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

by

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## Abstract

Approximately 349,000 tons of road salts (NaCl) are applied annually for road de-icing in the Twin Cities Metropolitan Area (TCMA) of Minnesota. To determine if and how 13 lakes in the TCMA respond to seasonal applications of road salt, the ionic composition of lake water samples was analyzed, and specific conductance and temperature profiles in the lakes were measured over a 45-month period. The lakes were selected based on four criteria one of which was their proximity to roadways.

Natural lakes in Minnesota are dominated by calcium, sulfate and carbonate ions. Sodium and chloride are, however, the dominant ions in the TCMA lakes studied. The one to one stoichiometry of sodium and chloride in the lakes suggests that NaCl is the source of both ions. Concentrations of the two ions were linearly related to specific conductance. Chloride concentrations in TCMA lakes have been increasing over several decades since the 1950 when road salt applications started to become popular. Long-term increasing trends in specific conductance in 39 lakes in the TCMA mimic amounts of rock salt purchases by the state of Minnesota. If current trends continue the chloride content of TCMA lake waters will continue to rise.

Chloride concentrations in TCMA lakes have a seasonal cycle; concentrations are highest during the winter and early spring months and lowest during the late summer and fall. This cycle matches road salt applications and snowmelt runoff in winter/spring, and flushing of lakes by rainfall runoff during the summer.

Concentrations in the lakes studied are highest at the bottom of the lake causing chemical stratification. This stratification can be strong enough to prevent complete vertical lake mixing (turnover) in the spring. In the lakes studied complete vertical lake mixing was only prevented in the spring, but not in the fall period, and varied from year to year.

There are no natural sources of NaCl in the geology of the TCMA. The salinity source for the TCMA lakes must therefore be man-made. The largest salt uses in the TCMA are for water softening and for road de-icing. Water softening backwash is typically disposed of in sanitary sewers and does not reach any lakes. Road salt, however, is a solute in snowmelt water which runs into lakes through storm sewers and small streams.

Chloride concentrations exceeded the chronic standard of 230 mg/L required for the protection of aquatic life at some point in time in 5 of the 13 lakes studied. These high concentrations were typically found during the winter and spring months and occurred in the deepest portion of the lakes.

Sodium and chloride ions penetrate into the lake sediment pore water by natural convection and diffusion. Lake sediment can therefore act as a sink or a source of sodium and chloride during stagnant and mixing periods, respectively. From the sediment pore water sodium and chloride may be conveyed into the groundwater, but this process was not investigated.

Taken together, these results clearly show a continued degradation of the water quality of urban lakes due to application of NaCl in the watersheds. No acute damage has been observed, but the trend of increasing lake salinity is disturbing. Violation of existing water quality standards appears to occur in a few lakes occasionally. Road salt seems to be required for driving safety, but road salt application practices need to be implemented that also take into account the water quality trends in lakes, and in the groundwater.

