). The sodium continues to exchange with calcium, magnesium and even potassium until equilibrium is reached; from then on sodium will act conservatively (Mason et al. 1999).

1.4 Research objectives

The overall objective of this project was to create knowledge about the environmental effects of de-icing salt, particularly sodium chloride on water quality in lakes, rivers, streams and groundwater in Minnesota. To this end, several specific goals were pursued:

(1) Data on the use of sodium chloride in the Twin Cities Metropolitan Area (TCMA) (Figure 1.2) as road salt, were assembled. The data were correlated with snowfall, road lengths and population.

(2) Data on sodium chloride concentrations in streams, rivers, lakes, and groundwater in Minnesota, especially in the Twin Cities area, were assembled and analyzed for regional differences and trends over time

(3) A chloride budget at the scale of the Twin Cities area was developed including all major chloride uses and discharges, to establish how much of the imported road salt is exported by the Mississippi River; a similar budget was developed at the scale of several small sub-watersheds for comparison.

(4) Several lakes in the Twin Cities area were monitored for chloride and temperature on a monthly timescale to see seasonal effects that could be related to road salt applications. Ionic composition of lake waters in the Twin Cities metro area were determined and compared to other water bodies to determine the prevalence of sodium and chloride. Historical data on lake salinity were assembled to determine lake salinity trends in the Twin Cities metro area.

(5) Data on chloride concentrations in Minnesota's groundwater were assembled and analyzed.

The results of the research conducted under this project will be summarized in this report. Detailed information can be found in four technical reports which cover

(1) an inventory of road salt uses in the Twin Cities Metro Area (TCMA),,
(2) a chloride budget for the TCMA,
(3) salinity measurements, variations and trends in lakes of the TCMA, and
(4) salinity distributions and trends in groundwater of Minnesota.

References of the four technical reports are:

Sander, A., E. Novotny, O. Mohseni, H. Stefan, "Inventory of Road Salt Uses in the Minneapolis/St. Paul Metropolitan Area". University of Minnesota, St. Anthony Falls Laboratory Report No. 503, December 2007, 46 pp.

Novotny, E., Sander, A., O. Mohseni, H. Stefan, "A salt (chloride) balance for the Minneapolis/St. Paul Metropolitan Area Environment". University of Minnesota, St. Anthony Falls Laboratory Report No. 513, August 2008, 23 pp.

Novotny, E., Sander, A., O. Mohseni, H. Stefan, "Road Salt Effects on the Water Quality of Lakes in the Minneapolis/St. Paul Metropolitan Area". University of Minnesota, St. Anthony Falls Laboratory Report No. 505, December 2007, 47 pp.

Sander, A., E. Novotny, O. Mohseni, H. Stefan, "Potential Groundwater Contamination by road Salt in Minnesota". University of Minnesota, St. Anthony Falls Laboratory Report No. 509, September 2008.

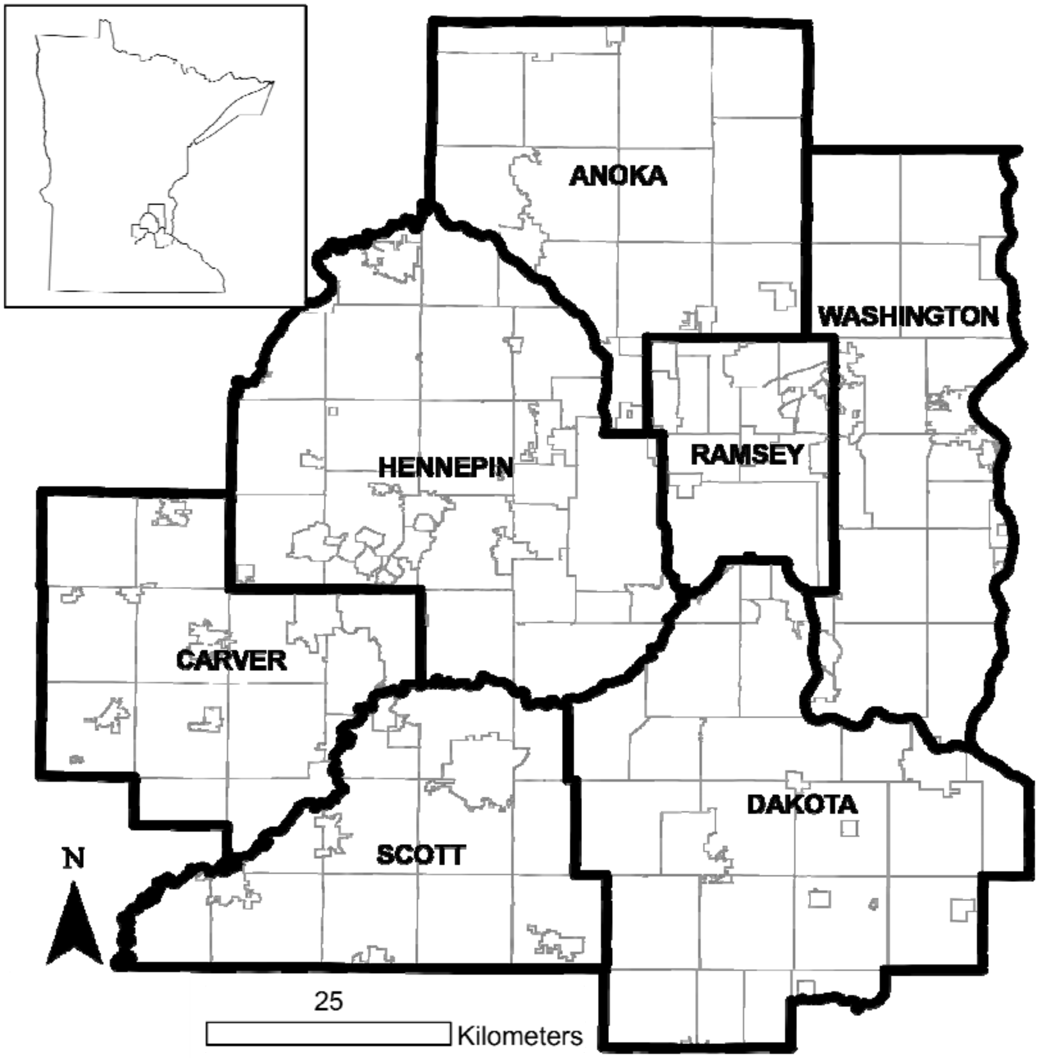

Figure 1.2 Twin Cities Metropolitan Area (TCMA), Minnesota.

Chapter 2

Use of Road Salt in the Twin Cities Metropolitan Area

2.1 Total road salt use in the TCMA

The Twin Cities Metropolitan Area (Figure 1.2) is home to 2.7 million people in 188 cities and townships. There are 949 lakes and 49 regional parks within the region. There are over 26,000 lane miles of roadways with impervious surfaces in the area, maintained by state, counties and municipalities. Interstate routes I35 and I94 pass through the area and are used extensively for the transport of goods and by daily commuters living or working in outer ring communities. Since the TCMA lies within the snow belt of North America, winter travel is a safety and economic concern for citizens and government officials. Nearly 12 million dollars are spent annually on road deicing products, mostly NaCl, by public agencies in Minnesota every year. This does not include any costs associated with equipment, maintenance or personnel.

Table 2.1 Summary of annual road salt application amounts in the TCMA.

User	Use (Tons)	Use (%)
Mn/DOT	80797	23%
Counties	70284	20%
Cities	114314	33%
Commercial Bulk	66349	19%
Packaged	17460	5%
Total	349204	100%

The total road salt use in the Twin Cities Metropolitan Area has been estimated and is summarized in Table 2.1. The amount of road salt that is applied by state, county and municipal agencies in the TCMA is on the order of 265,400 tons per season. This is approximately 2.8% of the total bulk deicing salt used by government agencies nationally (Salt Institute). The amount of bulk deicing salt applied by commercial snow and ice control companies is estimated to be on the order of 66,000 tons per season. Packaged deicer for home and commercial use is estimated at 17,460 tons per season, bringing the estimated total of deicing products to 349,000 tons per season for the 7-county Twin Cities Metropolitan Area (TCMA) . With a population of 2,780,000 living in the TCMA according to the last census, this amounts to 0.125 tons or 280 pounds of road salt per person per season. Road salt is applied by cities, by commercial users as bulk or packaged salt, Mn/DOT and counties (Figure 2.1 from Sander et al. 2007).

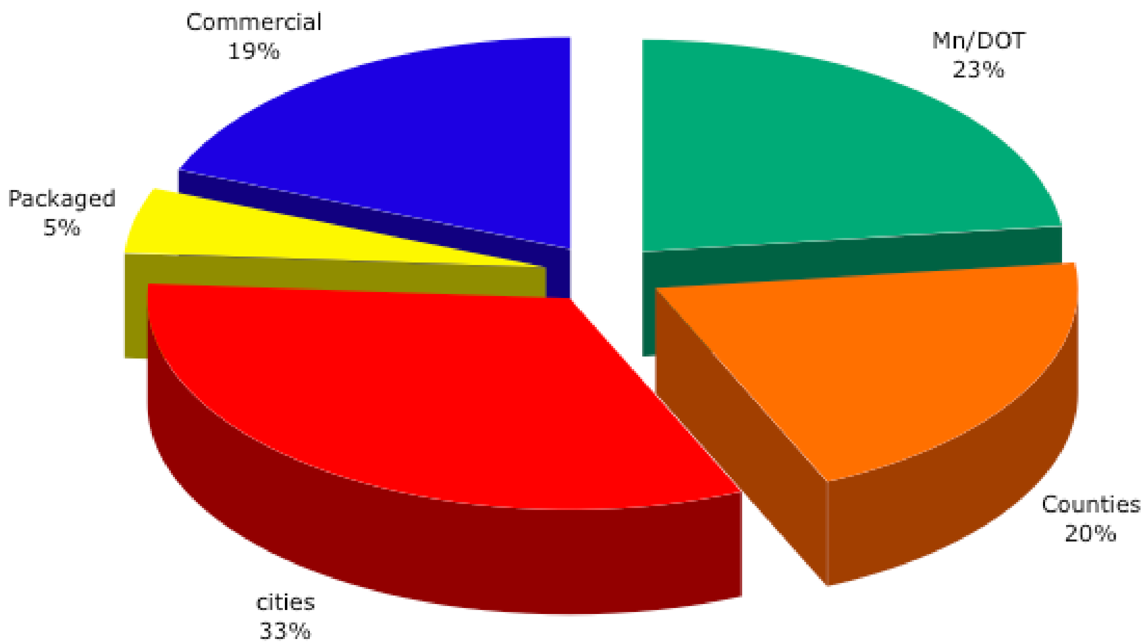

Figure 2.1 Distribution of road salt applications in the Twin Cities Metropolitan Area (TCMA). The total amount of road salt applied is approximately 350,000 (short) tons per season.

2.2 Salt use dependence on snowfall events, population and road length

There is a correlation between annual road salt use and the number of annual snowfall events as shown for Minneapolis and St. Paul in Figure 2.2. Weather data from the National Weather Service (NWS) were used to determine the number of days with snowfall in each year.

The data for twelve weather stations in the TCMA showed an overall average of 50 days (range from 30 to 65 days) with snowfall per year. When the annual road salt amounts were plotted against the average number of days with snowfall, a strong correlation was found (Figure 2.3).

Since the amount of road salt applied in the TCMA depends on the number of snowfall events (Figure 2.3) any snowfall increases in the future, due to global climate change (Seeley 2003), the need for road salt applications may increase as well.

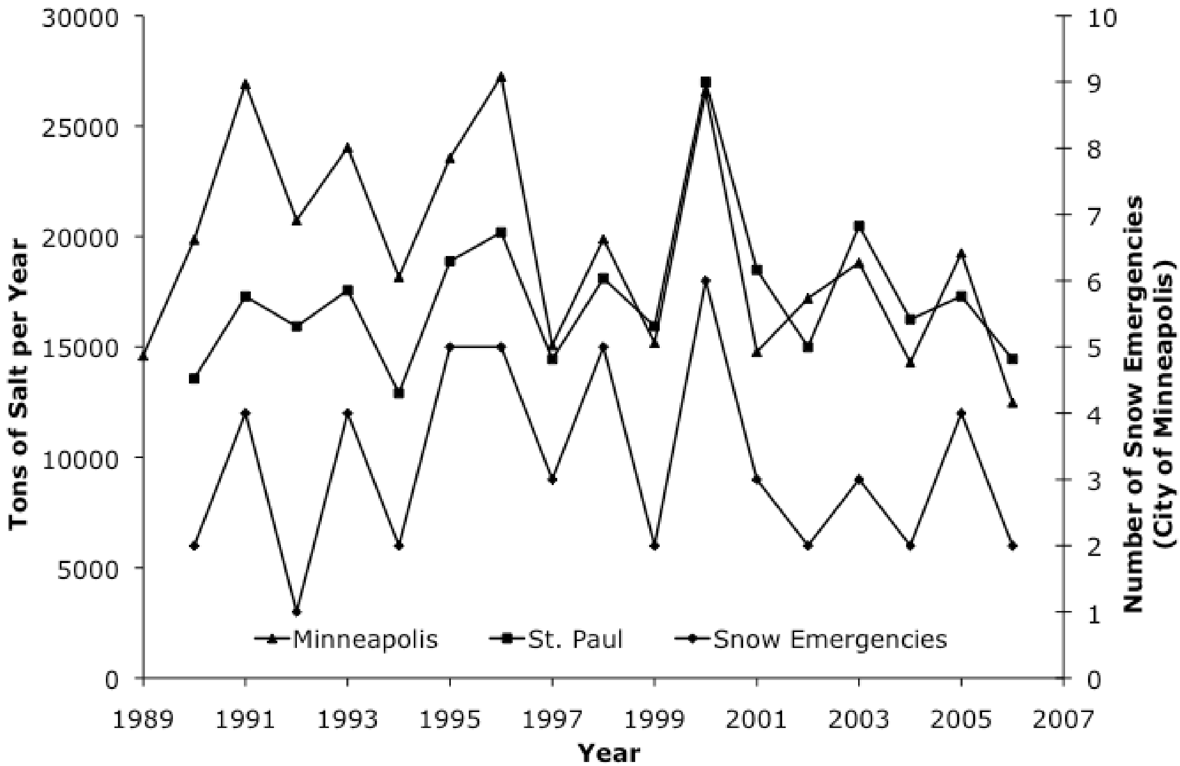

Figure 2.2 Road salt use (tons per season) and declared snow emergencies in Minneapolis and St. Paul.

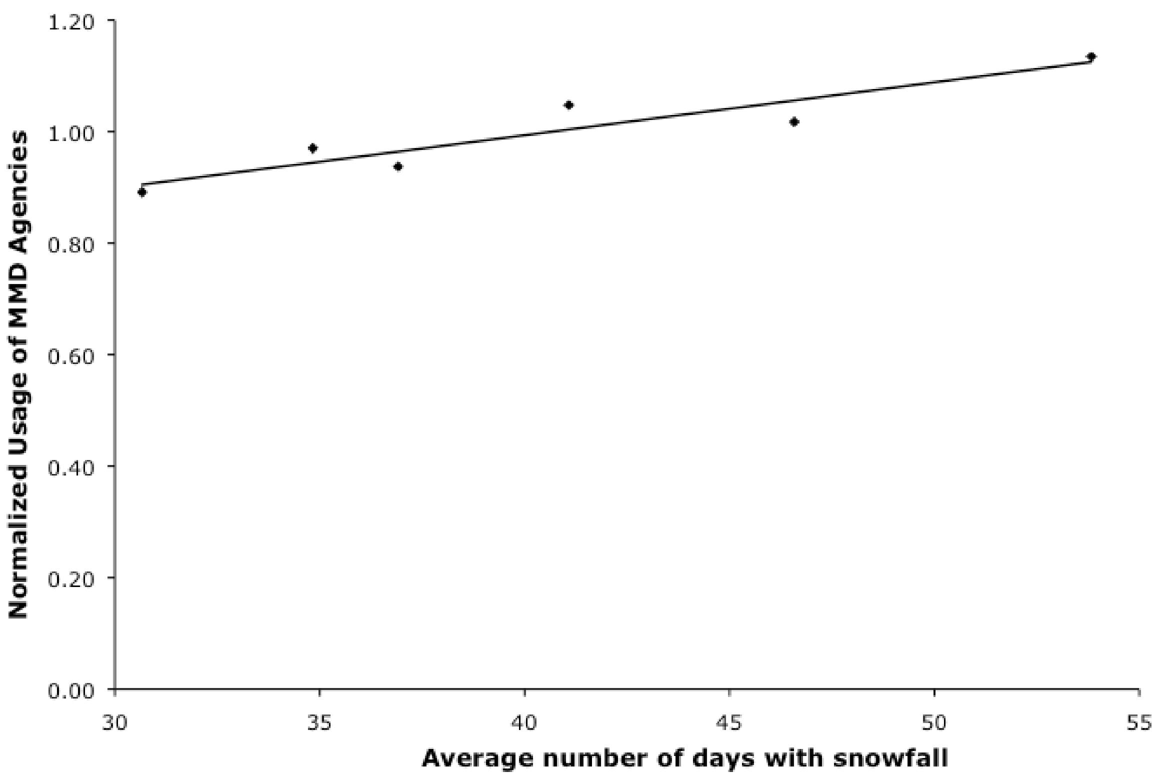

Figure 2.3 Annual road salt use in the TCMA by MMD contract participants vs. annual average number of days with snowfall.

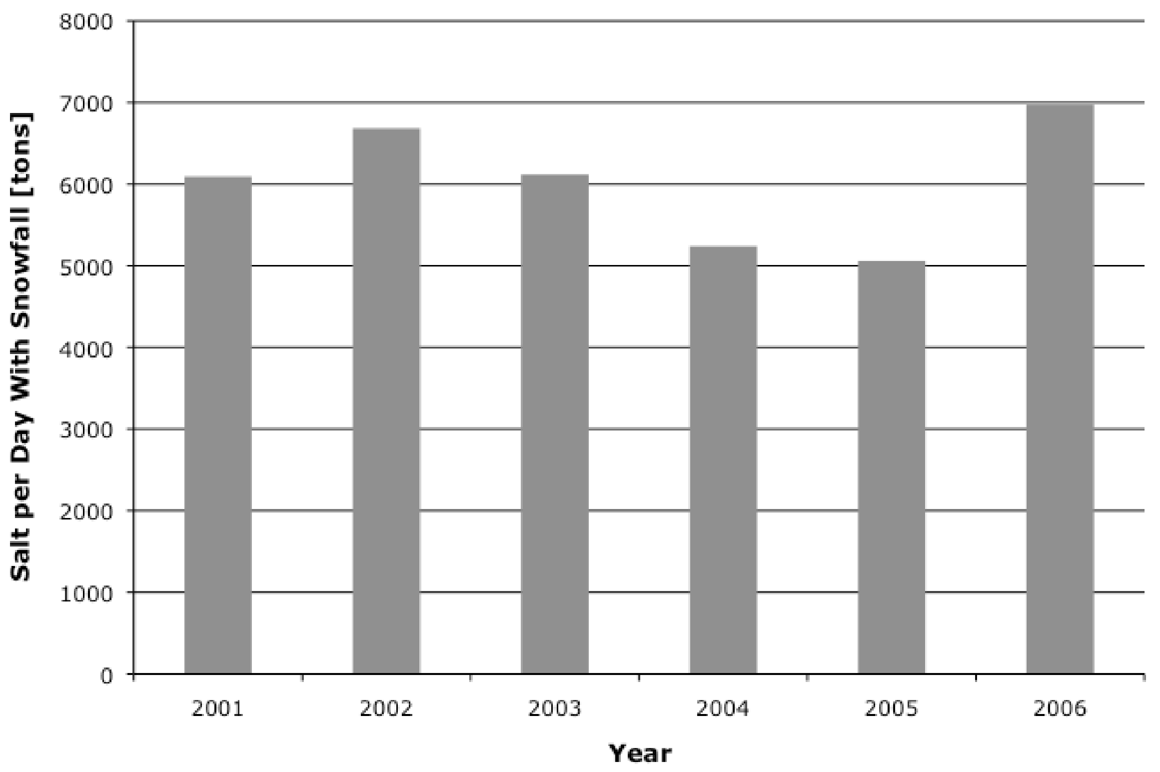

Figure 2.4 Salt use per day with snowfall.

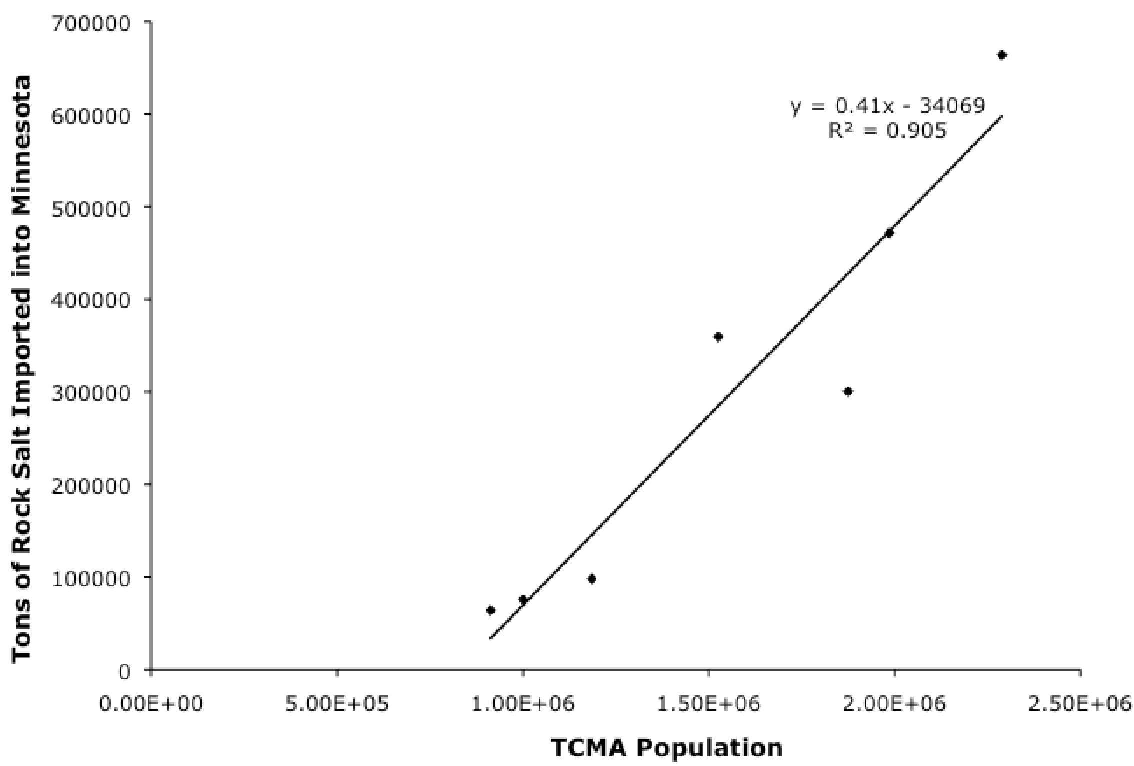

Figure 2.5 Rock salt imported into Minnesota and TCMA population 1930-1993.

There is also a strong correlation between road salt use and population. Trends that are seen on the national level are also found in Minnesota. The TCMA population shows a good correlation with the amount of rock salt imported into the state (Figure 2.5). This shows that the road salt use in Minnesota is mainly driven by the population of the TCMA.

The per capita road salt use for cities in the TCMA is shown in Figure 2.6. A larger population includes more roadway users and the possibility for more accidents. The per capita relationship agrees well with the relationship between road salt imported into Minnesota and the population of the TCMA (Figure 2.5). The amount of road salt applied by cities only (not the total) was estimated to be about 0.045 t/yr/capita.

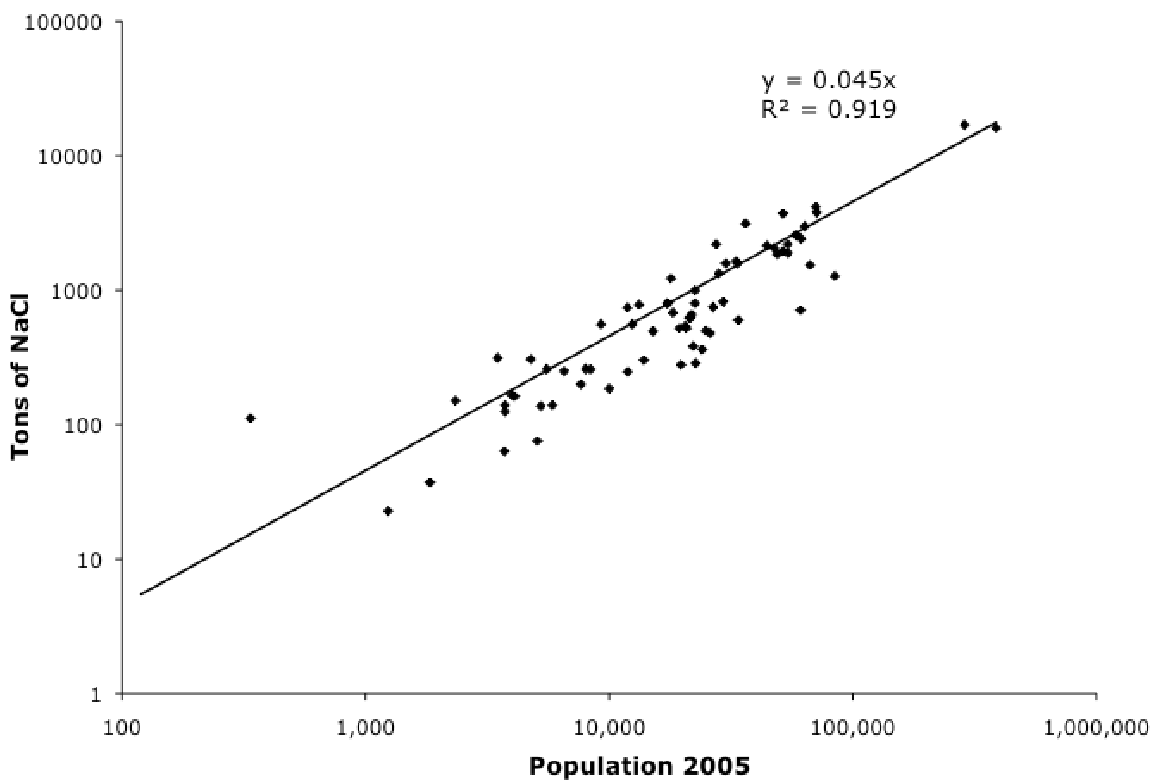

Figure 2.6 Road salt use (tons per season) in cities of the TCMA. The slope of the line is the per capita salt use by cities (not the total).