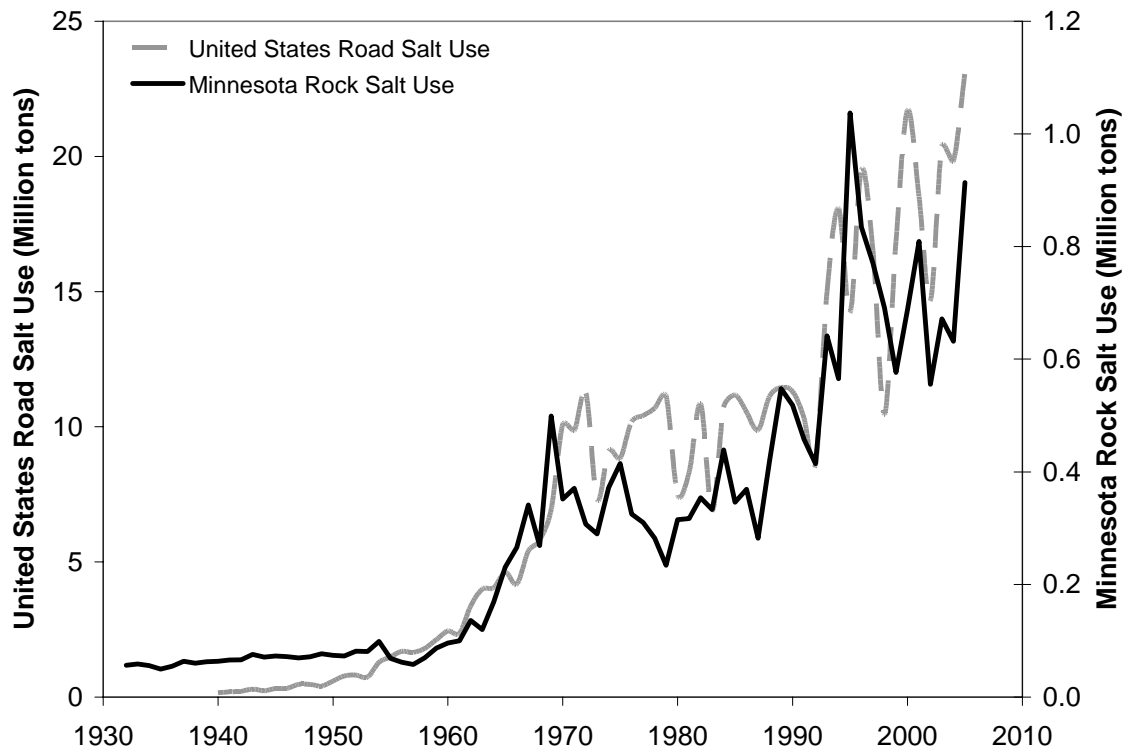
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## INTRODUCTION

In the snow-belt regions of the United States de-icing agents are used to remove snow and ice from roadways in winter. The primary agent used for this purpose is rock salt consisting mainly of sodium chloride (NaCl, 40% sodium and 60% chloride by weight). Its cost is considered moderate, and storage, handling and dispersing on surfaces are relatively easy (Novotny et al. 1999). Other agents in the road salt mixture, such as ferrocyanide, which is used as an anti-clumping agent, and impurities consisting of trace elements (phosphorus, sulphur, nitrogen, copper and zinc), can represent up to 5% of the salt weight (Marsalek 2003).



**Figure 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.**

In the U.S., annual rock salt use for road de-icing increased from 163,000 tons in 1940 to over 23 million tons in 2005 (Figure 1) according to the United States Geological Survey (USGS) mineral yearbooks (Jackson and Jobbagy 2005, USGS 2007). In the state of Minnesota annual rock salt purchases increased during the same time period from 60,000 tons to over 900,000 tons (USGS 2007).

Road salt applications keep roads free of ice for safe winter travel in northern climate zones. Besides sodium chloride (NaCl) many other deicing agents, e.g. calcium or magnesium chloride (CaCl<sub>2</sub>) or potassium acetate, are available, but because of a large difference in cost NaCl is applied most frequently.

Much of the rock salt applied to the roads is dissolved in the melting snow and ice; the salt containing water eventually infiltrates into the soil or is transported by surface runoff thus contaminating groundwater and surface waters while affecting the chemistry and biota in the soil and water (Thunquist 2004). Another pathway of road salt is as windblown dust from dry road surfaces through the air, and deposition on the land including many plants. Many studies have been conducted on the influence of road salt application on the environment. Comprehensive literature reviews (1999, Novotny et al. 1999, Ramakrishna and Viraraghocan 2005, Langen et al. 2006) have reviewed and summarized providing a vast amount of information on this subject

### **1.1 Sodium Chloride Sources**

Sodium and chloride are used for many other purposes in the United States than just road deicing. Major categories of NaCl use include:

- (1) agriculture,
- (2) chemical production,
- (3) road deicing,
- (4) food production,
- (5) metal production,
- (6) paper production,
- (7) petroleum,
- (8) textiles and dyeing and
- (9) water treatment (softening).