As to be expected, there is also a relationship between road length and annual road salt use. Figure 2.7 gives the relationship between road length and annual road salt use for the counties in the TCMA.

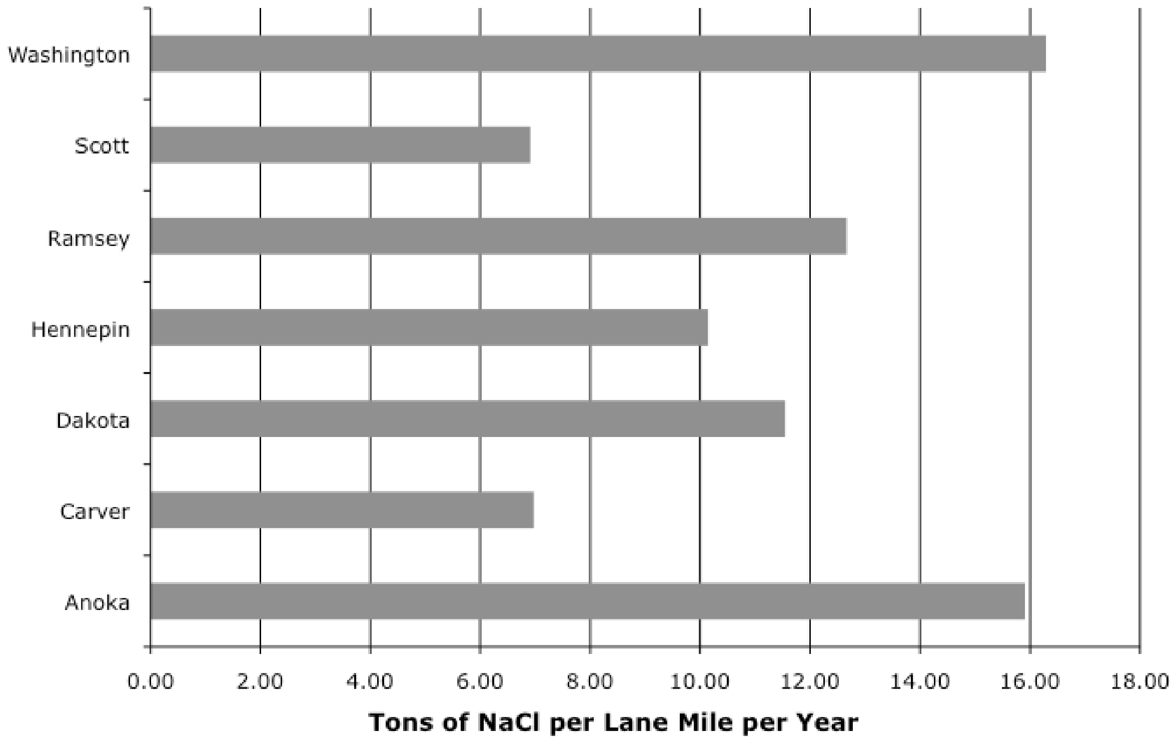

Figure 2.7 Annual road salt use by counties in the TCMA per lane mile.

There is a relationship with the population and the length of roads in a city. In the TCMA the length of impervious lane miles has increased as a result of a growing population. This correlation is important as it ties the two parameters used for determining the spatial application of road salt together.

2.3 Road salt applications In Minnesota

The Minnesota Department of Transportation is the largest user of road salt in Minnesota as their area of responsibility encompasses the entire state. Mn/DOT purchases approximately 40% of the road salt contract amounts in the Metro area as well as statewide. The total amounts from state, county and city contracts for the entire state based on the information from MMD are shown in Figure 2.8. This plot also indicates the total contract amounts for the TCMA and the corresponding amounts purchased by Mn/DOT.

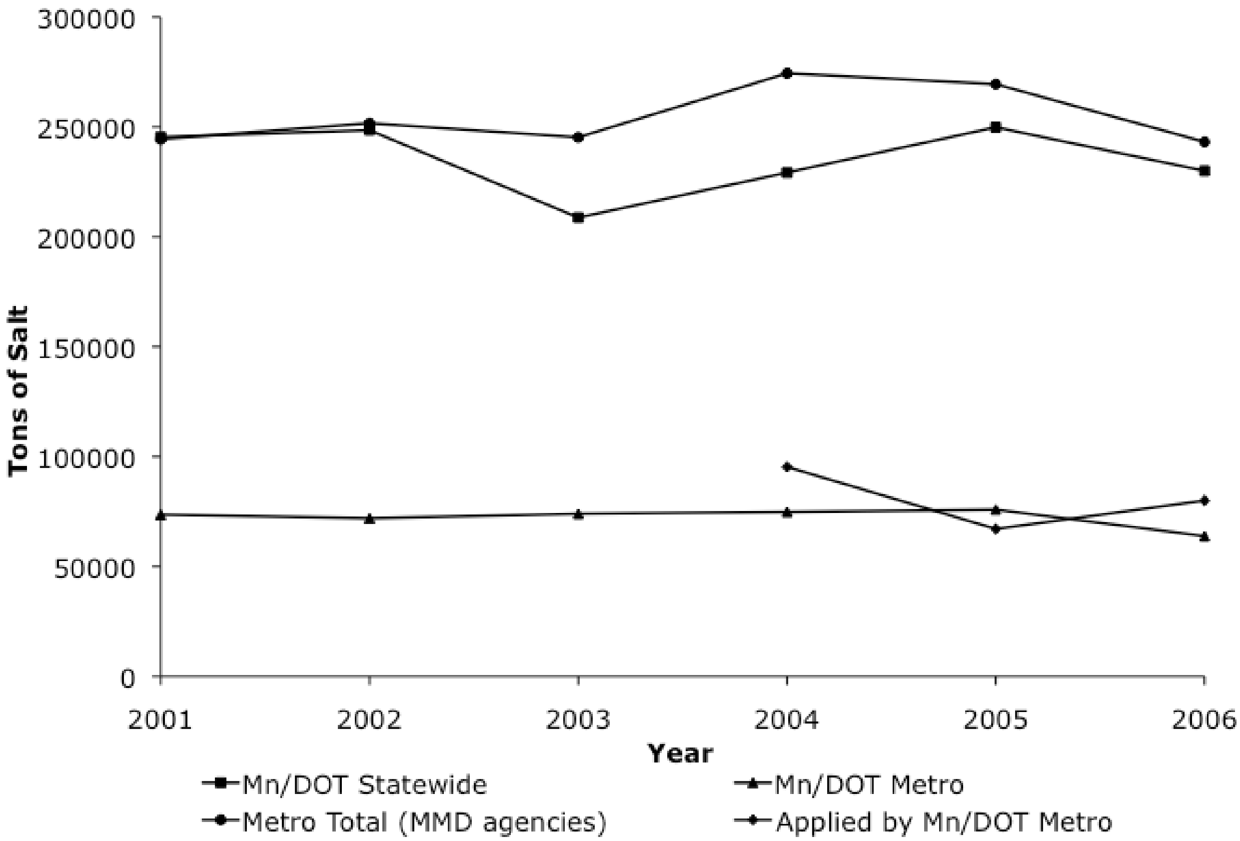

Figure 2.8 MMD salt contract amounts for the TCMA.

2.4 Road salt applications in the U.S.

The USGS Mineral Information office publishes a Mineral Yearbook annually. This document reviews the mineral and material industries of the United States. The mineral report on salt use breaks down the use of salt for ice control and for stabilization. From the amounts of salt in each sector, a percentage used by commercial users is determined. A summary is given in Table 2.2. The data are based on a survey of 27 salt companies in the United States. Natural Resources Canada has indicated that the USGS values on salt consumption could be used to estimate the corresponding consumption in Canada. (Natural Resources Canada-Materials Yearbook, Salt, 2005).

Table 2.2 Government and commercial use of road salt (metric tons per season) in the U.S. (USGS).

Year	*Government (Federal, State, Local)*	*Commercial*	*Total*	*Percent Commercial*
1993	12,700,000	896,000	13,596,000	7
1994	15,000,000	1,430,000	16,430,000	9
1995	11,800,000	1,030,000	12,830,000	8
1996	15,300,000	2,400,000	17,700,000	14
1997	13,100,000	1,900,000	15,000,000	13
1998	8,690,000	794,000	9,484,000	8
1999	13,500,000	1,820,000	15,320,000	12
2000	17,400,000	2,370,000	19,770,000	12
2001	14,800,000	2,030,000	16,830,000	12
2002	11,600,000	1,730,000	13,330,000	13
2003	16,200,000	2,320,000	18,520,000	13
2004	15,600,000	2,380,000	17,980,000	13
2005	18,200,000	2,740,000	20,940,000	13

In Table 2.2 the amount of road salt applied by the public sector for de-icing activities has to be augmented by the amount of road salt that is categorized as commercial and private. This market sector includes bulk and pre-packaged de-icers for:

- Homeowners (single family)
- Multi family dwellings
- Government offices
- Private roads and parking lots
- School Districts
- Airports
- Colleges
- Businesses

2.5 Trends in road salt use

2.5.1 Trends in the TCMA

The data provided by the public agencies were used to determine a trend in road salt use in the TCMA based on long-term average use (Figure 2.9). In this plot, yearly salt use was referenced to an average long-term use by each agency. These normalized values were then averaged to obtain the values plotted in the chart. According to Figure 2.9 the amount of salt used each year by the public sector has risen only slightly over the last two decades. In fact, it may have peaked in 1996..

The amount of road salt applied in the TCMA is influenced by a number of factors: Long-term salt use trends are correlated with population or road mile increases. Short-term variations follow weather patterns, e.g. how many days of snowfall occur in a season.

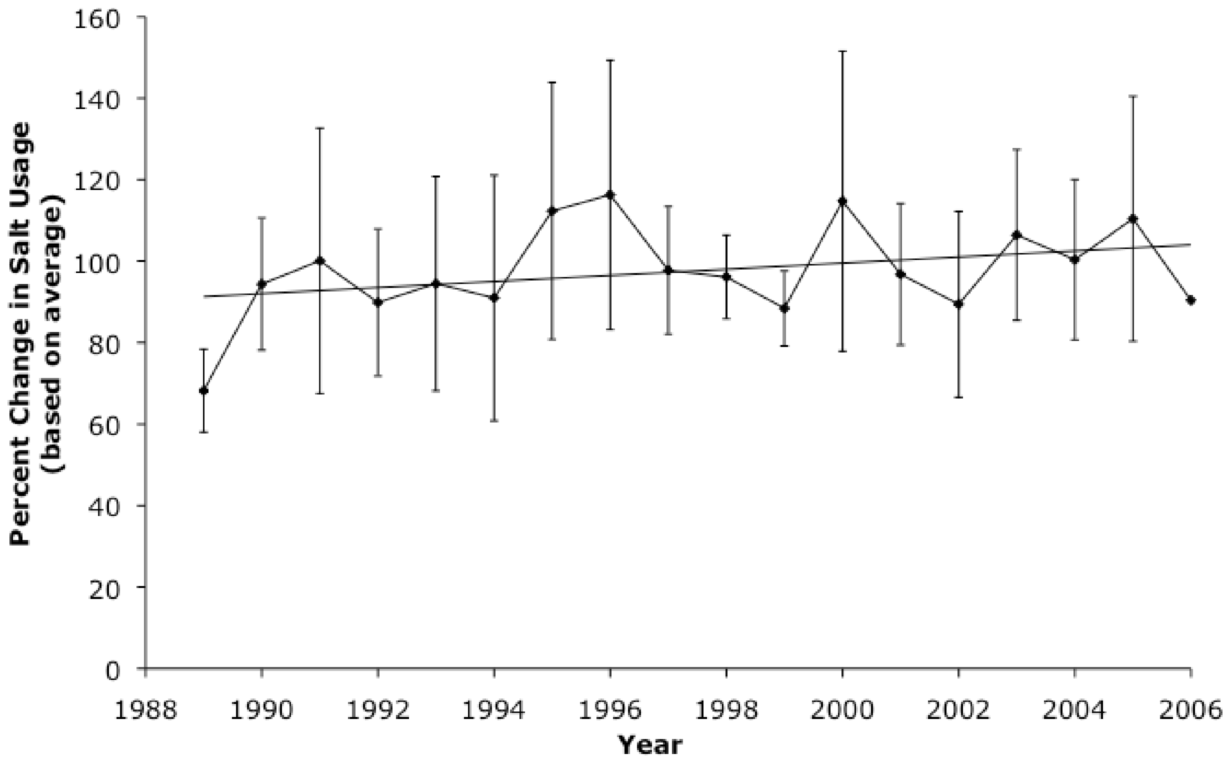

Figure 2.9 Annual road salt use as a percentage of the long-term (1989-2006) average.

2.5.2 Trends in Minnesota and the U.S.

Nationally, the use of salt for road deicing has risen considerably since the 1940s. The increase has been at a much faster rate than the growth of the US population (Figure 2.10). Minnesota has experienced the same trend, as is shown by the amount of rock salt imported into the state and used primarily for winter road maintenance (Note the logarithmic scales used to display the local and national data for comparison). There is a sharp increase in the amount of salt brought into the state from 1940 to 1970. The relationship between the national and Minnesota road salt use is shown in Figure 2.11.

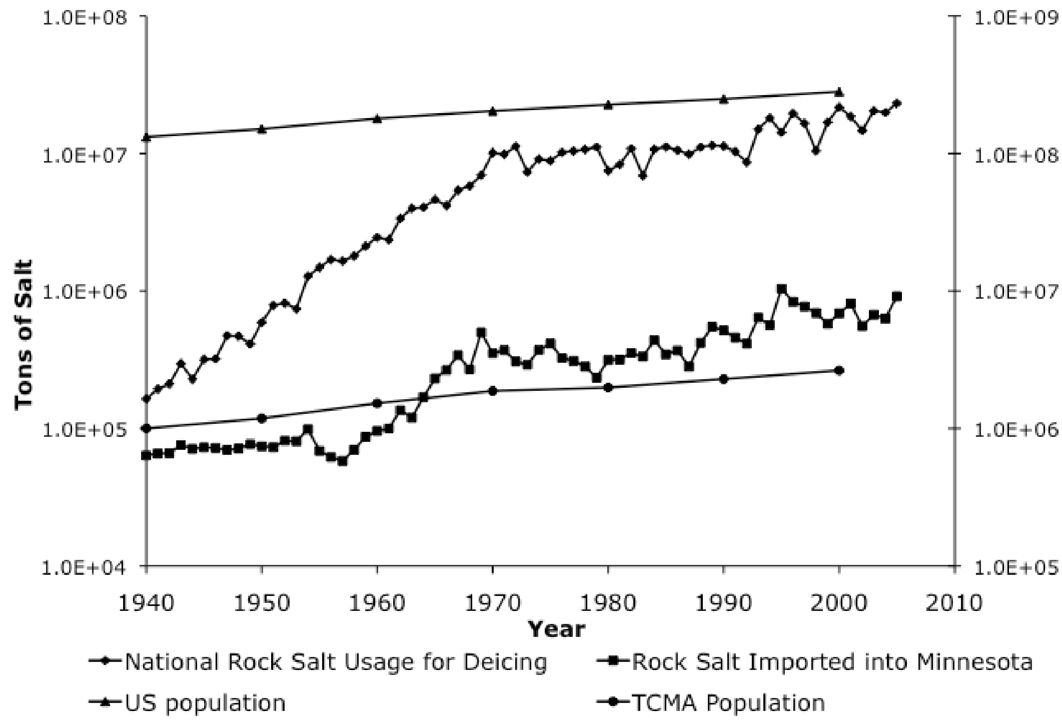

Figure 2.10 Road salt use in the U.S. and rock salt imported into Minnesota since 1940. For comparison population growth is also shown.

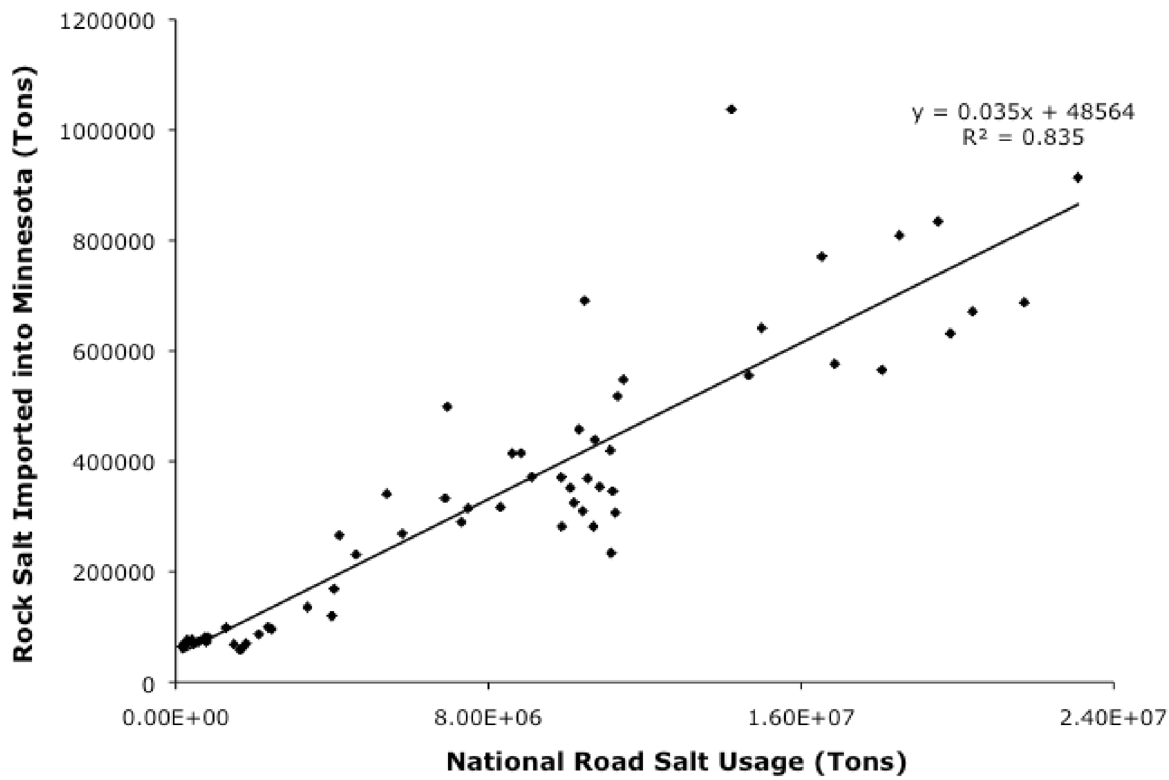

Figure 2.11 Correlation between national road salt use and rock salt imported into Minnesota.

Chapter 3

Salinity of Major Rivers and WWTP Effluents in the TCMA, and a Chloride Budget for the TCMA

3.1 TCMA watershed boundaries

The transport of sodium and chloride through the TCMA environment was investigated and a budget for the chloride ion in the greater TCMA watershed was developed. Four major sources of chloride were included in this analysis: road salt for de-icing, agricultural fertilizer applications, industrial effluents and domestic wastewater effluents.

The first step in the creation of a salt budget is to define the boundaries of the control volume. The boundaries shown as dark contours in Figure 3.1 were used as the TCMA watershed control volume.

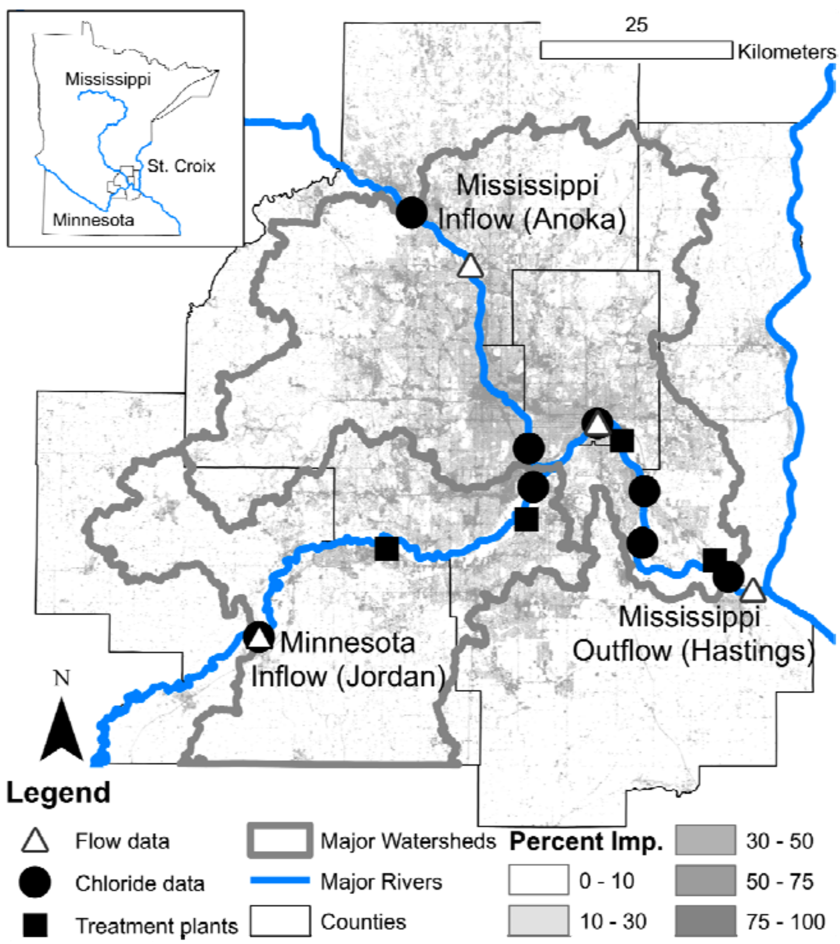

Figure 3.1 Boundaries of TCMA watershed (control volume) used for the salt (chloride) mass balance.

3.2 Chloride concentrations in the major rivers that flow through the TCMA

Two major rivers flow through the TCMA: the Minnesota River and the Mississippi River; the St. Croix River id a boundary of the TCMA. Sodium and chloride data for these three major rivers were obtained from the Metropolitan Council (Grab samples were collected at several points on the Mississippi and Minnesota River (Figure 3.1 top) two to five times a month throughout the year). Flow data were obtained from the United States Geological Survey (USGS) stream gauging stations at Jordan, Anoka, St. Paul, and Prescott. Daily average, and monthly average values were obtained for the period 2000-2007. A flow-weighted average concentration for each month between 2000-2007 was calculated.

Chloride concentrations change along the major rivers. The flow-weighted mean concentrations of chloride and sodium for the 2000-2007 period are shown in Figure 3.2. Major salt inputs to both the Minnesota and the Mississippi River occur at wastewater treatment plant discharges. As the Minnesota River approaches its confluence with the Mississippi River between Minneapolis and St. Paul, chloride concentrations increase from around 30 mg/L to over 40 mg/L. Sodium concentrations also increase. In the Mississippi River mean annual chloride concentrations are more than doubled by the inputs from the Minnesota River and the metro wastewater treatment plant discharge. (Figure 3.2). The St. Croix River has very low chloride concentrations (around 3 mg/L at the sampling locations in Bayport and Prescott) compared to the Minnesota and the Mississippi Rivers. Where the St. Croix joins the Mississippi River the chloride concentrations drop.