As well as many other uses (Kostick 2004). In 2004 sodium and chloride salts were used in the United States mainly for two purposes: chemical production e.g. chlorine and (b) 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). In other words 37% of the salt used throughout the United States was used for road deicing. 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). The majority of rock salt is used for road deicing which mean around 62% of the salt used in Minnesota in 2004 was used for road salt applications. All of these uses contribute NaCl to the environment. Sodium and chloride are released to the environment in deicing applications, domestic and/or industrial wastewater effluents, by chemical and petroleum industrial emissions, landfill leaching, fertilizer applications, salt storage facilities and from water softeners. All are anthropogenic point or non-point sources of sodium and chloride.

Techniques have been developed to identify non-point sources of chloride in the environment. One of these methods examines the relationship between total nitrogen and the Cl/Br ratio. N-enriched sources such as landfills, animal waste, and septic tank effluents can be distinguished from other sources with this relationship. Low N-values and high Cl/Br ratios are associated with road salt contamination. A plot of total N vs Cl/Br has therefore been successfully used to separate contamination by road salt



applications from other types of contamination (Panno et al. 2006). Similarly, saltwater intrusions of ocean water can be distinguished from road salt applications on Long Island, NY.

There are also natural sources of chloride and sodium in the environment: (1) Mineral sodium chloride deposits, (2) Weathering of geological formations (3) Wet deposition originating from ocean evaporation (Jackson and Jobbagy 2005). In many natural environments the natural source of chloride is very low. For example, in Canada, normal background concentrations of chloride are no more than a few mg/L (Environment Canada Health Canada 1999). The same can be said for SE Minnesota where there are no significant natural sources of chloride (Wilson et al. 2006). In a sand and gravel aquifer in northeastern Illinois background groundwater concentration were determined to be between 1 and 15 mg/L, much lower than concentrations found near roadways (Panno et al. 2006). Natural wet deposition of salts also contributes to sodium and chloride concentrations, but compared to deicing salt applications its effect is minor. The estimated value of natural wet deposition of Na and Cl over the entire United States was around 2.2Mt/year, much lower than 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 much lower in areas not located 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 at 0.3 mg/L (Panno et al. 2006) much lower than the national average (Andrews et al. 1997).

## **1.2 Transport of Sodium and Chloride through the Environment**

Salt applied to a road during the winter eventually finds its way into the soil, streams, lakes, wetlands and the groundwater. The waterbodies 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 (Environment Canada Health Canada 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 (Environment Canada Health Canada 1999).

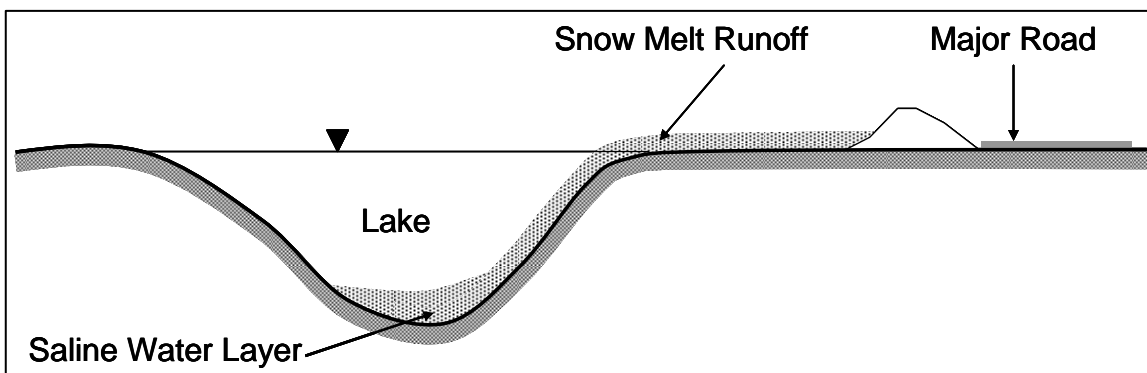
In snowmelt water the sodium and chloride ions dissociate from one another. Once dissolved in the runoff, the sodium and chloride ions are transported from urban areas to receiving waters in one of three pathways: (1) a rapid runoff pathway corresponding to storm water overland flow from impervious and pervious surfaces, (2) a shallow subsurface pathway defined as fast soil storage, and (3) a deeper and slower soil storage pathway know as baseflow (Novotny 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. On the other hand, if the snowmelt water is transported through the soil following pathways (2) and (3) the equivalents of sodium and chloride received will be different with more chloride present than sodium. The chloride ions are conservative in the soil and will pass readily into the groundwater and eventually into the