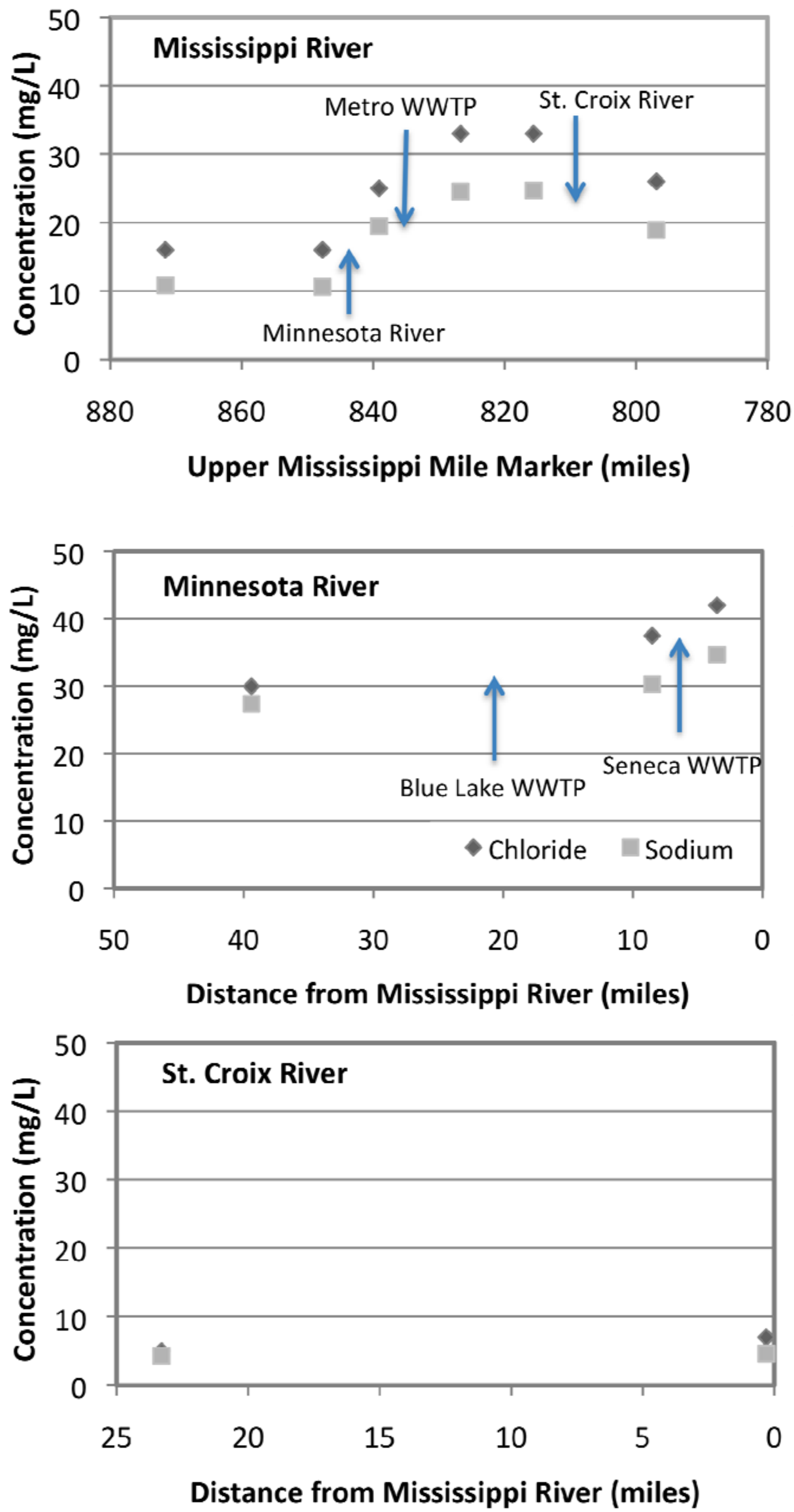

Figure 3.2 Median concentrations (2000-2008) of sodium and chloride for the three major rivers in the Twin Cities Metropolitan area.

The chloride concentration and flow data used for the construction of the TCMA chloride budget are plotted in Figure 3.3. The major river inflows to the TCMA are at (Minnesota 39.6, Mississippi UM 871.6) and the outflow at (Mississippi UM 815.6). Minnesota 39.6 is on the Minnesota River at Jordan, 39.6 miles upstream from its confluence with the Mississippi River. Likewise UM 871.6 is 871.6 miles from the confluence of the Upper Mississippi River with the Ohio River. In each case the mileage marker designates the position where the grad samples were taken.

In Figure 3.3 monthly average chloride concentrations for the period 2000-2007 are shown as a dark line and individual measurements as dots. For the flows only monthly averages are shown. The Mississippi River flowing into the TCMA has a fairly constant chloride concentration from month to month and even between years. By contrast, the Minnesota River flowing into the TCMA has significant variations in concentrations from month to month. For the most part, when the flow rates are high the chloride concentrations are low and vice versa. In Figure 3.4 monthly chloride concentrations for all of the sampling stations on the Minnesota and the Mississippi River are plotted against the average normalized monthly flow rates (normalized flow rate = monthly average flow rate / annual average flow rates) to illustrate the inverse relationship between low flows and high concentrations.

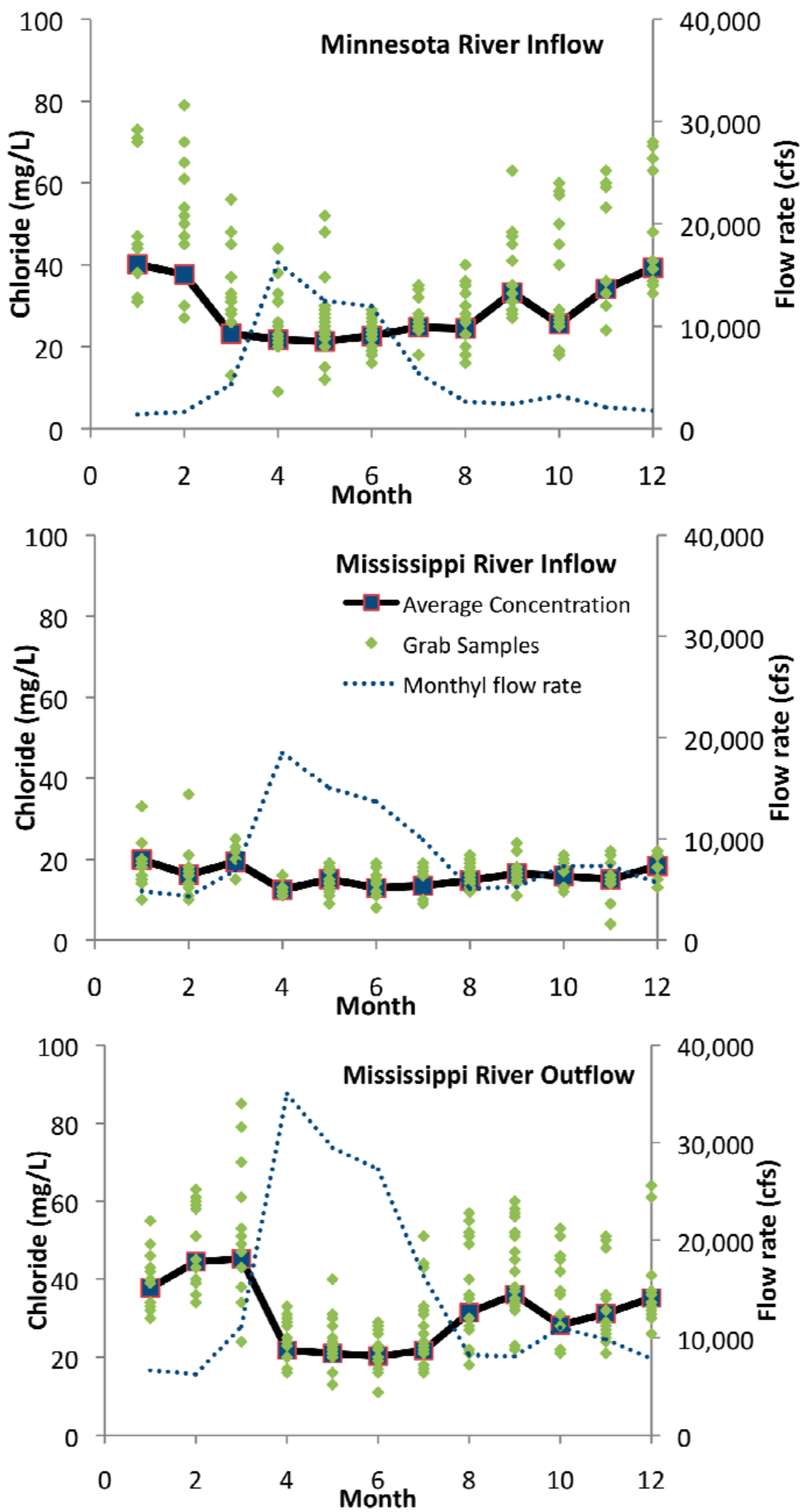

Figure 3.3 Chloride concentrations in individual grab samples from the Minnesota and Mississippi Rivers. Flow-weighted average monthly values for concentrations and flow rates are plotted as solid and dotted lines, respectively. All values are from measurements taken between the years 2000 and 2007.

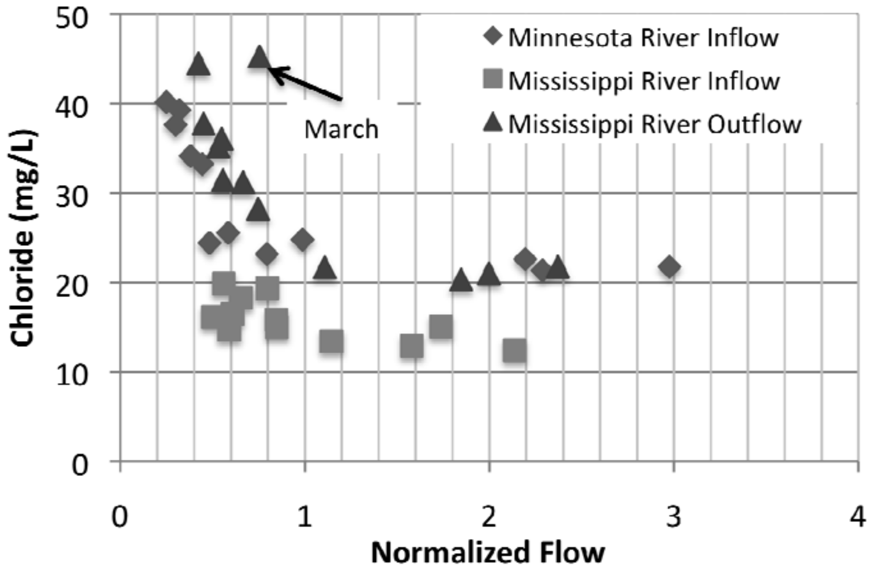

Figure 3.4 Monthly flow-weighted average chloride concentration vs. normalized monthly average flow at each of the sampling stations on the Minnesota and Mississippi Rivers.

The total mass coming into the metropolitan area through the Mississippi and Minnesota Rivers and the amount of mass exiting the control volume through the Mississippi River were determined. Figure 3.5 displays these two data series by plotting the amount of chloride entering the water shed and the amount of chloride exiting the watershed in terms of mass per/month for each month of the year.

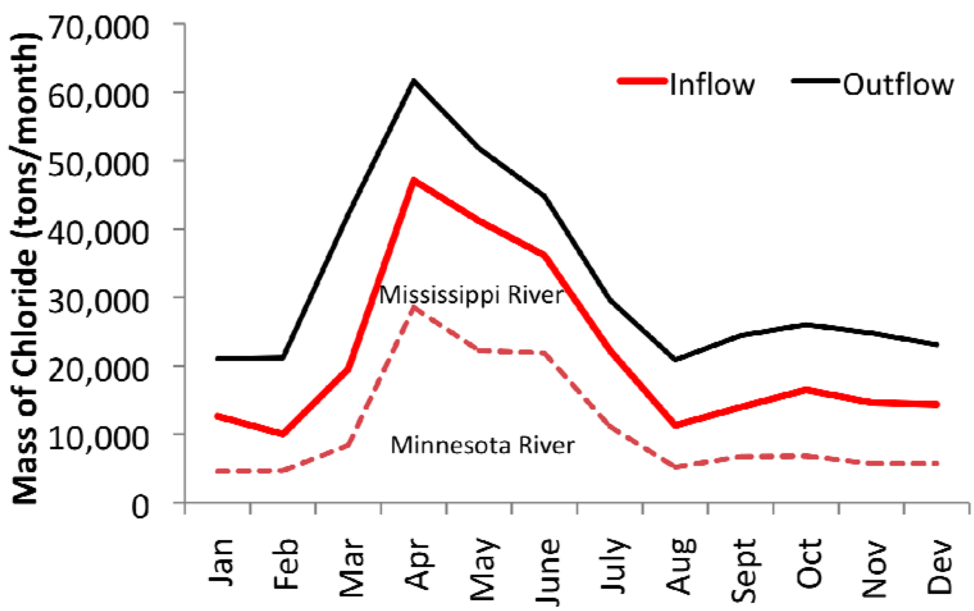

Figure 3.5 Mean monthly (2000-2007) chloride transport (tons/month) by the Minnesota and the Mississippi River into and out of the Metro watershed.

The total annual chloride inflow to the TCMA in the Minnesota and Mississippi Rivers were 132,000 and 128,000 tons/year respectively. The total annual amount of chloride exiting the TCMA watershed with the Mississippi River outflow was found to be 391,000 tons/year. These total annual amounts were calculated using the flow data and the flow weighted average concentrations.

3.3 Chloride sources in the TCMA

Natural sources of chloride inside the TCMA are insignificant. Three major man-made sources of chloride inside the TCMA watershed were considered in the study: (1) fertilizer applications, (2) domestic and industrial salt uses, and (3) road salt use.

(1) Farming in the outskirts of the TCMA is limited to 22% of the total land use area in the watershed. This percentage was calculated using land use data for 2005 provided by the Metropolitan Council. If all of this agricultural land (77,000 ha) was used for the production of corn, which according to the Minnesota department of agriculture requires 36 kg/ha of potassium chloride (Wilson, Crawford et al. 2006), the total input of chloride by fertilizers would only equal 2,800 tonnes/year. Since not all of the land would be used to grow corn and likewise not all of the land designated for farming is currently used for farming it would be expected that this value is actually lower. A value of 49.9 kg/ha per year was used in a study of fertilizer and manure contributions to streams in Sweden (Thunquist 2004).

(2) Domestic and industrial sodium and chloride users usually discharge excess or waste water into sanitary sewers which convey it to a wastewater treatment plant with an effluent discharge into either the Minnesota or Mississippi River. The vast majority of the population and industries in the TCMA uses a sewer system (Figure 3.6). Few households have septic systems. Wastewater treatment plants are not designed to remove sodium chloride from wastewater.

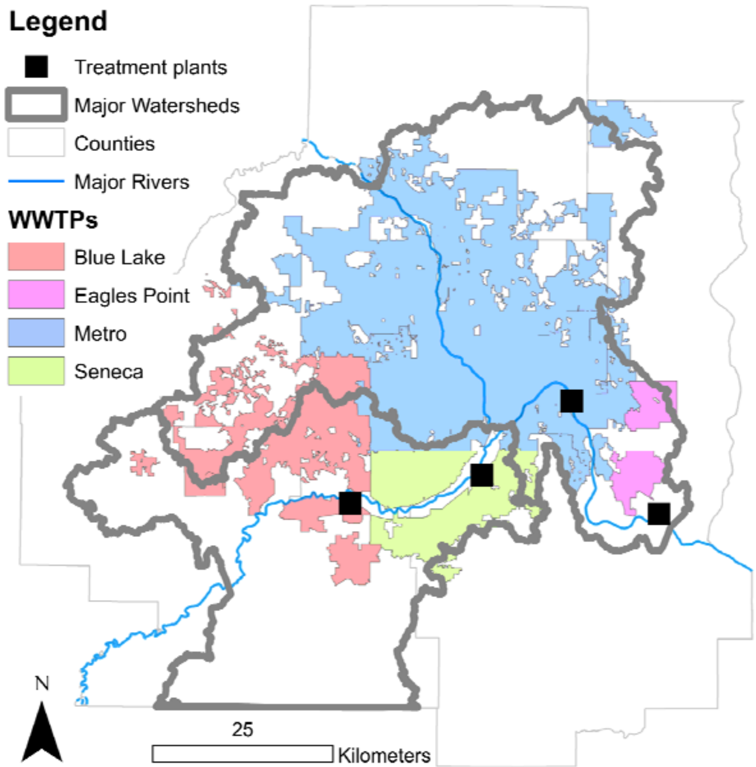

Figure 3.6 Coverage of the four WWTPs discharging into the watershed. Data layers obtained from Metropolitan Council GIS database.

Therefore a request was made to the Metropolitan Council Environmental Services (MCES) to sample effluents from the four wastewater treatment plants (WWTPs) located in the TCMA watershed for sodium and for chloride. Large amounts of salt (NaCl) are used in household for softening of water. Daily measurements were obtained for the period June 2007 to May 2008.

A plot of the bi-weekly (June 2007-May 2008) chloride concentrations in the WWTP effluents is shown in Figure 3.7. There are variations between the bi-weekly measurements and there is also a seasonal pattern in chloride concentrations at the Metro plant. The metro plant displays slightly higher concentrations during the winter then the summer. All other plants have similar concentrations throughout the year. It is possible that some or all of that increase is due to road salt that is collected in combined sewers or in car washes and other automobile related facilities which discharge through sanitary sewers to the metro WWTP. In the chloride budget computations we will use chloride concentrations in metro WWTP effluents that were measured in the warm season (May-October) only in order to avoid any road salt influences on WWTP effluent values. Values obtained throughout the year were used for the other three WWTPs.

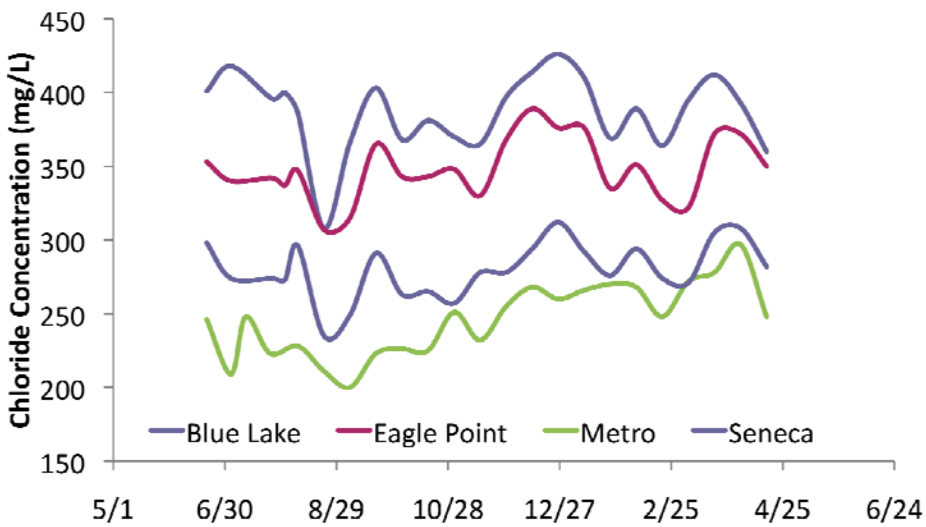

Figure 3.7 Chloride concentrations in WWTP effluents (June 2007-May 2008).

The annual average concentrations of chloride in the WWTP effluents along with the average flow rates are shown in Table 3.1. The total annual mass of chloride estimated to enter the TCMA river system from the four WWTPs is around 96,000 tons/year. The significant differences between the mean effluent concentrations in Table 3.1 are noteworthy.

Table 3.1 Average chloride concentrations and flow rates from the four major WWTPs in the TCMA. Also included is the total amount of Chloride estimated to pass through the WWTPs in the Mississippi or Minnesota Rivers each year.

	Chloride (mg/L)	Flow (MG/day)	Mass (tons/year)
Blue Lake	387	27	15925
Eagle Point	348	4	2122
Metro	227	197	68155
Seneca	280	23	9815

(3) A major source of chloride in the watershed is road salt. It is, of course a seasonal source. The amount of road salt used in the TCMA had been determined by Sanders et al. (2007). There are four main appliers of road salt in the TCMA: cities, counties, states and commercial applications. In that study values were determined by contacting cities, county, and state organizations. Commercial and packed salt use had to be estimated based on the percentages given in Figure 2.1. The final estimate of total road salt (de-icing) use in the TCMA was 349,000 tons per season

Since the watershed boundaries do not coincide with government boundaries of the TCMA (see Figure 3.1) the road salt application amount for the watershed needed to be estimated. Road miles were used to make the adjustment from political boundaries to watershed boundaries.

Total lane miles of city, county and state roads were determined for each city and county using GIS road data from the Metropolitan Council. Fractions of total road miles inside the watershed vs the total road miles inside the municipality were then multiplied by the total amount of road salt that each city, county or state agency had reported. The result gave an estimate of the amount of road salt applied in the watershed by state, city and government agencies. 24% was added to the amount of public road salt use to account for commercial and private road salt use and to determine the total amount of road salt used in the watershed.

Overall 266,000 tons of salt/year was estimated to be applied in the TCMA watershed (defined in Figure 3.1). Since this value is for NaCl the value is converted to chloride by using the molar mass ratio of 0.6068 grams of chloride for every gram of NaCl. This translates to 161,000 tons of chloride/year from road salt applications in the TCMA watershed area.

Table 3.2 Amount of road salt (NaCl) applied by each of the different groups in the TCMA and the watershed used for the chloride budget.

	Total (tons)	Watershed (tons)
Cities	114,000	98,000
Counties	70,000	42,000
Mn/DOT	81,000	62,000
Commercial	84,000	64,000
Total	349,000	266,000

After the application on the pavement road salt can follow various pathways. Most of the road salt application is applied in solid form as rock salt (crystals) usually with pre-wetting. Application as a concentrated solution of salt brine before snowfall is becoming a common practice. Since sodium chloride is a highly soluble substance, it is fair to assume that all of the road salt applied will dissolve in water. A portion of the water containing the dissolved road salt will run into storm sewers or drainage ditches from where it will flow into streams, rivers, storm water detention ponds, wetlands or lakes. Another portion will infiltrate directly into the soil on the shoulder of the roadway, or into the soil below a ditch or small stream. It may also infiltrate from storm water infiltration ponds or other man-made structures. Some storm water is still routed to WWTPs in combined sewers. In the TCMA sewers have been separated and combined sewers are rare. When road surfaces become dry, road salt appears as a white dust that becomes air-borne in the wake of vehicles. No studies have been found that document airborne road salt transport away from an entire urban area.

3.4 Chloride budget calculation for the TCMA

The total mass of chloride in the major river inflows to the TCMA (Mississippi and Minnesota Rivers) plus the total mass applied within the watershed (WWTP effluents plus road salt applications) minus the total mass leaving the TCMA by the Mississippi river gives a residual amount that is either staying behind in the TCMA or is being removed in other unaccounted ways, such as air-borne removal by wind.

Figure 3.8 gives the monthly amounts of chloride entering or leaving the TCMA water shed. The data series for the amount entering the watershed includes the Mississippi River at Anoka, the Minnesota River at Jordan and the WWTP effluents from the four WWTPs in the TCMA. The data series for the amount leaving the TCMA watershed is for the Mississippi River at Hastings. The WWTP discharge directly into either the Mississippi or Minnesota Rivers their effluents will exit the TCMA watershed control volume through the Mississippi River. Figure 3.8 illustrates that the major differences between the amount of chloride entering and exiting the watershed occur during the winter months when road salt is being applied. The question is whether all the road salt applied is carried away, of if any stays behind. Figure 3.9 gives the monthly differences between chloride export and import. The largest net export of chloride occurs in March (around 15,000 tons/month). Combining all of the months gives a net export of 35,000 tons/year of chloride.

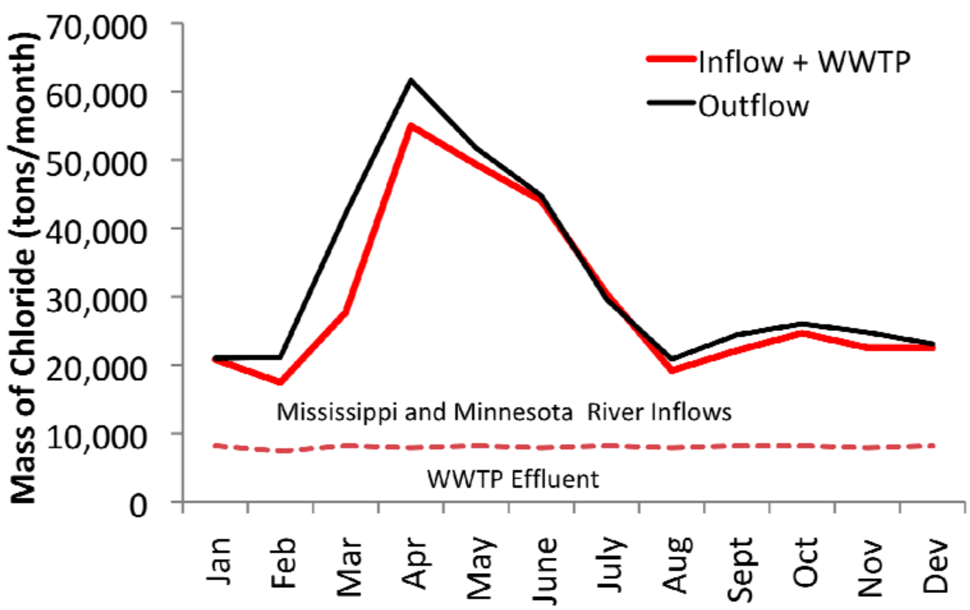

Figure 3.8 Mean monthly chloride transport (tons/day) into and out of the TCMA watershed including wastewater treatment. Road salt is not included.

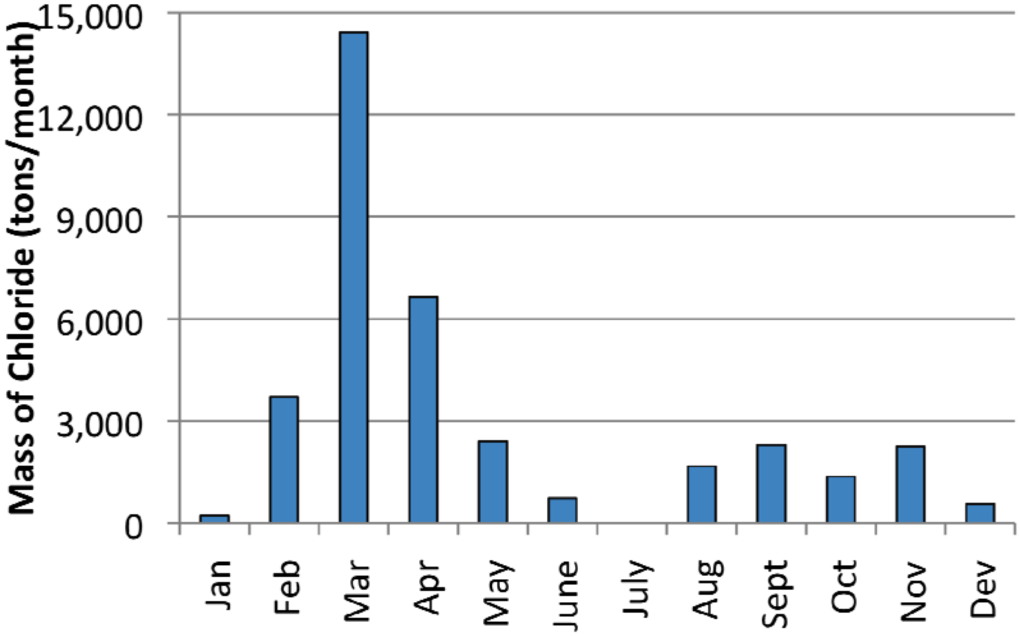

Figure 3.9 Net monthly chloride export from the TCMA watershed (Net export = difference between export and import in Figure 3.8).

Since road salt applications are the only other major chloride in the watershed, but not considered in the forgoing chloride fluxes and budget it is safe to assume that the net export of 35,000 tons of chloride exiting the watershed is from road salt. That most of the net export occurs in Feb, Mar and April would tend to support this assumption. This value can then be compared to the amount of chloride added to the TCMA watershed every year by road salt. It was estimated previously that 161,000 tons of chloride/year are being added to the TCMA watershed every year. If only 35,000 tons/year are leaving the watershed that means that around 126,000 tons/year is staying in the watershed. In other words only 22 % of the de-icing salt added to the roads every year is exiting the watershed wile 78 % is unaccounted for. This unaccounted amount could be leaving the watershed in the form of windblown dust, or in other unknown exports. More likely, it is staying in the in the soils, the lakes, the wetlands or the ground water of the TCMA.

3.5 Chloride (salt) budgets for watersheds of small streams

The road salt retention percentage given above appears high. To examine if indeed significant amounts of road salt applied in the TCMA are retained in the watershed and not reaching the major rivers, we examined the chloride budgets of several small streams and their watersheds. Chloride concentration and stream flow data were available at the outflow stations of ten stream watersheds located within the control volume of the TCMA. We determined the amount of the amount of road salt leaving with the stream and compared it to the amount of road salt applied in the watershed to establish a retention rate. The stream was the only surface water outflow from each watershed. The location of these streams in the TCMA watershed can be seen in

Figure 3.10. Information on the individual streams can be seen in Table 3.3. The streams are located entirely in the TCMA, and outflow concentrations and flow rates were available from the Metropolitan Council. The amount of road salt applied was determined as explained earlier using lane miles of roads in the watershed.

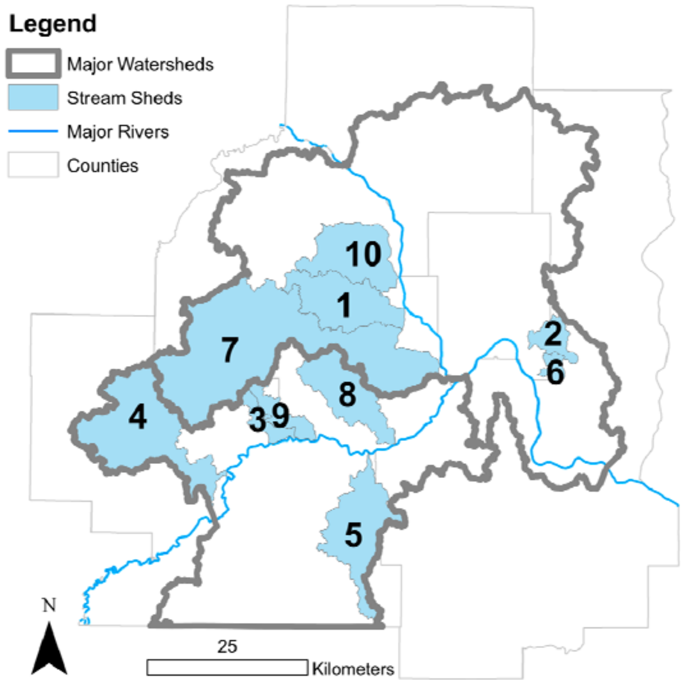

Figure 3.10 Location of small stream watersheds in the TCMA. Position numbers are referenced in Table 3.3.

Table 3.3 Stream watershed information.

	Position number (Figure)	Watershed Area (ha)	Percent Impervious	Annual Average Flow (m^3/s)	Annual Average [Cl^-] (mg/L)
Bassett	1	11,117	34	0.966	138
Battle Creek	2	2,952	32	0.221	147
Bluff Creek	3	2,316	11	0.105	65
Carver Creek	4	21,632	4	0.983	37
Credit River	5	13,300	9	0.498	44
Fish Creek	6	1,319	27	0.093	100
Minnehaha Creek	7	46,137	15	1.685	68
Nine Mile Creek	8	9,911	29	0.709	74
Riley Creek	9	3,386	18	0.113	52
Shingle Creek	10	10,770	35	0.493	185

The amount of road salt applied was calculated separately for city, county and state highways (Table 3.4). The amount of chloride applied per hectare in the watershed ranged from 0.04 tons/acre to 0.37 tons/acre. The flow rated annual average chloride concentrations in these streams ranged from 185 mg/L in Shingle Creek to 44 mg/L in the Credit River. The total mass of chloride exiting the watershed was calculated by multiplying the annual flow rate by the flow weighted annual average chloride concentrations. Two simulations were run: in the first simulation no adjustments were made for background concentrations, in the second simulation the annual average chloride concentrations were adjusted by subtracting 18.7 mg/L as a background concentration. This background concentration value is obtained from a plot of the average annual chloride concentrations (at the outlet of the ten small stream watersheds of the TCMA) vs. the amount of chloride applied per ha per season (Figure 3.11. A "background" chloride concentration of 18.7 mg/L is obtained from a linear fit to the data (R^2 = 0.79) when the road salt application rate is set to zero.)

Table 3.4 Road Salt applications rates for the 10 streams' watersheds.

	City Salt (tons)	State Salt (tons)	County Salt (tons)	Comm. Salt (tons)	Total NaCl applied (tons)	Total Cl^- applied (tons)	Cl^- applied per area (tons/acre)
Bassett	5,526	4,533	1,115	3,529	14,703	8,922	0.32
Battle Creek	1,828	1,069	463	1,061	4,420	2,682	0.37
Bluff Creek	244	399	84	230	957	581	0.10
Carver Creek	630	1,148	684	777	3,238	1,965	0.04
Credit River	1,158	186	870	699	2,913	1,768	0.05
Fish Creek	454	289	172	289	1,204	730	0.22
Minnehaha Creek	14,554	5,896	4,129	7,762	32,342	19,625	0.17
Nine Mile Creek	3,044	2,996	972	2,214	9,226	5,599	0.23
Riley Creek	384	403	187	308	1,283	778	0.09
Shingle Creek	5,475	2,335	1,839	3,047	12,697	7,704	0.29
					Total	50,354	

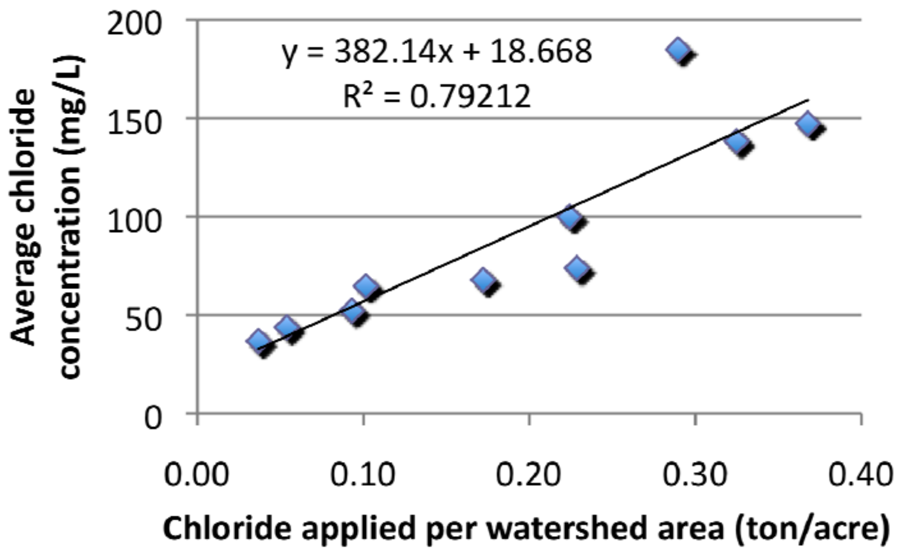

Figure 3.11 Mean annual chloride concentrations in small streams of the TCMA vs. seasonal road salt (NaCl) applications.

The amounts of chloride exiting the watersheds were found to be from 15 to 64 %. of the amounts applied in the watersheds (Table 3.5). In other words from 36 to 85 % of the road salt applied is not carried away by the surface runoff. It is either retained in the watershed in surface waters or groundwater, or it is removed, e.g. as a windblown dust. The total amount of chloride added to these ten watersheds is 50,354 tons/year, and the total amount of chloride exiting them in surface flow is with out a background concentration is 17,502 tons/year. On average, only 35 % of the road salt applied to the watersheds of the 10 streams are carried away by the ten streams, 65% are retained in the watershed using 0 mg/L as a background concentration. Using a background concentration of 18.7 mg/L results in 73% of the chloride being retained in the watershed. It may be noteworthy that the highest retention of 85% is in the watershed of Minnehaha Creek (Table 3.5) which includes Lake Minnetonka and numerous wetlands.

Table 3.5 Chloride budgets for ten individual stream watersheds in the TCMA.

	Mass No background (tons/year)	Percent Cl^- exported	Percent Cl^- retained	Mass background (tons/year)	Percent Cl^- exported	Percent Cl^- retained
Bassett	4,625	52	48	4,021	45	55
Battle Creek	1,128	42	58	988	37	63
Bluff Creek	236	41	59	169	29	71
Carver Creek	1,257	64	36	620	32	68
Credit River	759	43	57	436	25	75
Fish Creek	325	44	56	264	36	64
Minnehaha Creek	3,974	20	80	2,885	15	85
Nine Mile Creek	1,816	32	68	1,361	24	76
Riley Creek	206	27	73	133	17	83
Shingle Creek	3,176	41	59	2,849	37	63
Totals	17,502	35	65	13,725	27	73

Note: "Mass No background" gives results obtained without a background concentrations
"Mass background" gives results obtained using 18.7 mg/L background concentration.

3.6 Discussion of the TCMA chloride (salt) budget

Chloride concentrations increase in the major rivers as they travel through the Metropolitan area. The Mississippi River enters the TCMA at Anoka with mean monthly chloride concentrations on the order of 20 mg/L and leaves at Hastings with mean monthly chloride concentrations on the order of 20 to 50 mg/L. Concentrations of the inflow are much more uniform from month to month and year to year than those in the outflow from the TCMA. WWTP effluents located along the rivers have chloride concentrations between 200 and nearly 400 mg/L contributing to the rise in chloride concentrations as the Mississippi River travels through the metropolitan area. The Minnesota River enters the TCMA at Jordan with mean monthly chloride concentrations between 20 and 40 mg/L, but individual samples have had concentrations between 10 and 80 mg/L mostly dependant on the flow rate.

River flow rates and chloride (salt) concentrations in both the Minnesota River and the Mississippi River are inversely related. (Figure 3.3 and 3.4). During the winter and even late summer/fall months the flow rates are lower resulting in elevated chloride concentrations possibly due to WWTP effluents. From August to February the WWTPs provide about 1/3 to 1/4 of the mass of chloride passing through the outflow stations; during the peak flow in April this value is decreased to about 1/10.

The pattern of high flow resulting in low chloride concentrations is broken during the month of March at the Mississippi River in Hastings, In March air temperatures start to rise resulting in the melting of the accumulated snowpack. Road salt accumulated in the snowpack is transported into the Mississippi and Minnesota Rivers producing higher chloride concentrations even though more water is present for dilution.

According to the annual chloride budget for the TCMA watershed area, 260,000 tons of chloride are carried into the TCMA by the Mississippi and Minnesota Rivers, and 391,000 tons are exiting in the Mississippi River at Hastings. 131,000 tons are added to the rivers as they travel through the Twin Cities. Of these 131,000 tons of chloride, 96,000 tons come from wastewater treatment plants and 35,000 tons from road salt. Since 161,000 tons of chloride are applied to the roads in the TCMA watershed every year, an estimated 126,000 tons of chloride or 78% of the applied road salt are retained by the watershed. An independent estimate for small stream watersheds in the TCMA gave a 65 to 73% retention rate depending on the concentration used as a background concentration.

In summary, the chloride budgets for both the entire TCMA watershed and for the watersheds of ten small streams located inside the TCMA watershed indicate that over 70% of the road salt applied in the TCMA is not transported from the roads to steams and out of the metropolitan area by the Mississippi River. It is conceivable, but not proven, that a very small portion of this amount may be transported by wind as a powder out of the TCMA. A substantial portion of these 70% is presumably staying in the area of application, either in the soils, groundwater, lakes or wetlands. Even if the fraction of retained road salt were as low as 50%, it would be cause for alarm.

The Twin Cities area is covered with over 950 lakes. Salt accumulation in those lakes will be explored in the next section. Chloride concentrations in some 39 TCMA lakes have been observed to be increasing over the past 22 years, following a trend similar to the trend in road salt purchases by the state of Minnesota (Novotny et al, 2008). Some storm water management practices such as detention/retention ponds, infiltration ponds, or rain gardens, can also contribute to the retention of salt in the watersheds.

Chapter 4

Salinity of Lakes in the TCMA

4.1 Inflows to lakes

Much of the de-icing salt applied to roads is dissolved in the melting snow and ice. The water containing the salt runs into storm sewers and streams or infiltrates into the soil, eventually reaching the groundwater.

Several streams (Shingle Creek, Nine Mile Creek, Bassett Creek, Minnehaha Creek) in the Twin Cities Metropolitan Area are on the MPCA's 2008 list of "impaired waters" as impaired by chloride; a TMDL study of Shingle Creek has been conducted and other studies are in progress. Chloride concentrations in Minnehaha Creek are shown in Figure 4.1. Minnehaha Creek does not discharge to a lake, but the pronounced seasonal spikes during snowmelt runoff in spring are typical of many urban streams in the TCMA.

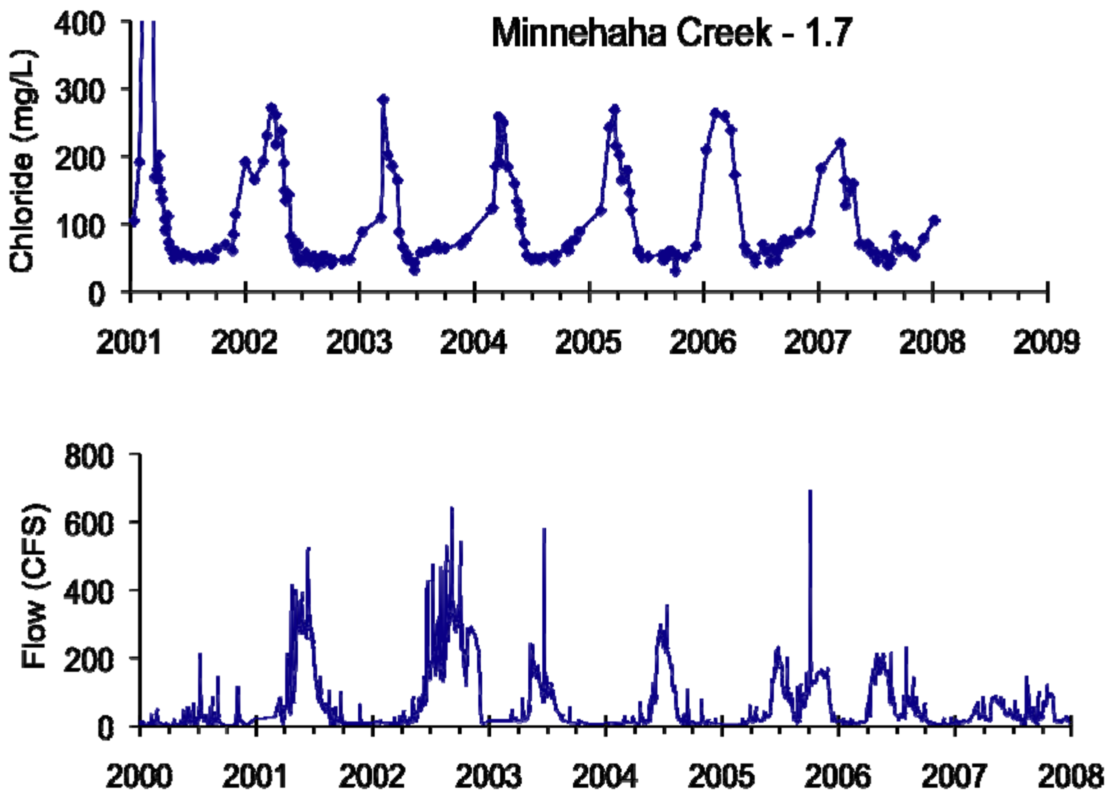

Figure 4.1 Chloride concentrations in Minnehaha Creek (1.7 miles from its outlet into the Mississippi River).

Saline water inflows from streams and storm sewers into lakes form plunging density currents (Figure 4.2) and cause the accumulation of salt water near the bottom of a lake. Snowmelt water accumulates at the bottom of urban lakes during the winter season when road salt is applied. Lakes in the vicinity of major roadways are most susceptible.

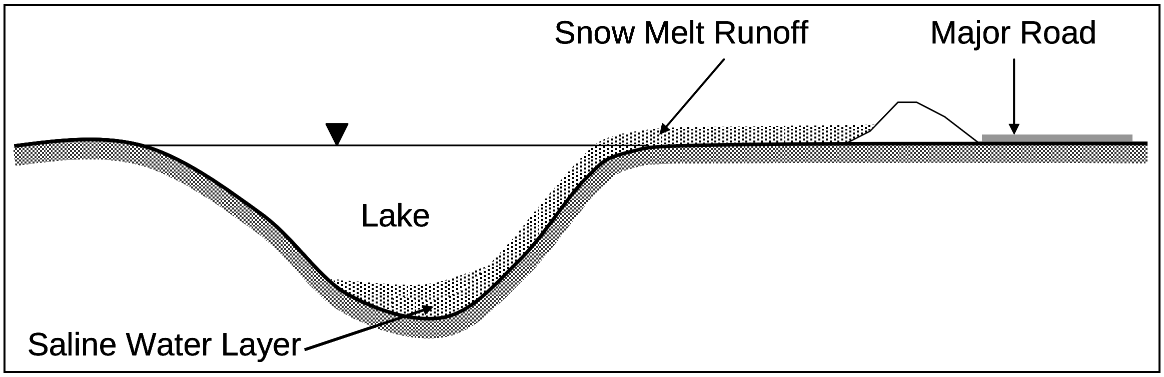

Figure 4.2 Schematic of a saline water intrusion into a lake.

Vertical mixing of this salty layer with the overlying water can occur during spring, summer or fall, especially during major storm events. Sometimes, the addition of the salt water layer on the bottom of a lake prevents the complete vertical mixing in spring or fall that is typical of many Minnesota lakes. If the saline layer remains at the bottom of a lake, oxygen supply to the lake sediment bed is reduced which in turn can have significant consequences for the benthic biota in the lake.

Salt is flushed out of lakes by water inflow from the watershed in the warmer season, i.e. during late spring, summer and fall. Because of the seasonal loading and flushing of salt from lakes, the average lake salinity has a seasonal cycle.

4.2 Field study of lakes

We conducted a field study of salinity in 13 urban lakes in the Minneapolis/St. Paul Twin cities Metropolitan Area (TCMA). The objectives of this study were to investigate several TCMA lakes with regard to

1) water chemistry,
2) presence of salinity stratification,
3) seasonal salinity cycles,
4) long-term trends in salinity.
5) potential long-term effects of road salt applications.

The seven-county Minneapolis/St. Paul Twin Cities Metropolitan Area (TCMA) has over 950 lakes (Metropolitan Council) and uses over 349,000 tons of road salt annually (Sander et al. 2007). With an expanding population and road system, more and more lakes in the TCMA are susceptible to contamination from storm water and snowmelt runoff. We collected data in 13 lakes from February 2004 to April 2005 and January 2006 to May 2008. The set of lakes was somewhat different but overlapped for the two periods.

From 2004 to 2005 eight lakes were sampled: Bass, Cedar, Lake of the Isles, Johanna, McCarron, Medicine, Ryan and Brownie. From 2006 to 2008 four of the previous lakes were sampled (Ryan, Cedar, Brownie and McCarron) and 5 new lakes were added (Tanners, Parkers, Bryant, Gervais, Sweeney). Lakes that did not show strong salinity stratification after the first sampling period were dropped, and other lakes with a high likelihood of salinity stratification were added. Lake selection was thus biased towards lakes that would receive high salinity runoff. Cedar Lake was kept as a reference lake that showed little stratification.

Locations of the selected lakes and their watersheds in the TCMA are shown in Figure 4.3. Lakes are listed in Table 4.1. Bathymetric characteristics (area vs. depth plots) are shown in Figure 5. Bathymetric data was obtained from the Minnesota DNR lake finder website (Resources 2007) and watershed delineations were gathered using the Metropolitan Council GIS database (MCES 2007b)

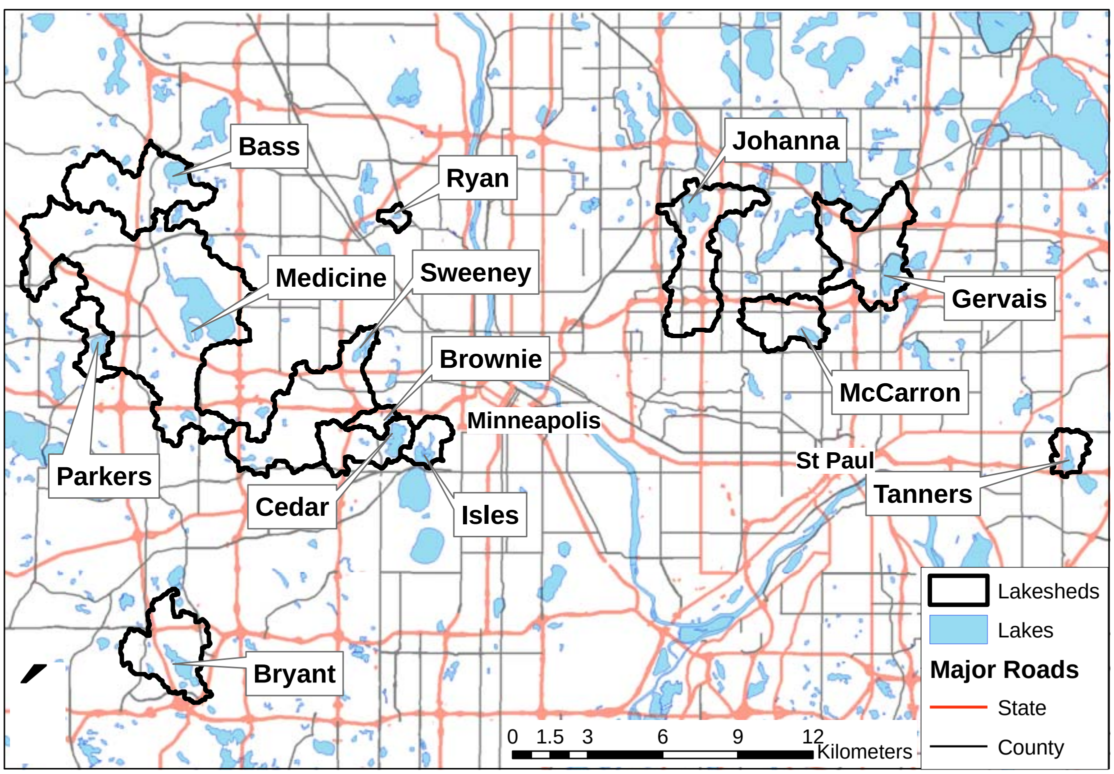

Figure 4.3 Locations of the study lakes and their watersheds in the Minneapolis-St. Paul Metropolitan Area (TCMA).

Table 4.1 Lakes studied and sampling periods.

	Max Depth (m)	Surface Area (Ha)	Volume (m^3)	Surface Area/Depth (Ha/m)	Watershed Area (Ha)	Watershed/ Surface Area	Percent Impervious (%)	Sampling Period (year/year)
Bass	9.4	70.4	673,000	7.5	1131	16	21	04/05
Brownie	14.3	5.0	200,000	0.3	136	27	33	04/07
Bryant	13.7	65.2	3,245,000	4.8	901	14	24	06/07
Cedar	15.5	68.4	4,433,000	4.4	537	8	28	04/07
Gervais	12.5	94.7	4,823,000	7.6	1144	12	30	06/07
Johanna	13.1	66.2	4,274,000	6.6	1168	14	39	04/05
Isles	9.4	44.1	1,120,000	4.7	252	6	29	04/05
McCarron	17.4	27.6	2,151,000	1.6	549	20	24	04/07
Medicine	14.9	358.6	18,589,000	24.0	4380	12	29	04/05
Parkers	11.3	36.9	1,414,000	3.3	340	9	27	06/07
Ryan	11.0	7.6	295,000	0.7	77	10	34	04/07
Sweeney	7.6	26.7	952,000	3.5	1512	57	37	06/07
Tanners	14.0	28.3	1,848,000	2.0	214	8	33	06/07

4.3 Ionic composition of solutes in TCMA lakes

The chemical analysis of 36 water samples from 9 urban TCMA lakes yielded the results summarized in Table 4.2. Chloride and sodium are the dominant ions in the water, followed by calcium and magnesium. Differences in Cl- and Na+ concentrations between surface and bottom waters of the urban lakes are significant. For all the other ions the differences between surface and bottom waters are insignificant (Table 4.2). This would suggest that Cl- and Na+ are associated with each other, and with the seasonal variations typical of dimictic lakes, while all the other ions respond to longer time scales.

Table 4.2 Ionic composition (mg/L) of 18 water samples taken on 2/22/2007 and 11/15/2007 in 9 urban lakes of the TCMA, 1 m below the water surface and 1 m above the bottom of the lake.