surface waters (Environment Canada Health Canada 1999), although retention in the soil capillary water results in residence times for Cl that exceed that of water (Mason et al. 1999). Sodium on the other hand does not act conservatively in soils. The sodium from the salt exchanges with other cations adsorbed to soil particles causing an increase in calcium, magnesium, potassium and hydrogen ions via cation exchange (Mason et al. 1999).

### 1.3 Lakes

Lakes receive sodium and chloride from snowmelt runoff directly by overland flow and through streams located within the watershed or indirectly through the soil and from groundwater. Roadsalt applications in rural areas have been shown to affect lakes a few hundred meters away (Environment Canada Health Canada 1999). When runoff or groundwater containing dissolve NaCl enters a lake density currents are often formed due to the intrusion of high density salt water. This phenomenon has been documented in a small lake in Minneapolis: a saline density current into the lake occurred synoptically with above freezing air temperatures and snowmelt runoff. The snow melt runoff proceeded to the deepest part of the lake where it remained until the lake finally turned over in the spring (figure 2) (Ellis et al. 1997).



**Figure 2. Schematic of a saline water intrusion into a lake.**

Density current intrusions have the ability to cause chemical stratification of a lake. NaCl concentrations of 1 g/L increase the specific gravity of water by approximately 0.0008 (Wetzel 2001). This change is significant in relation to temperature-induced density changes. For example, a temperature change from 4 to 5°C produces the same density change (0.000008) as a salt concentration of 10 mg/L (Wetzel 2001). Density stratification caused by salt can be much stronger than that caused by temperature causing lakes to become “meromictic”. This condition is typically found in lakes with a small surface area, yet fairly deep. Large lakes are less vulnerable to becoming meromictic than small lakes because large lakes have a greater fetch which can create more powerful wind mixing and dilution of intruding density currents (Environment Canada Health Canada 1999). Shallow lakes are less susceptible to

meromixis than deeper lakes due to the smaller amount of energy required to fully mix the lake.

The formation of meromictic conditions has been observed in a small lake in Ann Arbor Michigan after a heavy snow winter and high road salt applications; runoff containing road salt entered the lake causing a chemocline that remained and prevented mixing in the spring (Judd 1970). In Irondequor bay on the southern shore of Lake Ontario chloride concentration increased fourfold from 1950 to the early 1970s, to the point where complete mixing in the bay was prevented in the spring from 1970 to 1973 (Bubeck and Burton 1989). In 1975 shortly after a salt reduction program was implemented the bays waters mixed completely and total chloride stored in the lake decreased as road salt use decreased until 1980. From 1980 to 1984 road salt use increased again causing the chloride content in the bay to also increase to the point where complete mixing was again prevented in spring 1984, the last year in the study (Bubeck and Burton 1989).

The formation of meromixis can have several consequences for a lake. Chemical stratification impedes vertical mixing preventing dissolved oxygen (DO) from reaching the bottom layers and nutrients from reaching the top layers. Low DO below the chemocline can result in the loss of all but the most resilient deep water animal species. Meromixis will also affect sediment/water exchange of dissolved species. For example, phosphorus and other metals are more readily released from poorly oxygenated waters (Environment Canada Health Canada 1999).