	2/22/2007		11/15/2007	
	Top	Bottom	Top	Bottom
Ca^{2+}	48	51	42	43
Mg^{2+}	17	18	14	14
Na^{+}	73	105	59	59
K^{+}	3	3	3	3
NH_4^{+}	1	2	0	0
SO_4^{2-}	14	16	13	13
Cl^{-}	132	186	109	109
SC	745	988	612	639

The TCMA has no significant natural sources of chloride. Consequently, under natural conditions, Cl- concentrations would be expected to be very low. Indeed, the median Cl- concentration in TCMA lakes in 1800 and 1750 was calculated to be 3 mg/L by using diatom assemblages in sediment cores (Ramstack et al. 2004). If the area had remained undeveloped

Cl- concentrations in TCMA lakes could be expected to be similar to the ones seen in the Wisconsin North Temperate Lakes region, which has Cl- concentrations equivalent to rainwater (LTER 2000). More realistically the lakes could be projected to resemble the 4-10 mg/L values found in the North Central Hardwood Forests ecoregion of Minnesota which includes the TCMA (MPCA 2004). That sodium and chloride concentrations in TCMA urban lakes (Table 4.2) have increased well above expected background concentrations must therefore be related to human salt uses.

Comparison with other North American freshwater bodies

Ionic concentrations for rainwater, a pristine lake (Crystal Lake) in northern Wisconsin, typical lakes of central Minnesota, typical North American streams, the Mississippi River and the Minnesota River upstream of the TCMA are given in Table 4.3.

Table 4.3 Ionic composition (mg/L) of selective surface waters in North America and the nine lakes studied in 2006/2007.

	[a]Continental Rain	[b]Dilute Wisconsin Lake	[d]Minnesota Lakes	[a]North American Rivers	[c]Mississippi River at Anoka	[c]Minnesota River at Jordan
Ca^{2+}	0.2 - 4	13	29	21	50	103
Mg^{2+}	0.05 - 0.5	3	16	5	17	47
Na^{+}	0.2 - 1	2	6	9	12	32
K^{+}	0.1 - 0.5	–	3	1	3	5
NH_4^{+}	0.1 - 0.5	–	–	--	–	--
SO_4^{2-}	1 - 3	–	14	20	17	162
Cl^{-}	0.2 - 2	0.3	4	8	17	34
NO_3^{-}	0.4 - 1.3	–	–	1	0.8	6

[a] From Wetzel (2001). [b] From Long Term Ecological Research (LTER) site (North Temperate Lakes (Trout) Region). [c] Averages (2000-2007) from Metropolitan Council database. Locations are before the rivers enter the TCMA. [d] Averages from lakes in Minnesota (Gorham, Dean et al. 1982).

A comparison of Tables 4.3 and 4.2 reveals several significant differences:

First, the concentrations of all ions are much higher in the urban lakes than in other freshwater bodies except the calcium, magnesium and sulfate in the Minnesota River.

Second, ionic concentrations in the urban lakes are similar to those in the Mississippi River, except for sodium and chloride. The Mississippi River drains central Minnesota and its chemical water composition could be expected to bear a resemblance to the lakes in the area. Similarities in major ion concentrations such as calcium, magnesium, and sulfate can be seen. Sodium and chloride concentrations are very different, however. Sodium and chloride concentrations in the surface and bottom layers of the urban lakes are 6 to 11 times larger, respectively, than in the Mississippi River upstream of the TCMA.

Third, the dominance of chloride over other anions in the lake is unusual. Only rarely is chloride the dominant anion in an open water system (Hutchinson 1975). In lakes throughout Wisconsin, Minnesota, North and South Dakotas sulfate is the anion which dominates changes in conductivity (Gorham et al. 1982).

Fourth, The increased sodium and chloride concentrations in urban lakes of the TCMA are also apparent in a comparison with lakes located throughout the state of Minnesota (Gorham et al. 1982). This set includes 91 lakes overall, excluding lakes in western Minnesota where high specific conductance is due to rich sulfur bearing minerals (gypsum and pyrite) and lakes in northeastern Minnesota (Canadian shield area) with very low specific conductivity values. Chloride and sodium concentrations in the TCMA lakes during the fall are between 10 and 25 times higher than in these other lakes (Table 6). By comparison, calcium concentrations in the TCMA lakes are only 1.4 times higher than in the other lakes throughout Minnesota.

Overall, the lakes in the TCMA appear to be chloride and sodium dominated waters differing from other water bodies in the region, which are calcium and sulfate dominated.

4.4 Relationship of specific conductance to chloride concentration

Specific conductance measures the electrical resistance of an aquatic solution and depends on ionic strength. Since the water in the urban lakes had a high chloride and sodium content, specific conductance in those lakes is expected to depend primarily on the concentration of these two ions. If a relationship between specific conductance and Cl- and Na+ concentrations exists, specific conductance profiles can be measured to determine profiles of chloride concentrations in the TCMA lakes. The data plot in Figure 4.4 shows a linear relationship between specific conductance and chloride concentrations. As the concentration of chloride increases, so does the specific conductance of the water. A linear equation was fitted to the data (Figure 4.4), and was used to convert specific conductance measurements to chloride concentrations.

If the chloride ion is derived solely from salt (NaCl), then the molar concentrations of Cl- and Na+ should match one to one. It was found that the molar ratio of Cl- to Na+ was 1.08 :1. It is speculated that the molar relationship is different from 1:1 because Na+ is known to be adsorbed onto soil particles whereas Cl- is not (Shanley 1994, Mason et al. 1999, Lofgren 2001, Norrstrom and Bergstedt 2001, Oberts 2003).

Since the water samples had been analyzed not only for chloride and sodium but many other ions, their influence on specific conductance was also analyzed. Specific conductance was only weakly correlated with other ionic concentrations such as potassium, calcium, sulfate and magnesium.

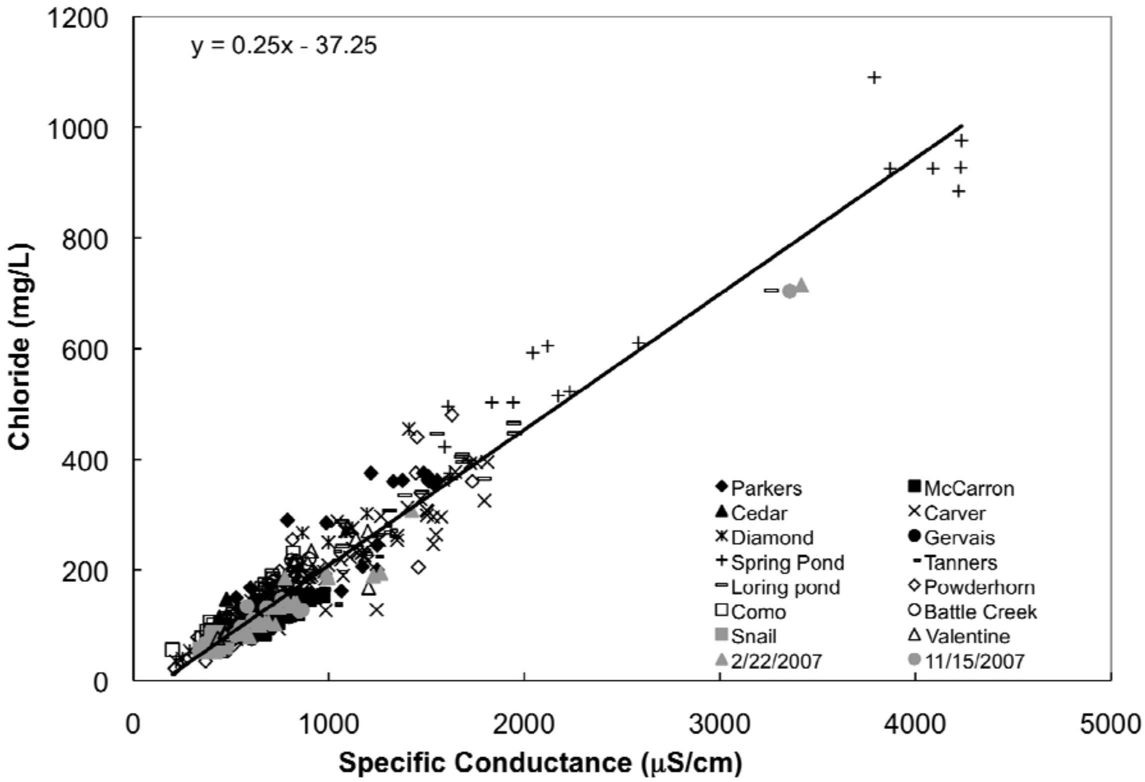

Figure 4.4 Relationship between specific conductance and chloride concentration in TCMA lakes. Data from 14 lakes in the MPCA Environmental Data Access (listed by names), and water samples from 9 TCMA lakes (2/22/2007) were used.

The relationship between chloride or sodium and specific conductance is high - with correlation coefficients above 0.97 for both ions. Correlation coefficients between the specific conductance values and the other individual ionic concentrations sulfate, potassium, calcium and magnesium were -0.09, 0.93, 0.12 and 0.28, respectively. The high median values in mg/L for sodium and chloride (Table 4.2), coupled with the high correlations with specific conductance justify the conclusion that sodium and chloride are the dominant ions in the urban lakes analyzed. The only other ion with a high correlation potassium has very low concentrations. Our study shows increases in chloride concentrations as well as increases in the dominance of chloride in the lake waters with increases in specific conductance. These findings and the lack of natural chloride sources lead to the conclusion that chloride and sodium in the lakes of the TCMA are due to road salt applications.

4.5 Seasonal lake salinity cycles

Specific conductivity/temperature profiles were measured in 13 lakes over several years. Specific conductivity measurements were converted to chloride concentrations. The chloride profiles measured at different times of the year, allow us to explore if there is a seasonal salinity cycle in the lakes. We would expect such a cycle because road salt is applied only in the colder months of a year. Lakes that receive salt-laden snowmelt runoff in winter and spring, and rainfall runoff without road salt content in summer and fall would be expected to have a seasonal salinity cycle. Seasonal variations in salinity for an entire lake should be detectable in volume-weighted average chloride concentrations. These values were therefore calculated for each individual lake and plotted against time in Figures 4.5 and 4.6.

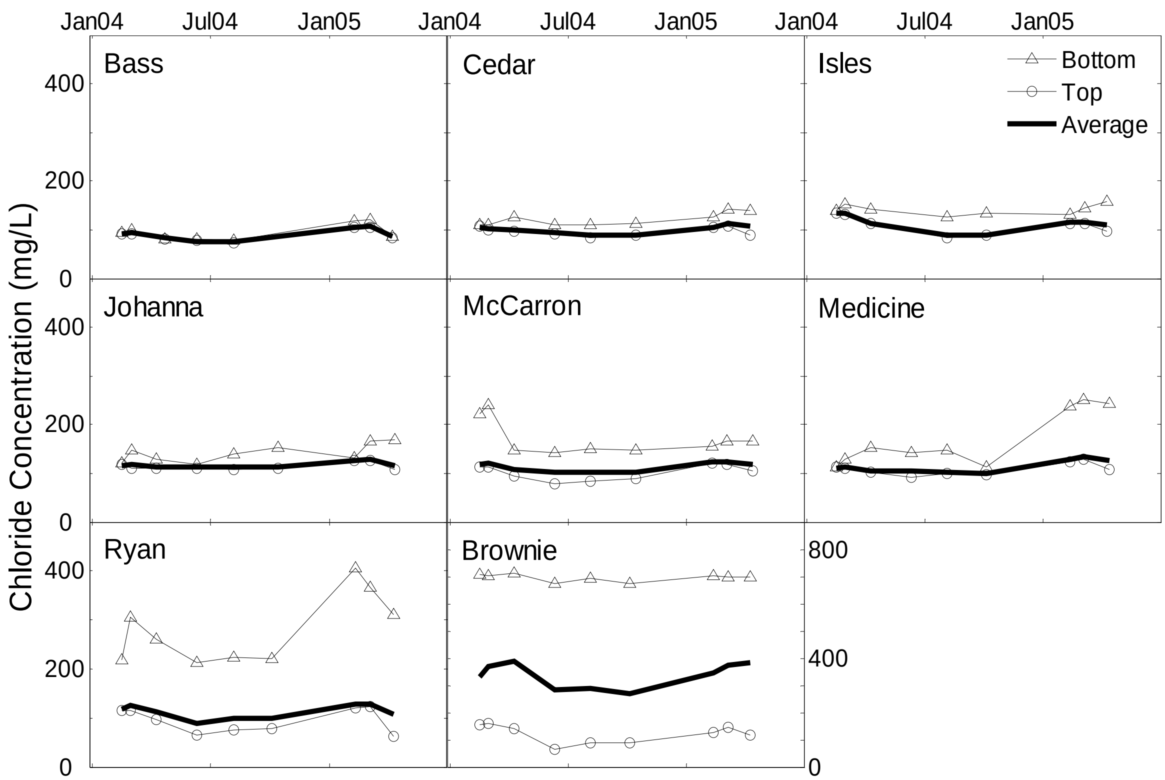

Figure 4.5 Chloride concentrations 0.5 m below the surface and 0.5 m above the bottom of 8 TCMA lakes, and average chloride concentrations in each lake sampled from Feb 2004 to April 2005.

To document salinity stratification we plotted the time series of the salinity values near the top and near the bottom of each lake, as is also shown in Figures 4.5 and 4.6. Salinity stratification can be seen in all 13 lakes. High concentrations of chloride occur during the winter and early spring near the bottom of the lakes. Lower concentrations were measured during the late summer months especially in the surface mixed layer (epilimnion) of the lakes. The strongest salinity stratification was found in Brownie, Parkers, Tanners and Ryan Lake; the least in Bass Lake and Cedar Lake. A detailed discussion of the seasonal salinity cycle and stratification observed in those lakes is given by (Murphy and Stefan 2006). Similar seasonal patterns occurred in the lakes sampled from 2006 to 2008 period (Figure 4.6).

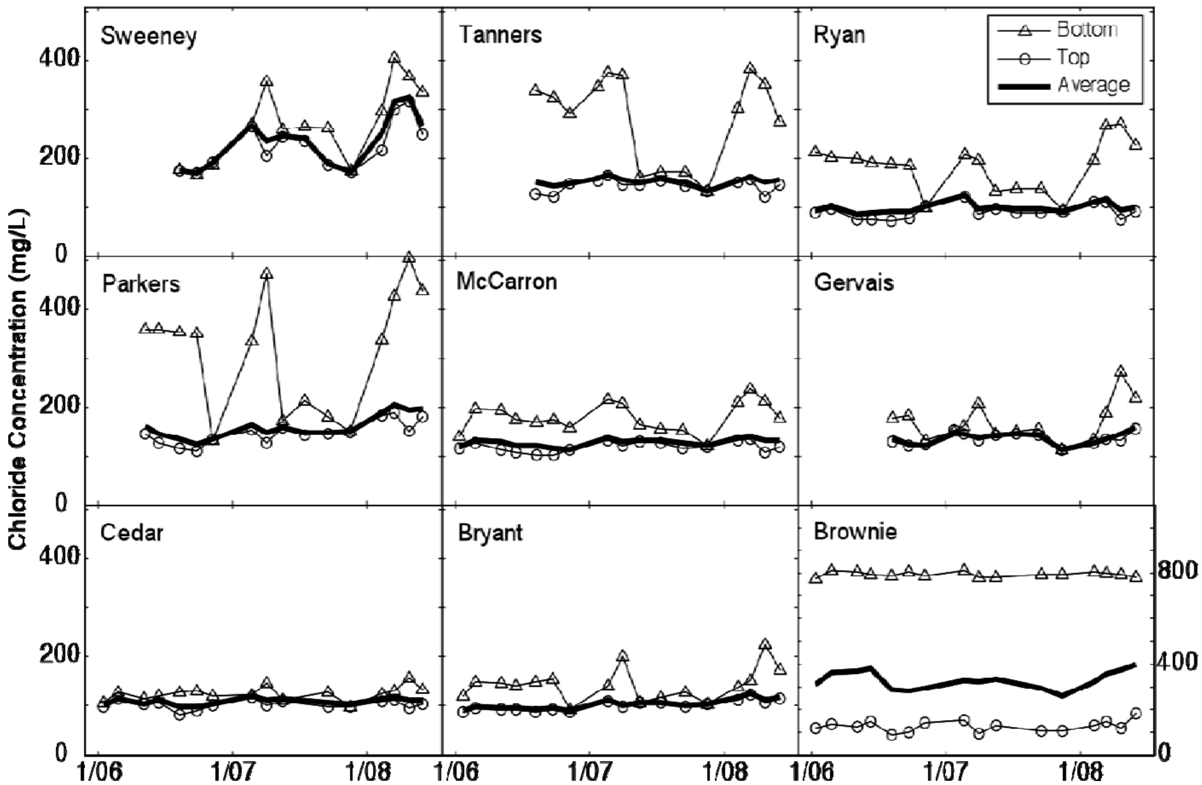

Figure 4.6 Chloride concentrations 0.5 m below the surface and 0.5 m above the bottom of 9 TCMA lakes, and average chloride concentrations in each lake sampled from Jan 2006 to May 2008.

Salinity in Parkers Lake was measured for the first time in the summer of 2006. Because a salinity difference between the bottom layer and top layer existed at that time it is assumed that Parkers Lake did not mix fully during the spring of 2006. In the winter of 2006/2007 the bottom layer of the lake increased from 150 mg/L chloride in November 2006 to over 400 mg/L chloride in April 2007. In spring 2007 the lake fully mixed. The salinity concentrations near the bottom and near the top of the lake matched in the fall of 2007, suggesting that full mixing had occurred. Despite of this short record, Parkers Lake is a good example of the variability in lake mixing: in one year the lake has chemical stratification throughout the summer, but the next year the lake is fully mixed by the end of May, resulting in no chemical stratification during the summer.

Tanners Lake is another lake that has strong salinity stratification between the surface and the bottom layer. As in Parkers Lake, stratification can be seen throughout the summer of 2006. Tanners Lake (unlike Parkers Lake) did not fully mix by the time a profile was taken in November 2006. A salinity increase occurred during the winter months and full mixing occurred in the spring of 2007. Similar seasonal patterns can be seen to a lesser extent in the other lakes, such as Ryan, McCarrons, Bryant, and Gervais.

In the complete data set, Brownie Lake and Sweeney Lake are special. They are at the extreme ends of lake dynamics:

Brownie Lake is a meromictic lake, i.e. it has a permanent salinity stratification. Solute concentrations in the bottom layer of the lake are higher than concentrations in the surface waters throughout the entire time period of sampling with very little variation in the bottom concentrations. Brownie Lake has been known to be meromictic since 1925 (Swain 1984, Tracey et al. 1996), and road salt runoff has only contributed to the previous meromictic conditions. Brownie Lake has a permanent chemical stratification and does not mix fully. Only the lake portion above the chemocline mixes seasonally. Brownie Lake displayed the same meromictic behavior from 2006 to 2008 as from 2004 to 2005.

Sweeney Lake is an artificially mixed lake. High concentrations of salt can be observed in the lake. An aeration system was installed and operated to reduce algal blooms. When this system was shut off in April 2007 to conduct a phosphorus TMDL study, a chemical stratification formed during the following winter, and chloride concentrations reached 400 mg/L near the bottom of the lake.

For a more comprehensive view of the salinity cycles in all of the lakes, the volume-weighted average concentrations for each survey date were normalized. For the set of lakes in Figure 4.6 the average concentration from Sept 2006 to August 2007 was used as the reference for normalization; for the set of lakes in Figure 4.5, the average concentration from May 2004 to April 2005 was used for each lake. The normalized data sets were then averaged for each sampling date to get a representation of the seasonal cycles in all of the lake combined (Figure 4.7). Although the results are for two different time periods and different lakes are used for each of the periods, similar results can be seen. The highest normalized concentrations occur in the winter - when road salt is being applied - and the lowest concentrations occur in the summer and fall when fresh rainwater runoff enters the lakes and flushes some of the salt away.

Seasonal salinity cycles are more pronounced in some of the lakes than others, although they were present in all the lakes studied. The strength of the seasonal salinity cycle can be quantified as the difference between the highest and lowest volume-weighted average concentration in a year. It can be normalized by the minimum average concentration. This definition also expresses the annual change in (removal of) salt storage between the highest and the lowest salt content of a lake relative to the baseline amount of salt stored in a lake. With this definition we can obtain the results in Table 4.4 for the strength of the seasonal salinity cycle:

Table 4.4 Salinity (Cl-) cycles in TCMA lakes. Percent change = ((Max-Min)/Min)*100%.

	Jan 2004 - Nov 2004			Jan 2006 - Nov 2006			Jan 2007 - Nov 2007		
	Min (mg/L)	Max (mg/L)	Percent change	Min (mg/L)	Max (mg/L)	Percent change	Min (mg/L)	Max (mg/L)	Percent change
Bass	76	94	**24**	--	--	--	--	--	--
Isles	88	135	**54**	--	--	--	--	--	--
Johanna	112	127	**14**	--	--	--	--	--	--
Medicine	101	128	**27**	--	--	--	--	--	--
Brownie	270	386	**43**	279	381	**36**	256	338	**32**
Cedar	88	106	**20**	96	109	**14**	101	118	**17**
McCarron	102	123	**21**	113	132	**17**	121	139	**15**
Ryan	88	128	**45**	85	103	**21**	92	123	**34**
Bryant	--	--	--	89	97	**9**	100	110	**10**
Gervais	--	--	--	--	--	--	113	146	**29**
Parkers	--	--	--	--	--	--	147	163	**11**
Sweeney	--	--	--	--	--	--	172	266	**55**
Tanners	--	--	--	--	--	--	131	167	**27**

The maximum concentrations occurred all between January and March, except for Brownie Lake, which had higher concentrations later in the year. This could be caused by upwelling of saline water from below the chemocline under high winds. The minimum concentration in all of the lakes, including Brownie Lake, occurred in the late fall (November).

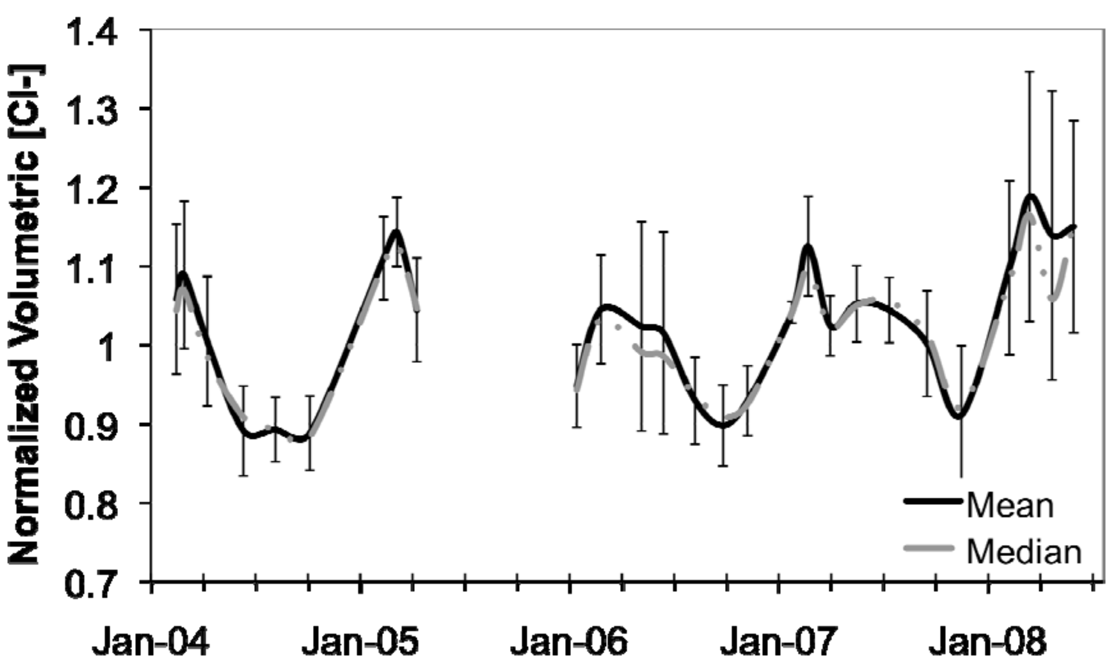

Figure 4.7 Seasonal salinity (Cl^-) cycles illustrated by normalized (volume-weighted) average chloride concentrations. Averages are for all lakes in each time period. Bars represent the standard deviation for the set of lakes. Reference for normalization is the (volume-weighted) average concentration for each lake during the sampling period.

Brownie Lake, Ryan Lake, Lake of the Isles and Sweeney Lake had the strongest seasonal salinity cycles of all the lakes studied. Brownie is the most saline lake studied. It is also meromictic, whereas Sweeney Lake was artificially mixed. All four lakes are fairly shallow and have a small surface area. This would allow for a stronger flushing effect due to shorter hydraulic residence time. In Brownie Lake salinity changes due to snowmelt runoff occur only in the top 6 m allowing for a shortened hydraulic residence time. The strongest salinity cycle was found in Sweeney Lake, which drains large portions of Interstate 394 and Highway 100. Sweeny Lake is also a shallow lake with aerators that allow for complete mixing throughout the year. This results in a stronger flushing effect of the lake by rainwater runoff in the summer.

Two of the four lakes analyzed for the entire sampling period (2004-2008) show increases in the annual minimum concentrations from year to year. Both Cedar Lake and Lake McCarron display higher minimum and maximum concentrations each year representing an accumulation of road salt in the lake. Bryant Lake also displays this behavior, but has been studied for two years only.

Seasonal salinity cycles had already been found in the grab samples of surface waters collected over a five-year period (1982 to 1987) from lakes near highways in the TCMA (Sadecki 1989). This study was limited to grab samples from the lake surface and did not include volumetric average concentrations or concentrations at the bottom of the lakes. The concentrations in the 13 lakes sampled in th1989 study were highest in the winter and spring and lower in the summer and fall. The study concluded, without quantification, that chloride concentrations in lake surface waters were directly related to runoff lane miles and inversely related to lake surface area and volume.

4.6 Salinity and temperature stratification profiles

The salinity dynamics in the surface and the bottom layer of each lake have already been illustrated in Figures 4.5 and 4.6 and also discussed. The complete set of measured temperature and salinity profiles cannot be given here, but may be found in reports by Murphy and Stefan (2006) and Novotny et al. (2007).

Three examples of measured temperature and salinity profiles from the 2006-2008 surveys are shown in Figures 4.8, 4.9 and 4.10. They are for Brownie Lake in Minneapolis, Tanners Lake in St. Paul and Parkers Lake in Plymouth. These profiles illustrate the seasonal salinity stratification cycles in more detail than Figures 4.5 and 4.6.

The stratification dynamics are highly correlated with weather dynamics. Snowfall amounts and number of snowfall events influence the timing and the amount of road salt applications. In addition, air temperatures and sunshine influence snowmelt and therefore the concentration, the amount and the timing of salt entering a lake. The higher the concentration of salt in the snowmelt water entering a lake, the stronger the potential for chemical and density stratification becomes. Wind blowing over a lake supplies the energy to break the chemical stratification in the fall or spring when thermal stratification is weak. Wind speed and direction are highly variable. Hence chemical stratification and lake mixing are not repeated exactly from year to year.

Brownie Lake (Figure 4.8) is the only meromictic lake analyzed. The water above the chemocline in Brownie Lake behaves like water in any other lake. A pattern of spring and fall overturns occurs in this lake only above the chemocline. The chemical stratification in the lake is so strong and the salinity and therefore the density of the lake water below the chemocline is so high that snowmelt runoff containing road salt enters the lake without sinking to the lake bottom. Instead, the permanent saline layer above the lake bottom deflects the plunging saline density current into the middle of the lake as an interflow.

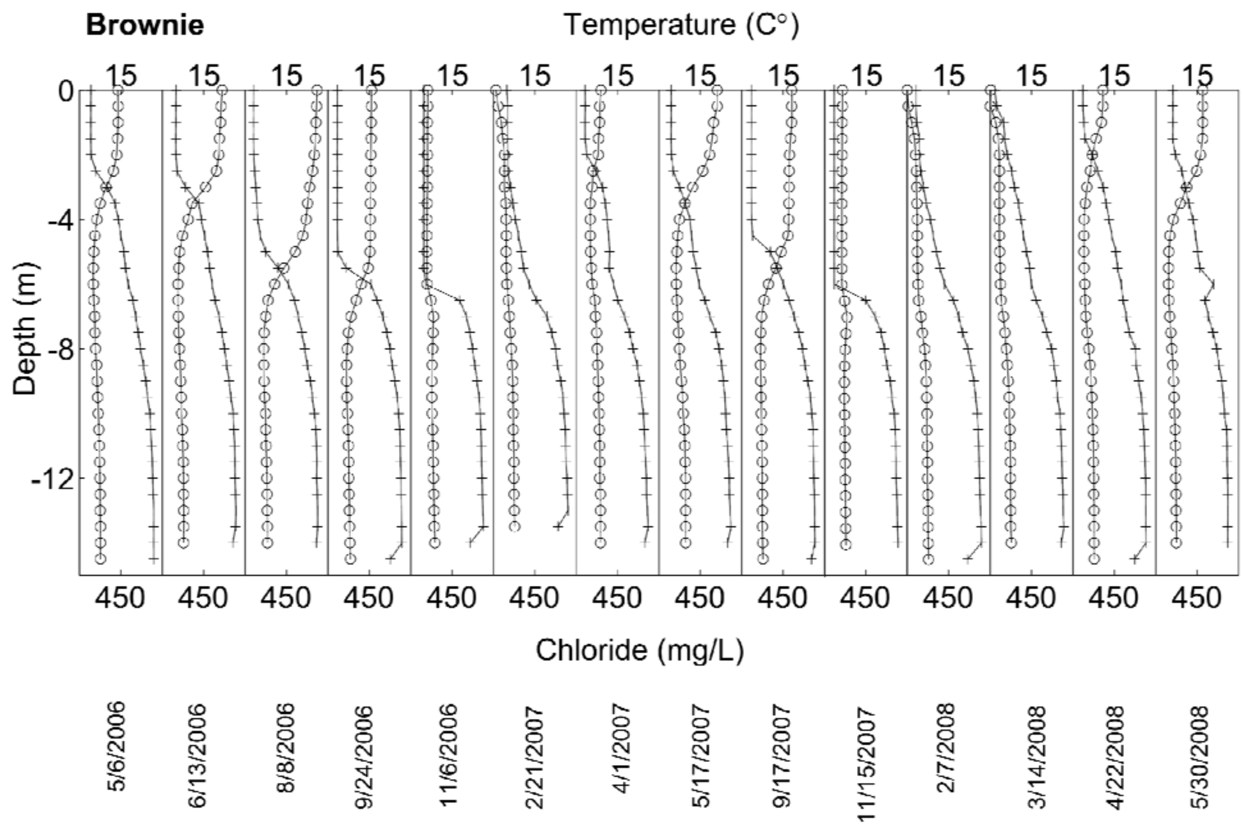

Figure 4.8 Chloride and temperature profiles for Brownie Lake.

Tanners Lake (Figure 4.9) does not appear to be meromictic, but monomictic at times. During the summer chemical stratification is present in Tanners Lake. In September when the temperatures at the surface of the lake begin to decrease, and the erosion of the thermocline begins, the chemocline also begins to degrade and moves to greater depths in the lake. In November when the thermocline has been completely eroded the lake becomes almost fully mixed except for a small saline layer at the bottom of the lake. During the winter months the chemocline forms in the deepest portion of the lake. The highest concentrations of chloride and the thickest layer of increased chloride concentration is seen in April. This is significant because the thermocline has already begun to form; if the mixing of the lake was triggered by density differences due to temperature only, the lake would have fully mixed by April, but Tanners Lake has not mixed, because of the added density in the bottom layers due to the presence of salt. Sometime between April and May the lake finally mixed completely resulting in uniform chloride concentration through all depths in the summer. Similar patters are seen in Parkers Lake (Figure 4.10) except that full mixing occurred as late as November 2006.

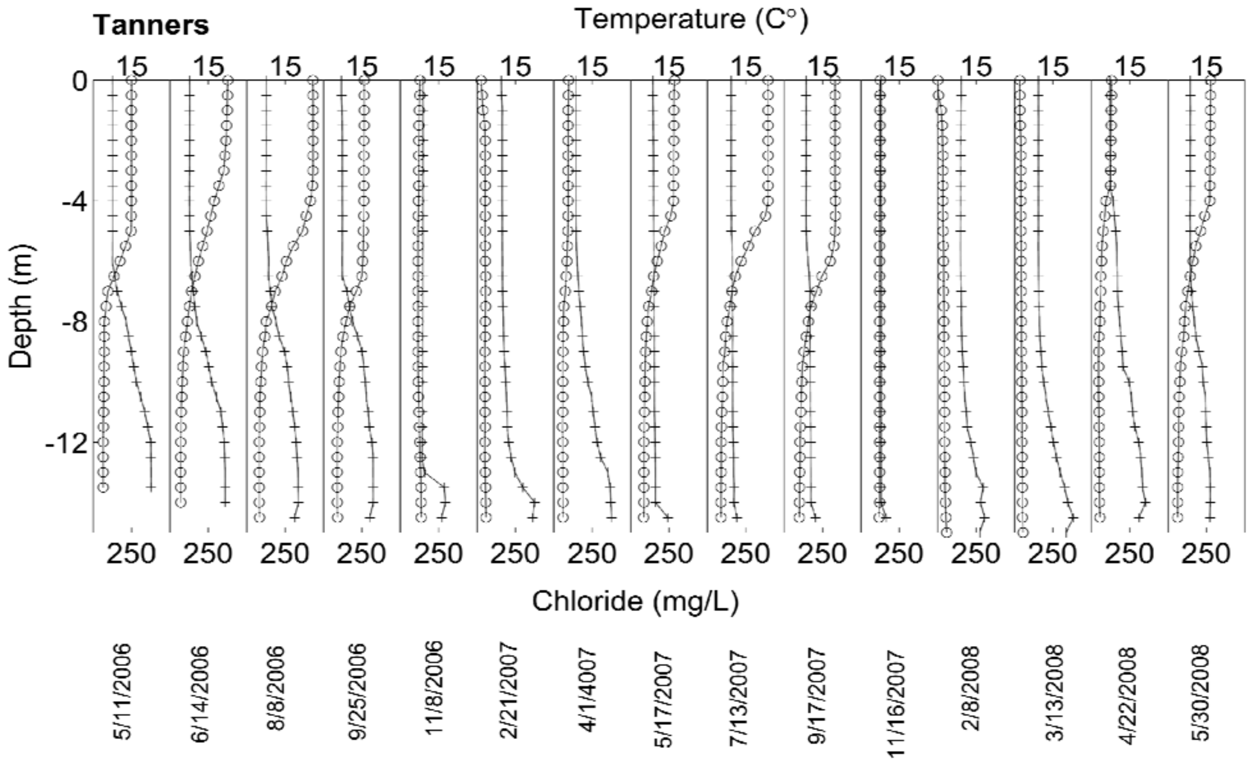

Figure 4.9 Chloride and temperature profiles in Tanners Lake.

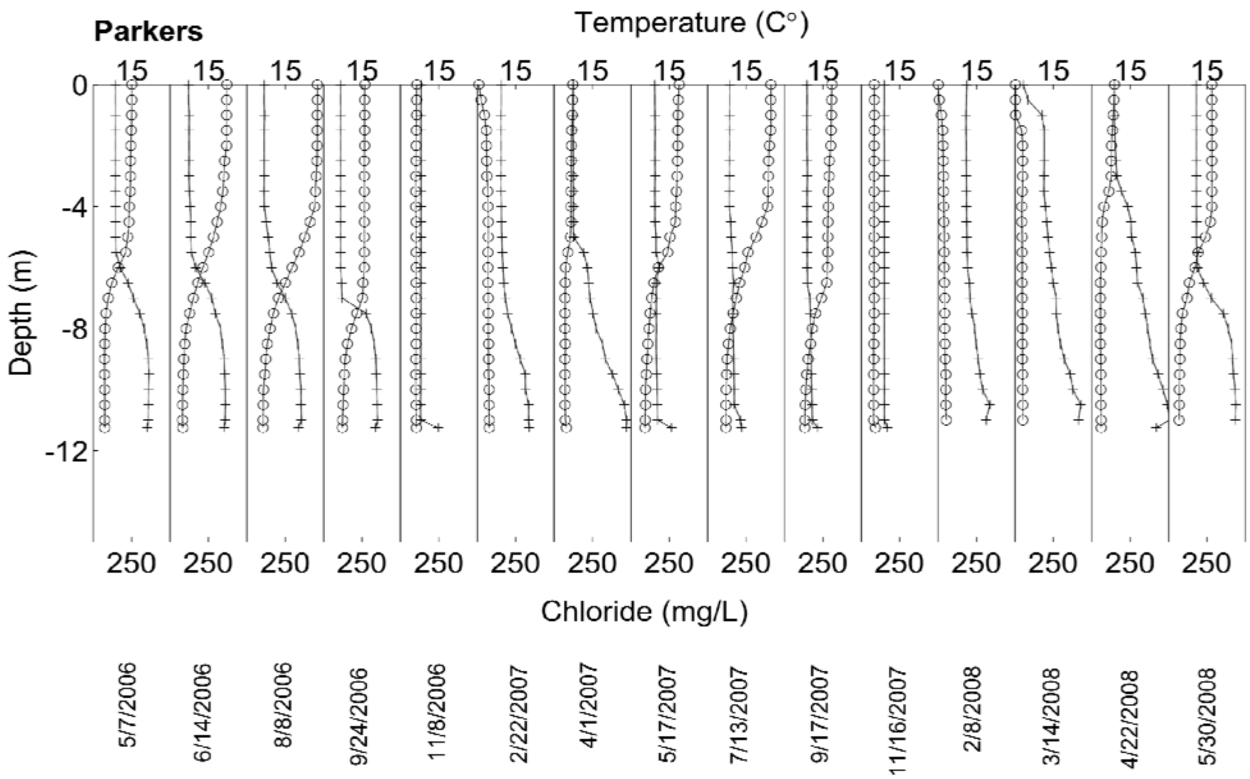

Figure 4.10 Chloride and temperature profiles in Parkers Lake.

Lake McCarron is an example of a lake receiving salt, but not enough to prevent full mixing either in the spring or fall. Salinity profiles in Lake McCarron were similar to those in Cedar, Bryant, Ryan and Gervais. In all of these lakes inflows of high density salt water can be seen to enter the lakes during the winter causing chemical stratification. This chemical stratification is not as strong as in Tanners Lake and Parkers Lake; therefore full mixing still occurred during the spring and fall. McCarron and Ryan Lake formed stronger chemoclines than Gervais, Bryant and Cedar Lake.

Sweeney Lake has salinity profiles that are different from the other lakes because it has an aeration system. During the summer no stratification is seen in the lake either thermal or chemical. The concentration of chloride remains constant with depth through the summer and fall. In winter (February) the concentration of chloride throughout the lake increases. The influx of salt laden runoff is easily detected in the fully mixed salinity profiles of the lake. Between February and April the aeration system was shut off and a clear chemocline formed at the bottom of the lake.

The chemoclines in the lakes form during the winter and spring when snowmelt runoff carrying sodium and chloride enters the lakes. The timing of the chemocline formation in lakes corresponds with peak salt concentrations in streams in the metro area. Sometimes these chemoclines are strong enough to prevent mixing in the spring resulting in monomictic instead of dimictic lake conditions. If full lake mixing does not occur in the spring, it was found to occur during the fall. So far the added salinity at the bottom of the lakes has not resulted in the formation of meromictic lakes in the TCMA. Only one of the study lakes in the TCMA (Brownie Lake) is known to be completely meromictic, but the meromixis is strongly linked to the particular physical characteristics of the lake, and was caused before road salt application became common (Swain 1984).

4.7 Salinity in lake sediment cores

Leakage of saline water into the sediment at the bottom of lakes can influence the chemical stratification from year to year. If the density of the water above the sediments is high enough mixing with the sediment pore water by density-driven natural convection can occur. Water with a lower concentration of salt and therefore lower density will move upwards in the sediment pores and water with a higher salinity will move downwards into the sediment pores. The net result is a loss of salinity and decreasing stratification of the lake**.**

To see if saline water is penetrating from the lake bottom into the lake sediment pore water, sediment cores were extracted from Lake McCarron and Tanners Lake. These lakes were chosen because they represent two different types of lakes. Tanners Lake turned monomictic during the 2006/2007 season resulting in the exposure of the lake sediments to lake water with an increased density for a long period of time. Lake McCarron has much less salinity in the bottom layer than Tanners Lake. In Tanners Lake the saline layer above the bottom of the lake is up to 7m thick and has concentrations reaching 400 mg/L chloride compared to the maximum concentrations of 240 mg/L chloride in Lake McCarron.

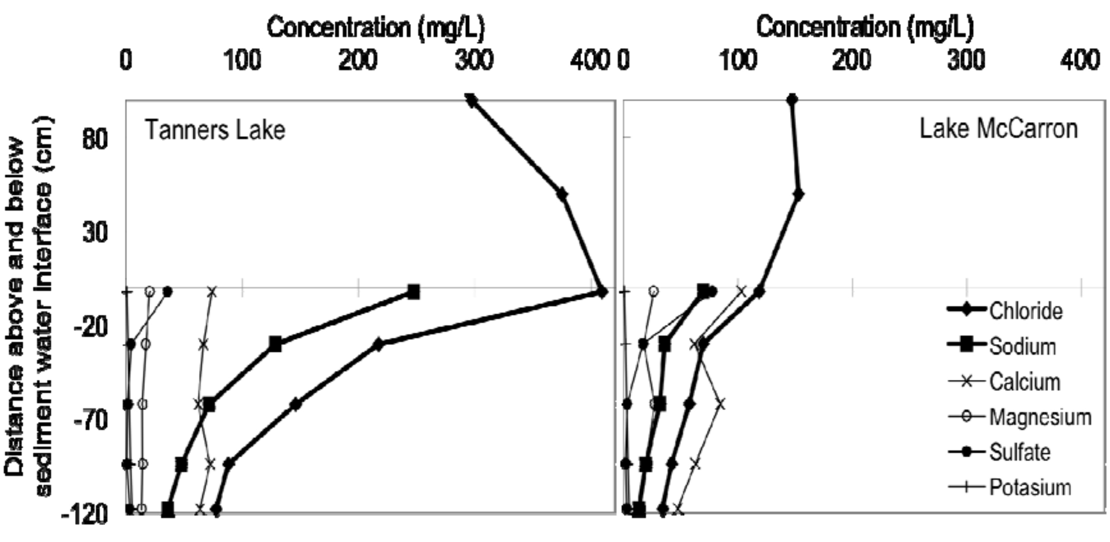

Figure 4.11 Ionic composition of pore water from sediment cores extracted at the deepest locations of Lake McCarron and of Tanners Lake.

Sediment cores of 1.2m length were extracted on 28 Feb 2007 with the help of the LacCore research staff at the University of Minnesota. The cores were sectioned and the pore water was extracted and analyzed for major ions. The profiles of ionic strength (Figure 4.11) show that the sodium and chloride concentrations decrease exponentially with depth in the sediments of both

Lake McCarron and Tanners Lake. They start at the sediment surface with concentrations equal to those of the saline water layer at the bottom of the lake. This leads to the conclusion that there is indeed convective circulation of salt water into the lake sediment pores. The concentrations of the other ions appear to stay about constant with depth into the sediment, but sodium and chloride do not. The concentrations of sodium and chloride start at around 250 and 410 mg/L respectively in Tanners Lake and around 113 and 186 mg/l respectively in Lake McCarron. Over the length of the core (1.2 meters) these values are reduced to 36 and 78 mg/L in the Tanners Lake core and to 14 and 34 mg/L in the Lake McCarron core, respectively.

4.8 Salinity trends and correlations in TCMA lakes

It is apparent from the seasonal salinity cycles and all the other information presented above that road salt is entering the lakes in the TCMA. Not detectable in the monthly measurements presented are long-term trends in lake salinity. Short term trends were detected in 3 of the lakes studied but a more comprehensive analysis is needed. To accomplish the trend analysis specific conductance measurements obtained from the MPCA Environmental Data Access website were analyzed. The average annual chloride concentration in the surface layer (top 3m) of 39 TCMA lakes with more than 10 years of record is plotted in Figure 4.12. The top 3 meters was used since concentration patterns in the surface layer of the lakes closely matched the volumetric average concentrations in Figures 4.5 and 4.6. Values are normalized (referenced) relative to the average for the period 2001-2005. After all 38 lake time series were averaged together the combined normalized time series was multiplied by the median concentration of the 38 lakes (average concentrations between 2001-2005) to get the resulting data series. Also plotted are rock salt purchases by the state of Minnesota from 1984 to 2005 (over 30% of those amounts are used in the TCMA (Sander et al. 2007)). The trends for both the chloride concentrations (salinity) of TCMA lakes and for the rock salt purchases by the state are strikingly similar. Both time series show an increase from 1984 to 2005 and a correlation coefficient of 0.72. The slope of the chloride concentrations is 1.48 mg/L/year. Extending this trend into the future would produce a doubling in salinity in these lakes in about 56 years. Hind-casting at the rate would give a near zero concentration in the 1950s corresponding to the time when road salt application were started.

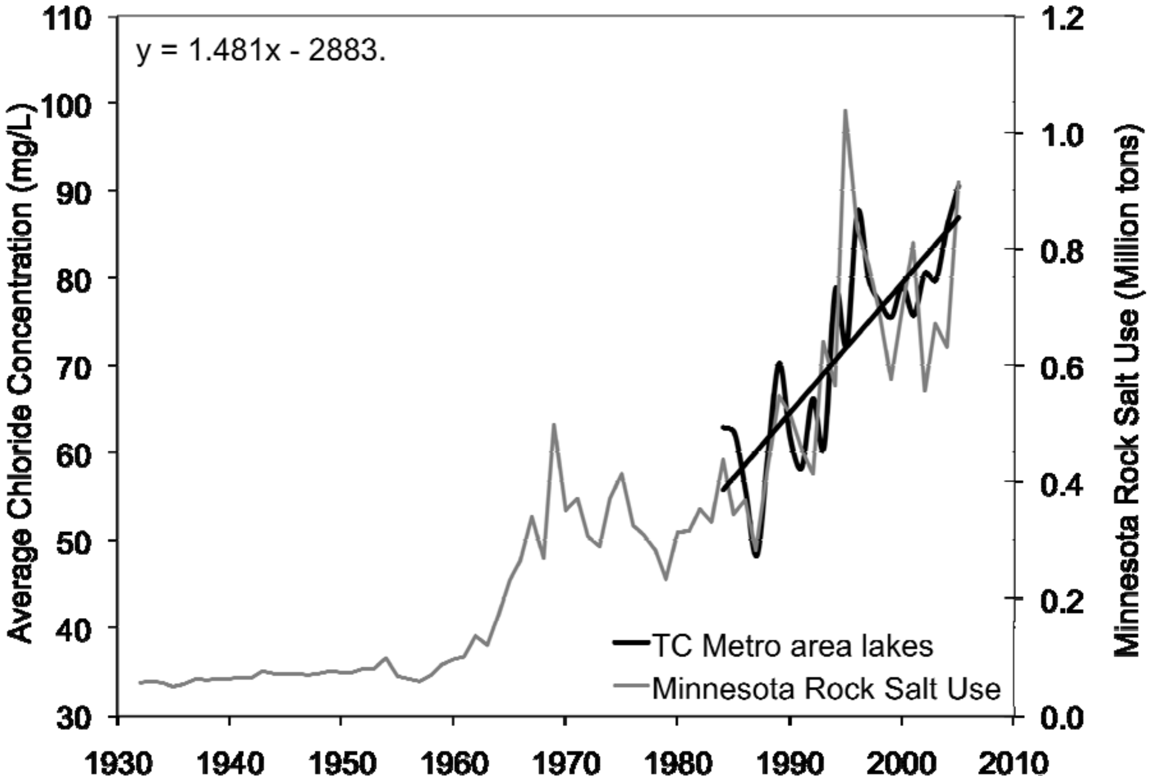

Figure 4.12 Comparison of lake chloride concentrations in 39 TCMA lakes and rock salt purchases by the state of Minnesota (Novotny et al. 2007).

An even clearer correlation was obtained by using 5-year running averages for both the specific conductivity and the rock salt data. This removes some of the variability due to changes in total snowfall and number of snowfall events. It also removes variations in road salt applications and effects of hydraulic residence times in the lakes. The 5-year running averages of the two dependent variables have a correlation coefficient of 0.93.

Information on the 38 individual lakes used in the trend analysis is given in Table 4.5. Lakes with at least 10 years of data from 1984-2005 were analyzed. Specific conductance profiles were typically measured between April and November by watershed districts, consulting companies or government agencies.

Table 4.5 Historical average, trend and maxima of chloride concentrations, and bathymetric and watershed data for 38 TCMA lakes.

	Max Depth (m)	Surface Area (ha)	Watershed Area (ha)	Percent Impervious (%)	[Cl-] Top 3 Meters (mg/L)	Trend Top 3 Meters (%/year)	[Cl-] Annual Max (mg/L)	Years of data (years)
Bald Eagle	11.0	513	2843	9	42	0.6	87	22
Beaver	3.4	26	1446	26	90	1.8	117	22
Bennet	2.7	9	293	36	63	2.2	100	22
Brownie	14.3	5	136	33	105	2.1	798	15
Calhoun	25.0	162	1408	35	103	1.2	158	18
Cedar	15.5	68	537	28	84	0.8	142	18
Como	4.6	25	591	32	89	2.1	166	22
Diamond	1.8	47	268	44	142	2.1	467	17
Gervais	12.5	95	1144	30	100	2.4	178	22
Harriet	26.5	136	737	28	93	1.2	119	18
Hiawatha	10.1	22	2378	45	91	1.7	221	17
Independence	17.7	342	1630	3	43	0.1	71	12
Island South	3.4	24	77	20	44	1.1	77	22
Isles	9.4	44	252	29	87	1.0	134	18
Johanna	13.1	86	1188	39	107	2.2	167	22
Josephine	13.4	47	350	23	48	1.7	81	21
Keller	2.4	29	329	23	87	2.4	113	21
Kohlman	2.7	30	629	27	87	1.7	160	22
Long NB	9.1	74	3781	25	99	2.3	202	22
Loring	4.9	3	144	77	340	2.7	760	11
Mccarron	17.4	28	549	24	85	1.7	189	22
Medicine	14.9	359	4380	30	88	1.4	204	14
Nokomis	10.1	83	1467	36	66	1.1	99	18
Otter	6.4	134	382	7	25	0.6	50	18
Owasso	11.3	141	1047	24	44	1.2	81	22
Phalen	27.7	80	580	30	89	2.3	127	22
Powderhorn	6.7	5	94	44	86	0.7	361	13
Round	2.4	12	251	29	94	2.4	231	22
Snail	9.1	61	477	22	57	2.4	102	22
Spring	2.1	2	30	47	505	3.0	1018	10
Tanners	14.0	28	214	33	104	1.1	288	11
Turtle	8.5	166	316	12	42	1.2	70	22
Valentine	4.0	24	664	33	117	2.5	208	20
Wabasso	20.1	19	103	32	36	1.2	74	22
Wakefield	3.0	9	563	32	97	2.9	178	22
Weaver	17.4	60	203	17	53	0.7	85	11
West Silver	14.3	29	208	30	57	2.2	225	21
White Bear	25.3	978	3059	11	31	0.9	43	22
Median Values	**10.1**	**45**	**543**	**30**	**87**	**1.7**	**150**	**21**

Note: Chloride concentrations for the top 3 meters are annual average value for the period 2001-2005.

Trend is based on the time series of annual average concentrations from 1984 to 2005 for the top 3 meters of each lake and normalized with the average value from 2001 to 2005 to obtain a percent change per year.

Annual maximum chloride concentration is the average of the maximum concentration in the lake for each year between 2001 and 2005, measured at any depth.

Chloride concentrations in the surface layer throughout the TCMA ranged from 31 mg/l in White Bear Lake, a large lake located in the northern suburbs to 505 mg/l in Spring Lake which is practically a storm detention pond located near I-394 in Minneapolis. The maximum chloride concentrations occurred during the winter months and were recorded near the bottom of the lakes. These values ranged from 43 mg/L again in White Bear Lake to 1018 in Spring Lake. Every lake has an increasing trend ranging from 0.57 percent/year to almost 3 percent/year. The data clearly display that increasing chloride concentrations in lakes of the TCMA are common throughout the metro area and not necessarily specific to a small number of lakes located close to highways.

Correlations of chloride concentrations values with lake and watershed parameters are given in Table 4.6. Chloride concentration values correlate best with the impervious surface area of the watershed. This seems correct since impervious surfaces are characteristic of roads and parking lots on which road salt would be applied in the watershed. Lake surface area and depth as well as watershed area have no correlation with chloride concentration. The ratio of impervious surface area in the watershed to lake volume (i.e., lake surface area times lake depth) has the highest correlation coefficient with the average chloride concentration and the max concentration. As the volume of the lake increases there is more water to dilute the snow melt runoff causing lower concentrations. Conversely, as the impervious surfaces increase the potential for road salt applications also increases.

Table 4.6 Correlation coefficients between chloride concentrations with lake and watershed information. PI (Percent Impervious), SA (Lake surface area), D (Lake depth).

	Lake area (ha)	Depth (m)	watershed area (ha)	Percent Impervious	PI / (SA *D) ($1/m^3$)
[Cl-] top 3 meters	-0.25	-0.29	-0.18	**0.67**	**0.94**
[Cl-] average annual max	-0.28	-0.26	-0.24	**0.66**	**0.79**
Trend	-0.44	-0.40	-0.18	**0.54**	0.43

The location of the 39 lakes and all 71 lakes for which information was available is also of interest. Figures 4.13 displays where the lakes are located in the TCMA. In addition it also indicate where the lakes with the highest ave, max, chloride concentrations can be found (Figure 4.13). It seems fairly evident that lakes with high chloride concentrations are found predominantly in the core region of the TCMA, and lakes with low are more common towards the periphery of the TCMA. It seems very reasonable that lakes located in the heavily populated areas of the TCMA have higher chloride concentrations. The further away the lakes are from the heavily populated areas, the lower the concentrations and the trends are.

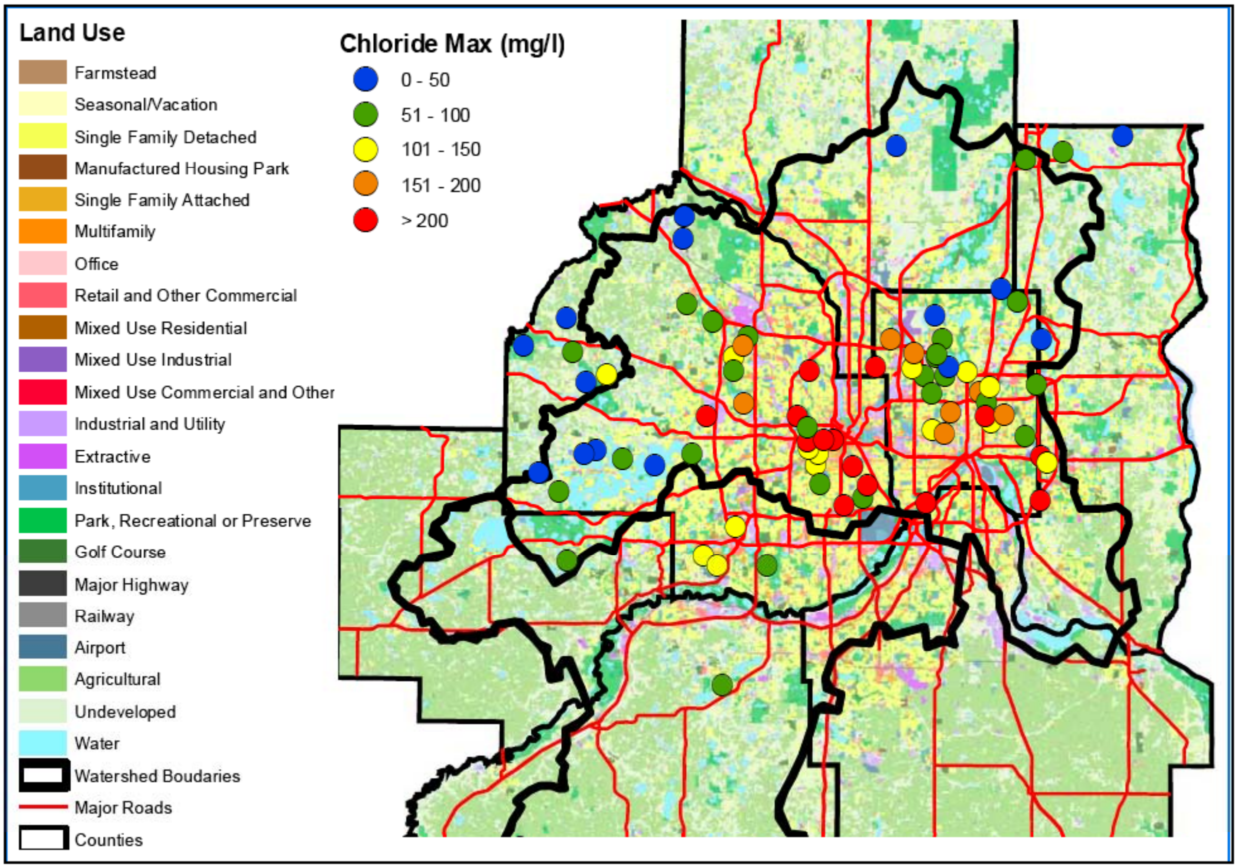

Figure 4.13 Maximum chloride concentrations in 71 lakes of the TCMA.

Chapter 5

Salinity of Groundwater in Minnesota

5.1 Objectives of investigation

The purpose this part of the study was to assemble, review and interpret data on sodium and chloride concentrations in aquifers (wells) in Minnesota, particularly the Minneapolis-St. Paul Metropolitan Area, and to relate this information to road salt uses. The total amount of NaCl applied to roads in the TCMA per season is estimated at 349,000 tons per year, and 70% is expected to be retained in the TCMA. The State purchases over 900,000 short tons of road salt annually. Changes in groundwater salinity in the TCMA and Minnesota over time, particularly the last 50 years are of particular interest, because it is suspected that aquifers are the ultimate recipients (sinks) of some of the road salt applied at the ground surface. Of specific interest are:

- current chloride concentrations in aquifers,
- effects of urban development and road density on chloride concentrations in aquifers (spatial dependence),
- historical trends in chloride concentrations in aquifers (temporal dependence).

5.2 Groundwater information sources in Minnesota

There are over 200,000 wells registered in the County Well Index (CWI) in Minnesota. The wells serve a variety of purposes such as monitoring, municipal, domestic, agricultural and industrial water supply. Depths range from 2 ft to 8080 ft. Wells are concentrated in several areas as shown in Figure 5.1.

Many sources of information on groundwater quality in the TCMA and the state of Minnesota were consulted: the Minnesota Pollution Control Agency (MPCA), Minnesota Department of Health, Minnesota Geological Survey, U.S. Geological Survey and the water departments of several municipalities. Counties have information on groundwater resources. Statewide groundwater quality surveys by the MPCA from 1992 to 1996 and from 2004 to 2007 provided the largest amount of data.

The Minnesota Geological Survey (MGS) has mapped the state’s geology and aquifer systems. The MGS also has information on groundwater geochemistry.

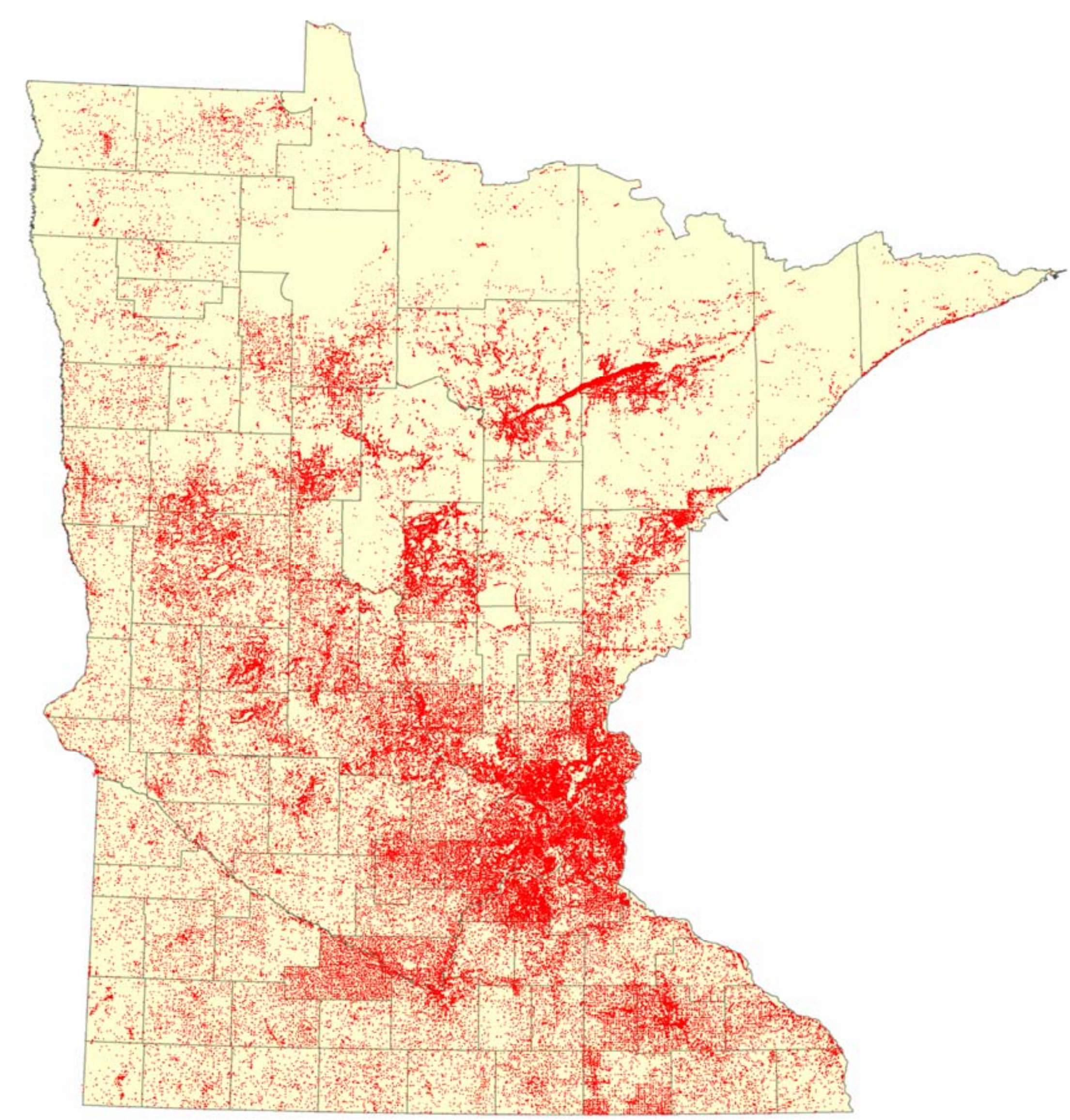

Figure 5.1 Wells in Minnesota.

The Minnesota Department of Health (MDH) is the controlling agency for programs in Health Risk Assessment, Drinking Water Protection, Hazardous Sites and Substances, and Well Management. The latter of these includes maintaining the County Well Index (CWI), a record of wells in Minnesota. The MDH is also responsible for measuring Priority One contaminants in all municipal water supply systems in the state. Chloride is a secondary contaminant, mainly associated with aesthetics (taste), and is not subject to regular testing.

The Minnesota Department of Agriculture (MDA) is responsible for the monitoring of surface and groundwater for contaminants associated with agricultural practices. Of interest is long-term evaluation of regular pesticide applications on water quality. Consequently, the MDA only samples in areas of agricultural runoff, not including the TCMA.

The Minnesota Department of Natural Resources (DNR) is charged with managing groundwater quantities in the state. The DNR currently operates the Ground Water Level Monitoring Program, and the Ground Water Mapping Program, which collect data on the presence, direction of flow, and natural quality of groundwater and on regional geology.

The Minnesota Pollution Control Agency's (MPCA) runs a major groundwater monitoring program, the Groundwater Monitoring and Assessment Program (GWMAP), which was initiated in 1989. Under the GWMAP’s ambient groundwater program over 800 wells in the state were sampled once between 1992 and 1996 to determine background concentrations of chemicals in groundwater. This data collection was repeated starting in 2003 when the MPCA initiated a trend analysis study on contaminants in Minnesota. These two data sets are very comprehensive and provide chloride concentrations as well as physical characteristics of wells, i.e. location, well depth, and geological formations present.

The USGS monitors groundwater levels and quality in addition to stream flow and lake levels throughout the state. The USGS maintains the Active Groundwater Level Network as well as the National Water Quality Assessment Program (NAWQA). The NAWQA program is similar to the efforts of the MPCA: water quality metrics and contaminant tracking.

5.3 Chloride in Minnesota groundwater

Long-term groundwater quality data on chloride concentrations do not seem to be available for the TCMA region or the state of Minnesota. A report by the MPCA (1979) on highway de-icing chemicals reviews adverse effects of chloride on biota. Statewide groundwater quality surveys by the MPCA from 1992 to 1996 and from 2003 to 2006 provided the largest amount of useful data. The former was part of the MPCA’s Ambient Ground Water Monitoring and Assessment program that sampled over 800 wells for the four year period. In 2003, the MPCA restarted its groundwater sampling program, concentrating on trend analysis of chloride and nitrate concentrations in wells primarily located in the TCMA, the Rochester region and the St. Cloud region. In the fall of 2007, the MPCA published a document which states that:

- Median chloride concentration for the period 1992-1996 was 4.9 mg/l
- Median chloride concentration for the period 2004-2005 was 12 mg/l

Chloride concentrations in wells of southeastern Minnesota in 1992-96 and again in 2004-2005 are given in Figures 5.2 and 5.3, respectively. The water samples taken in wells of the TCMA, the Rochester and the St. Cloud areas had higher chloride concentrations.

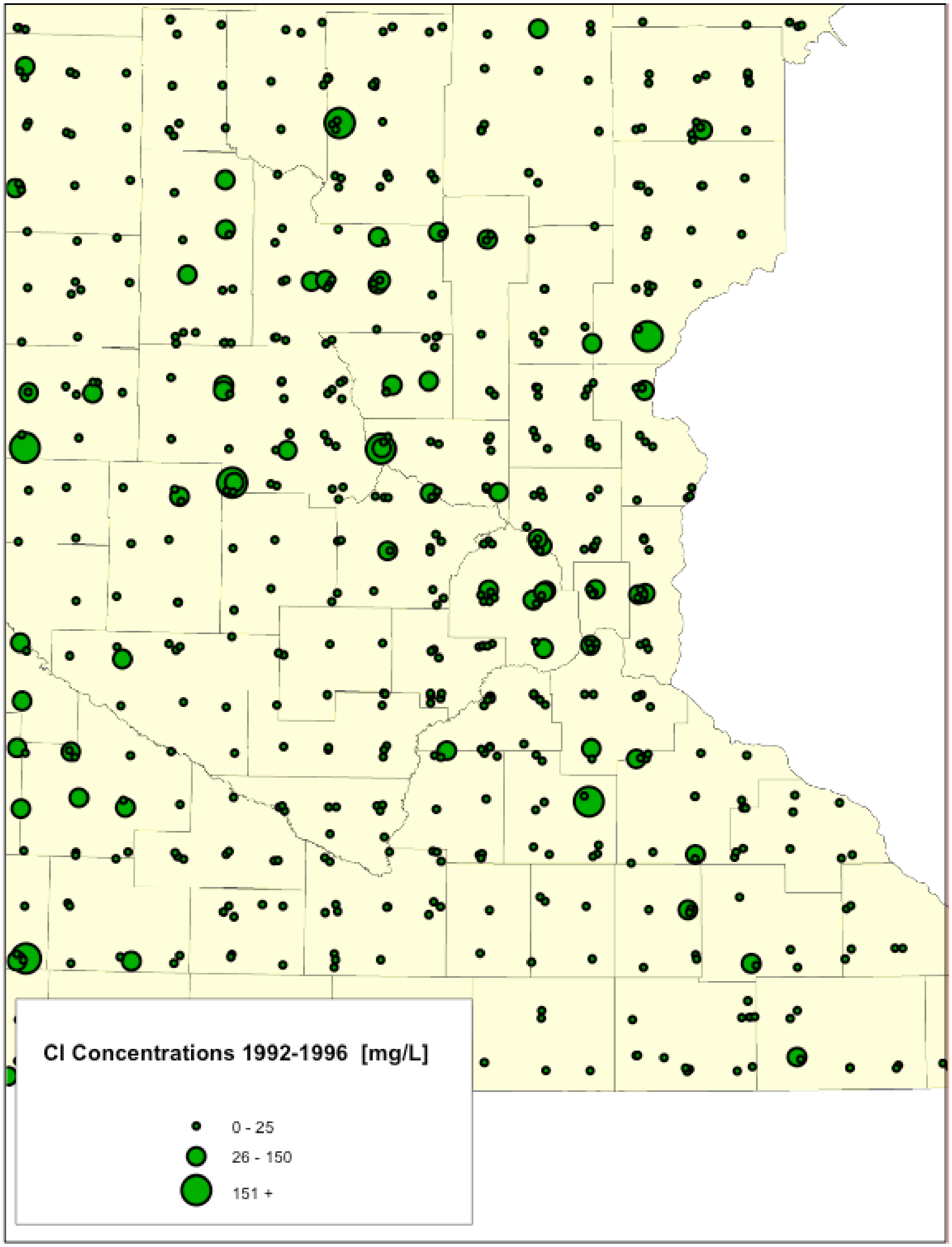

Figure 5.2 Chloride concentrations in wells of southeastern Minnesota. The largest circles represent over 150 mg/L of chloride, the smallest less than 25 mg/L of chloride (1992-1996 data from MPCA).

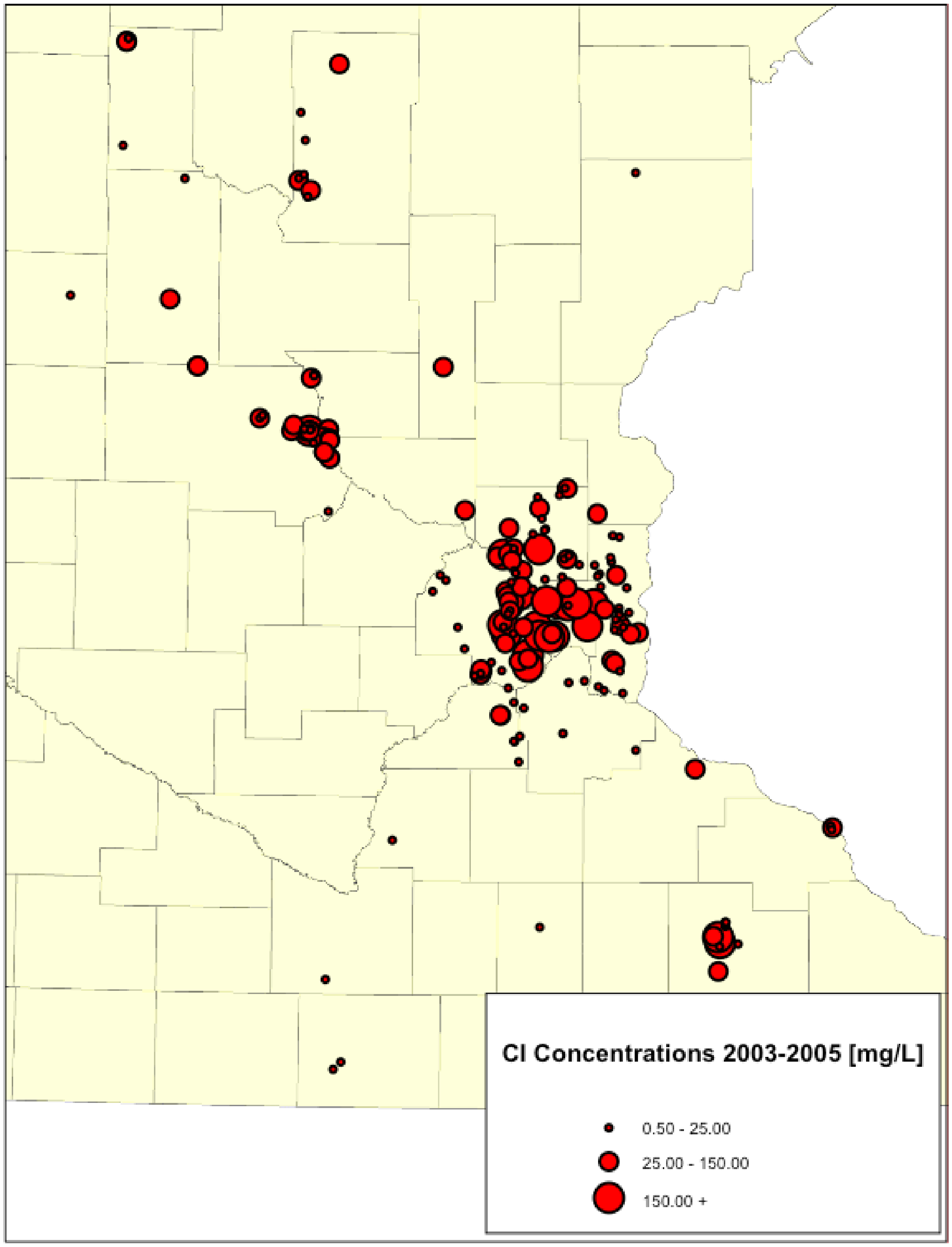

Figure 5.3 Chloride concentrations in wells of southeastern Minnesota, especially near St. Cloud, Minneapolis/St.Paul, and Rochester. The largest circles represent over 150 mg/L of chloride, the smallest less than 25 mg/L of chloride (2003-2005 data from MPCA).

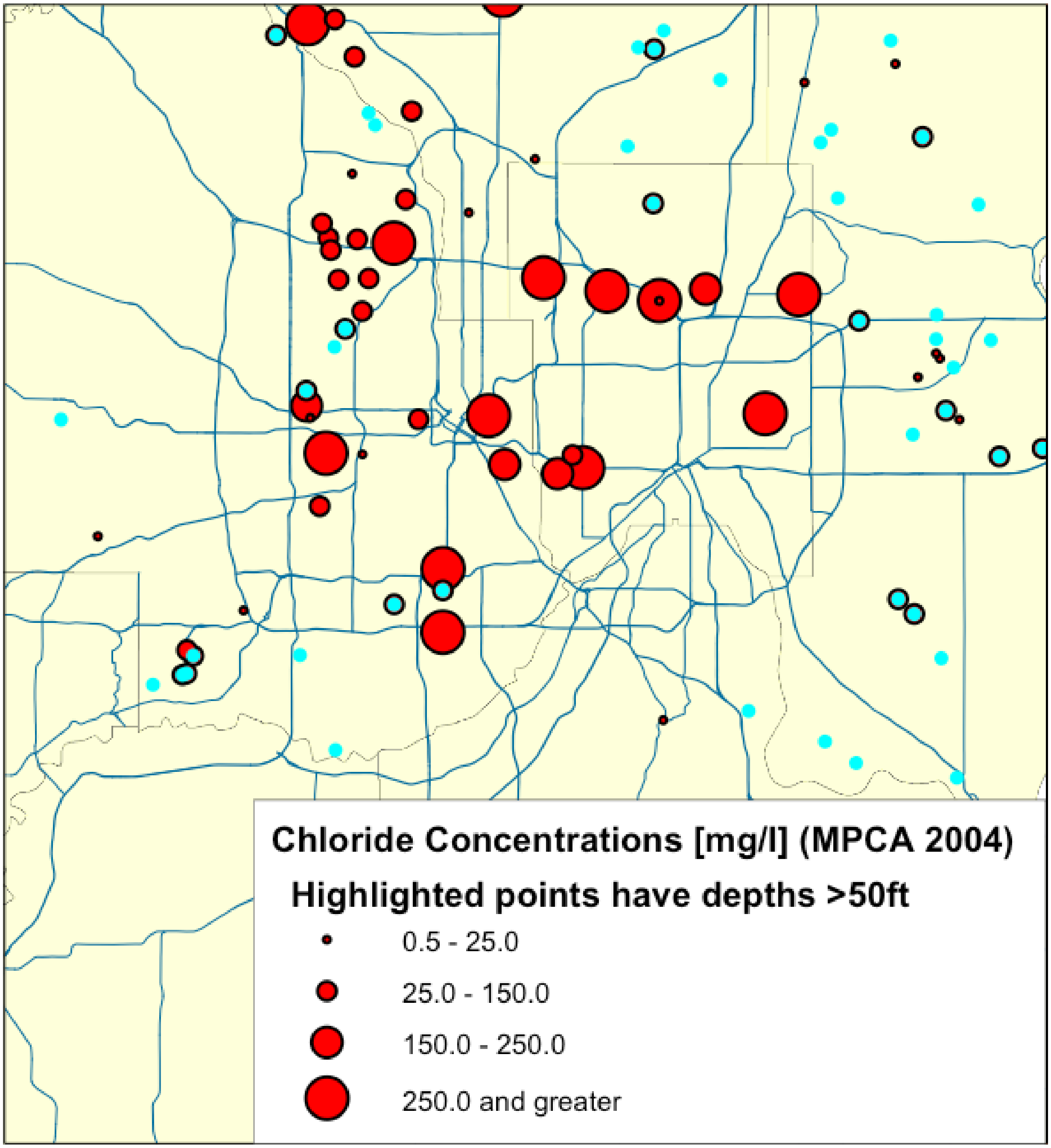

Figure 5.4 Chloride concentrations in TCMA wells. Dark (red) circles represent shallow wells (depth < 50ft). Light (blue) circles represent deep wells (depth > 50ft) (2003-2005 data from MPCA).

Using GIS, and data for road networks and wells throughout the TCMA, Figure 5.4 was generated. The largest circles represent wells with chloride levels above 250mg/l. These wells are in close proximity to major roadways in the TCMA and have depths less than 50 ft. Wells which are deeper than 50 ft have chloride concentrations of less than 150 mg/L.

In 2003 the MPCA published results of a land use study in the St. Cloud area. Figure 5.5 gives chloride concentrations in shallow groundwater for different land uses. The mean chloride concentration in groundwater below undeveloped areas is ~3mg/l (background), in groundwater below urban and developed areas it is between 50mg/l and 80 mg/L.

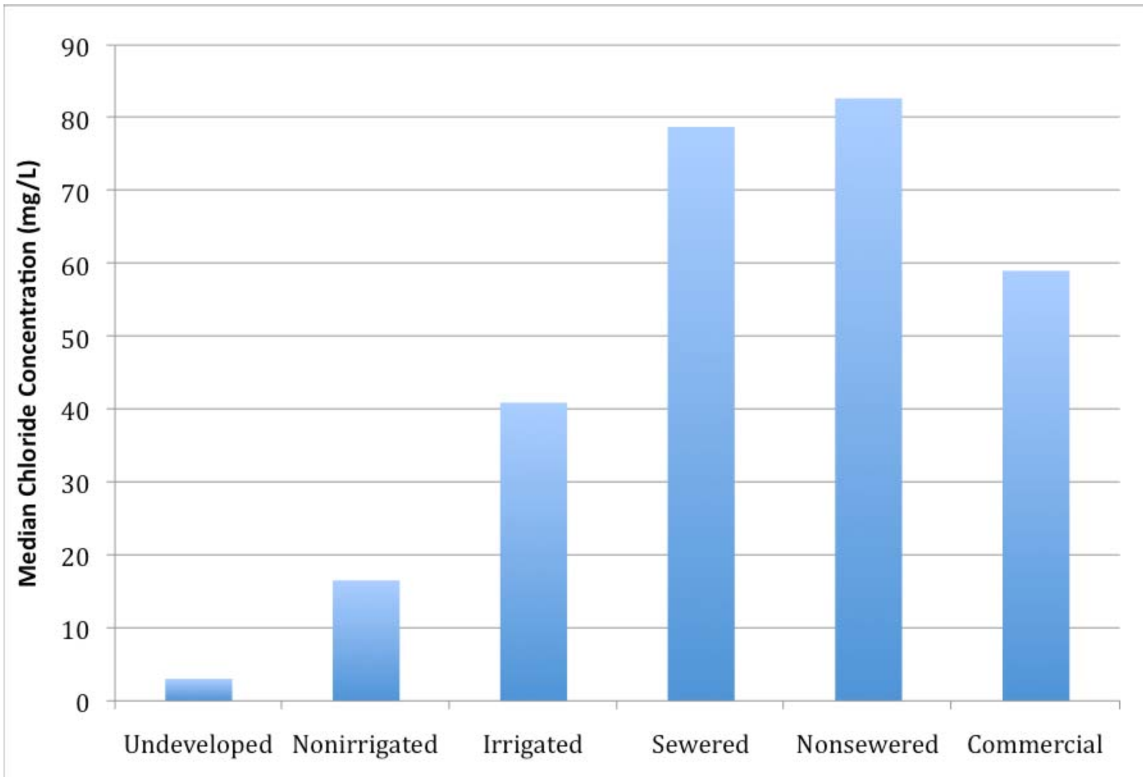

Figure 5.5 Chloride concentrations in groundwater below different land covers/uses (Trojan et. al. MPCA 2003).

The distribution of chloride with depth in an aquifer can give a clue whether the source of chloride is anthropogenic rather than geological/natural. Figure 5.6 gives a plot of chloride distribution in the Twin Cities Metro Area.. Higher concentrations are found near the ground surface, i.e. in shallow wells, indicating that infiltrating water is high in chloride. The flux of chloride is diluted by mixing with more groundwater at greater depths. Figure 5.7 shows that mean and median concentrations decrease as the well depth increases.

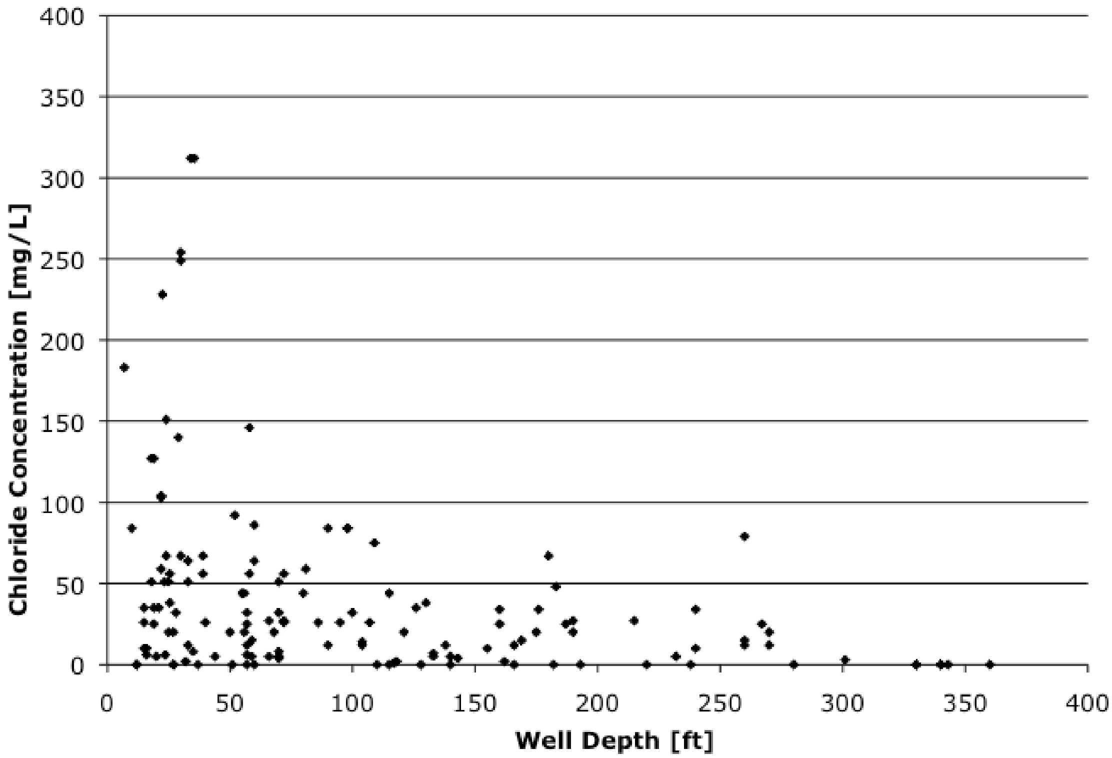

Figure 5.6 Chloride concentrations in groundwater of the TCMA.

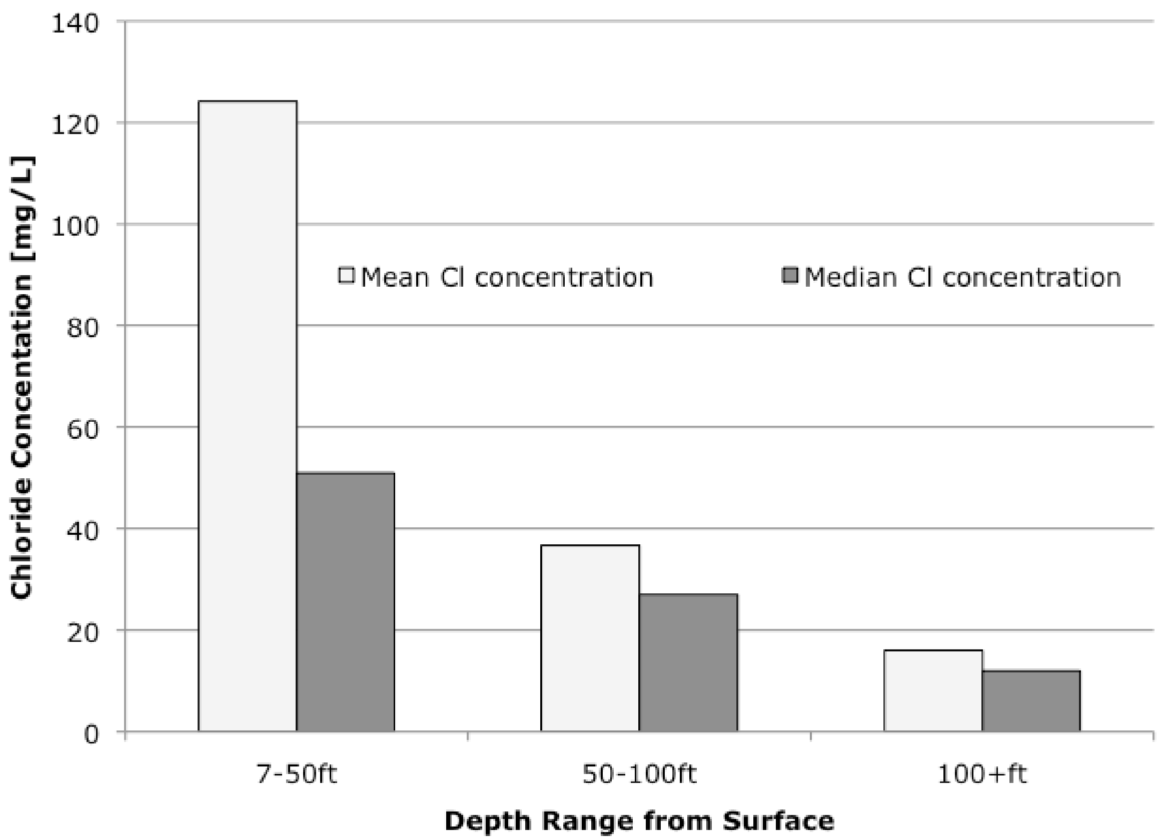

Figure 5.7 Chloride concentration vs. depth of groundwater in the TCMA (MPCA 2004-2005 DATA).

5.4 Comparison with another northern region

Several studies pertaining to road salt use and chloride in groundwater were conducted in the Toronto area. Toronto is similar to the TCMA with regard to latitude (Greater Toronto Area at 43° 40' N, TCMA at 45° 00' N), population, transportation networks, snowfall and aquifer systems. Studies of sources and of long-term trends in groundwater chloride concentrations were of particular interest.

In the U.S., chloride in drinking water is considered a secondary contaminant. Its limit is set primarily based on aesthetics (taste), and water supply utilities are not mandated to test drinking water for chloride regularly. As a result, we could not find long-term data from wells in Minnesota to document if there were any long-term trends in chloride concentrations in groundwater. In Canada, chloride is considered a contaminant, In Toronto, Canada, there have been several studies on chloride contamination in surface waters as well as in ground water. Figure 5.8 illustrates the long-term increase in chloride in wells in the Toronto area. The wells are located in the glacial aquifer system of southern Ontario.

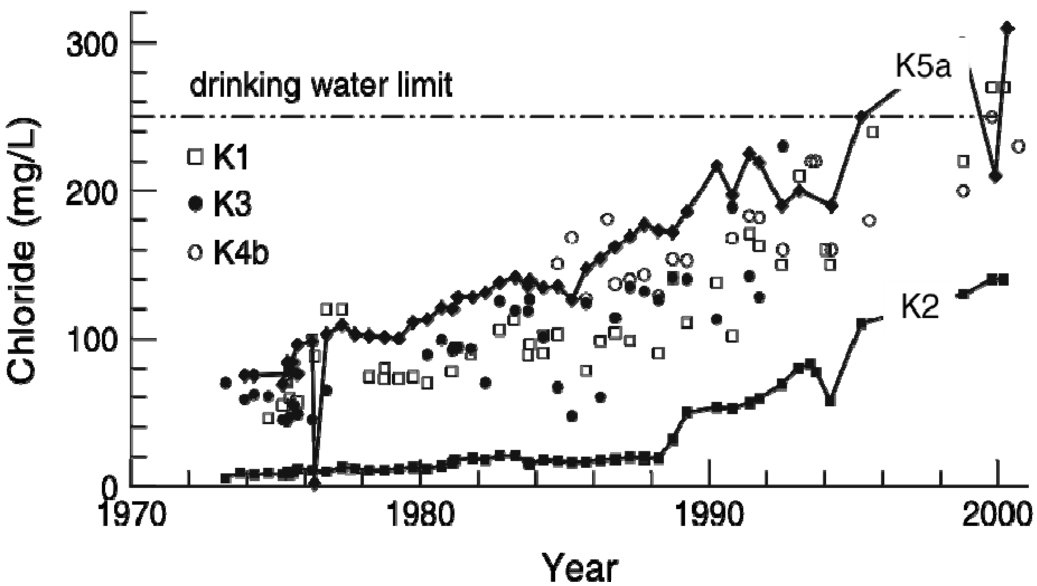

Figure 5.8 Canadian measurements of chloride concentrations in five groundwater wells (K1, K2, K3, K4b and K5a) in the Toronto area (Bester et al. 2006).

To identify the source of the chloride compound several indicators can be used, in particular the ratio of chloride to other ions; Na, P, Br and I (Panno et al. 2006; Howard and Beck 1993). Figure 5.9 illustrates the relationship between Na and Cl from road deicing salt in the Toronto area. Figure 5.10 gives the same kind of data plot for the TCMA. The relationships are similar, but not identical. Further analysis with other major ions is ongoing.

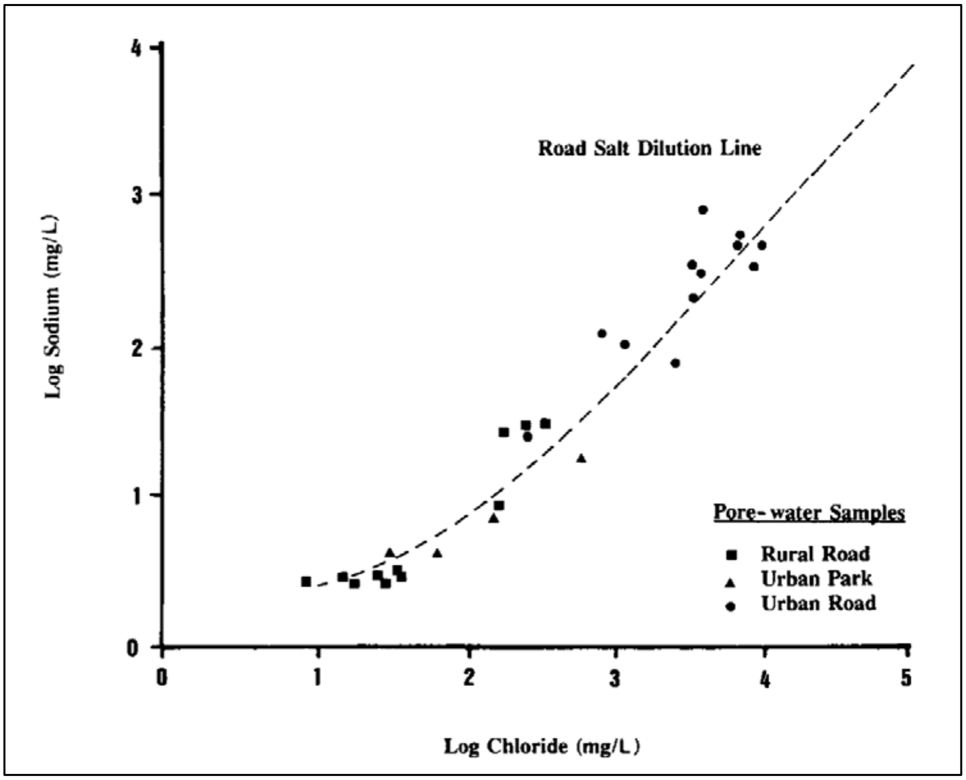

Figure 5.9 Sodium vs. chloride relationship attributed to NaCl use for winter road maintenance (Howard and Beck 1992).

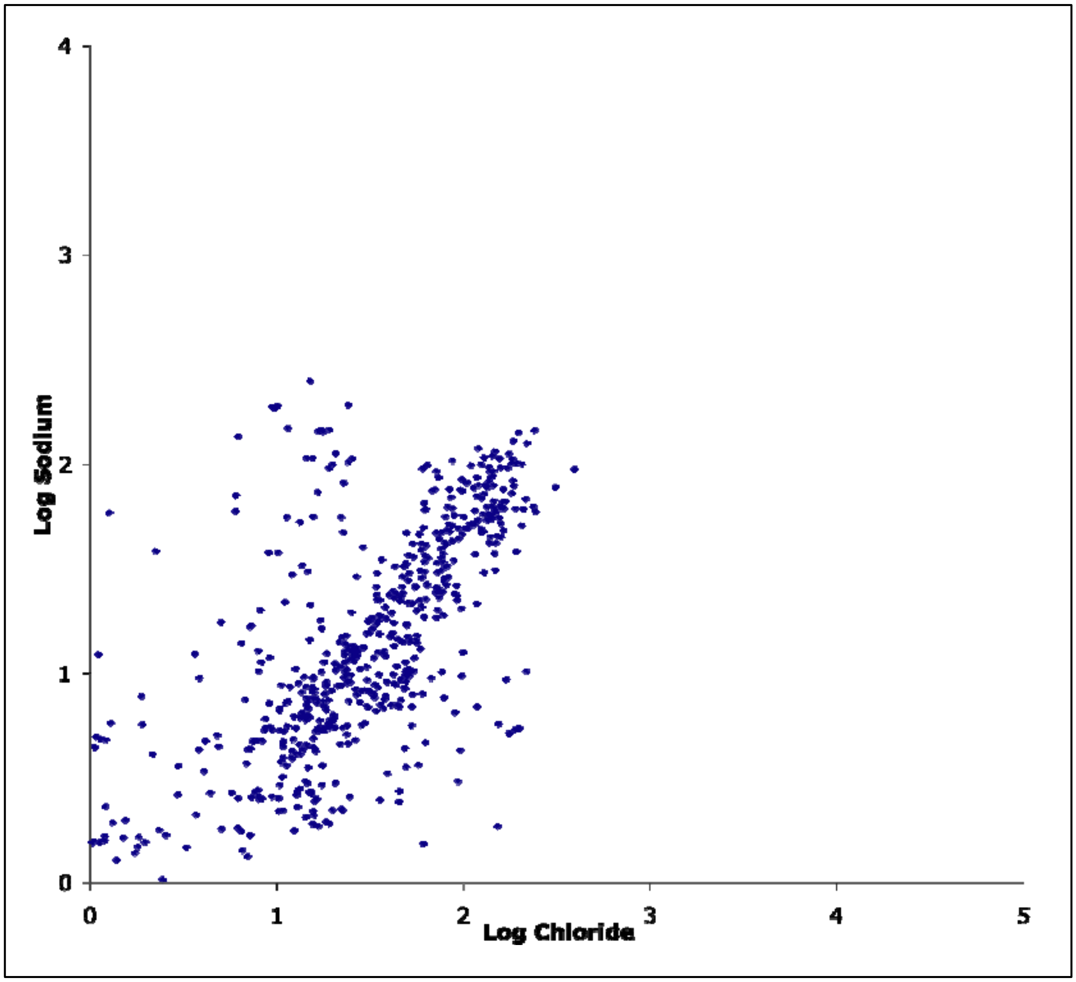

Figure 5.10 Chloride vs. sodium concentrations in groundwater of the TCMA.

Chapter 6

Reduction and Mitigation of Road Salt Impacts

The benefit of road salt applications in terms of crash avoidance, injury prevention and lives saved is undoubtedly very high. We do not know of a monetary value for it. The purchase cost of 350,000 tons of salt applied annually in the TCMA is about $ 45 per ton (Minnesota Materials Management Division), the cost of spreading it is perhaps on the order of $150 per ton. A study by Vitaliano (1992) estimates infrastructure costs of at least $615 per ton, vehicle corrosion costs of at least $113 per ton, aesthetic costs of $75 per ton applied near environmentally sensitive areas, plus uncertain human health costs. Adjusting for inflation brings this total cost to around $1200. The American Society of Corrosion Engineers estimates that one ton of road salt results in $1460 in corrosion damage to bridges and that the indirect costs may be 10 times the direct cost (Sohanghpurwala 2008). If one accepts these numbers, the annual costs for the TCMA are on the order of $15 Million for road salt purchases, $50 Million for application, and $ 450 Million for corrosion and other damage to infrastructure and public and private properties.

Our efforts should be directed towards a reduction of the rates of road salt application while maintaining the level of road safety. There are many ways by which such a reduction can be achieved: education of the driving public, education and certification of road salt applicators, changes in application technology, and changes in road deicing techniques.

In addition we also need to think about mitigation and reversal of adverse impacts. One example of potential remediation is the removal of saltwater layers from the bottom of some urban lakes. We may not be able to go back to 1950s conditions or natural conditions, but we may be able to stop or reverse the trends and avoid truly adverse effects in the future. Some of those threats were spelled out 30 years ago in a document by the MPCA (MPCA 1979).

Chapter 7

Conclusions

Road Salt Applications:

349,000 short tons of road salt (NaCl) are applied for road de-icing the Twin Cities Metro Area (TCMA) every year; 76% by cities, counties and the state and 24% by private and commercial users

Twin Cities Metro Area Chloride Budget:

1) Around 70% of the salt being applied in the TCMA watershed is retained in the watershed. A similar percentage of salt applied in 10 watersheds of small streams of the TCMA is retained in those watersheds.
2) Salt residence time is short-term (days and weeks) in streams, intermediate-term (months and years) in lakes and long-term (years and decades) in groundwater.
3) Road salt transport as dust by wind has not been explored.

Lakes:

1) Lake chloride concentrations (volume weighted) are increasing on average by 1.4 mg/L/year in the TCMA. Increasing trends were found in 39 lakes of the TCMA.
2) Chloride concentrations in lake water are highest near the bottom during the late winter and early spring, and lowest near the surface during fall.
3) Saline water seeps into the pores of lake sediments. Observations were made in two lakes.
4) A seasonal salinity cycle has been observed in 13 TCMA study lakes.
5) Few lakes studied had chloride concentrations above the 230 mg/L standard set by the MPCA (Sweeney, Tanners, Parkers, and Brownie).
6) Chloride concentrations in individual lakes are positively correlated with the percent of impervious surface area in the watershed, and inversely correlated with lake volume.
7) 8 to 55% of the minimum salt content of the 13 study lakes is flushed out every year.

Groundwater:

1) Chloride concentrations in shallow groundwater wells near major roads are higher than in other wells.
2) Chloride concentrations in some shallow groundwater wells of urban areas have increased over the last 15 years.
3) Higher chloride concentrations have been found by the MPCA in shallow groundwater monitoring wells than in deep wells in the TCMA.
4) Samples with chloride concentrations above 250mg/L have been found by the MPCA in shallow groundwater wells less than 50ft deep in close proximity to road networks in the TCMA

Overall:

The overall conclusion has to be that some deterioration of the water quality of Twin Cities Metro Area lakes due to increasing chloride levels is in progress. No acute problems have been documented yet, but present trends will lead to violations of water quality standards in some urban lakes. Similarly shallow groundwater in the Twin Cities Metro Area appears to receive sufficient salt input annually so that water quality deterioration is beginning to be evident.

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Appendix A:

Title pages of four detailed technical reports

UNIVERSITY OF MINNESOTA
ST. ANTHONY FALLS LABORATORY
Engineering, Environmental and Geophysical Fluid Dynamics

Project Report No. 503

Inventory of Road Salt Use in the Minneapolis/St.Paul Metropolitan Area

by

Andrew Sander, Eric Novotny, Omid Mohseni, and Heinz Stefan

Prepared for

Minnesota Department of Transportation
Local Roads Research Board (LRRB)
St. Paul, Minnesota

December, 2007
Minneapolis, Minnesota

UNIVERSITY OF MINNESOTA
ST. ANTHONY FALLS LABORATORY
Engineering, Environmental and Geophysical Fluid Dynamics

Project Report No. 505

Road Salt Effects on the Water Quality of Lakes in the Twin Cities Metropolitan Area

by

Eric Novotny, Dan Murphy and Heinz Stefan

Prepared for
Local Road Research Board (LRRB)
Minnesota Department of Transportation
St. Paul, Minnesota

December, 2007
Minneapolis, Minnesota

UNIVERSITY OF MINNESOTA
ST. ANTHONY FALLS LABORATORY
Engineering, Environmental and Geophysical Fluid Dynamics

Project Report No. 509

Potential Groundwater Contamination by Road Salt in Minnesota

by

Andrew Sander, Eric Novotny, Omid Mohseni, and Heinz Stefan

Prepared for

Local Road Research Board/
Minnesota Department of Transportation
St. Paul, Minnesota

September 2008
Minneapolis, Minnesota

UNIVERSITY OF MINNESOTA
ST. ANTHONY FALLS LABORATORY
Engineering, Environmental and Geophysical Fluid Dynamics

Project Report No. 513

A Salt (Chloride) Balance for the Twin Cities Metropolitan Area Environment

by

Eric Novotny, Andrew Sander, Omid Mohseni and Heinz Stefan

Prepared for
Local Road Research Board (LRRB)
Minnesota Department of Transportation
St. Paul, Minnesota

June, 2008
Minneapolis, Minnesota