In New Hampshire chloride and sodium levels in a small lake have been observed to steadily increase since a highway was constructed in the watershed. The increase has been at a rate of 2.4 ueq (micro equivalents) yr<sup>-1</sup> for sodium and 3.3 ueq yr<sup>-1</sup> for chloride (Rosenberry et al. 1999). In Toronto Canada chloride concentrations were found to increase in Don River reservoir although the outflow drains the bottom layer (Scott 1979). Before the flooding of the reservoir the soil at the reservoir bottom had the same chloride concentrations as soil collected at a distance of 45 meters from a road. After the runoff waters of one winter had been impounded in the reservoir, the average concentrations of sodium and chloride in the soils had doubled suggesting that the salt in the water infiltrated into the soil and remained in the soil when the reservoir was drained (Scott 1979).

In Minnesota diatom species were used as an indicator of lake chloride levels. Sediment cores from lakes throughout the state were analyzed for diatom species in order to determine trends in chloride concentrations during two time periods: 1750-1800 and 1800-1970 (Ramstack et al. 2004). From 1750-1800 trends in chloride concentration were generally weak and non-directional in three of the ecoregions examined. In contrast, half of the urban lakes showed a significant increase in chloride from 1800-1970. The trend was strongly correlated with the percent of urban development in the watershed. In forested areas, during this same time period, the chloride levels showed little change after 1800, similar to the period from 1750 to 1800 for all lakes (Ramstack et al. 2004). Another study showed significant change in the Chloride concentrations

from 1970 to 2000 in the same 55 lakes. Trends in chloride concentrations were confined to lakes located in the Twin Cities metropolitan area; it can be inferred that these changes are most likely caused by road salt usage on roads in the city (Ramstack et al. 2003).

#### **1.4 Streams**

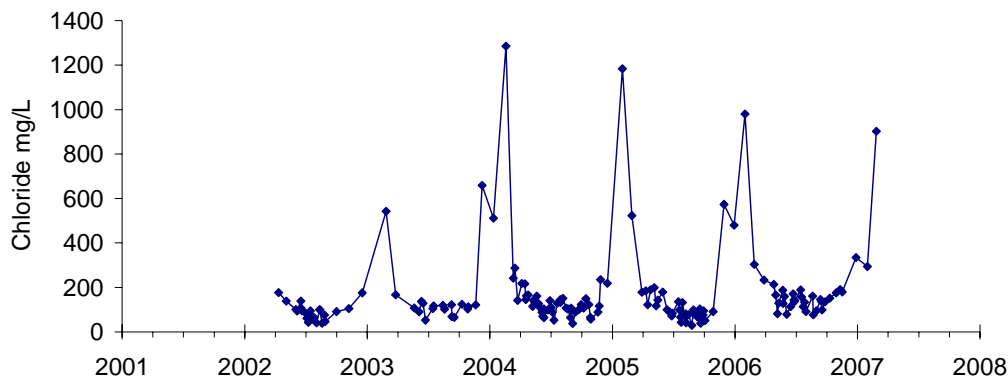
Chloride concentrations in streams have been on the increase. Although stratification is not a concern in streams and rivers, high chloride concentrations can have an effect on the biota. The type of watershed and runoff influences the concentration levels. For example, if a stream receives snowmelt runoff directly from an urban area, concentrations of sodium and chloride will spike during the winter months and spring thaw, and decline quickly once the salt application has stopped (Scott 1981). If the primary water source is groundwater the concentrations in the streams will be more steady, with little seasonal variability; concentration may still be high during low flow in summer and late fall due to the limited dilution by runoff from rainfall.

Many studies on chloride and sodium concentrations in streams have been conducted. In streams in New York, Maryland and New Hampshire concentrations as high as 5 g/l (25% of the concentration of sea water) were measured in some urban streams during the winter; during the summer months concentrations were up to 100 times higher than in unimpacted streams in forests (Kaushal et al. 2005).

In the Northeastern United States the baseline salinity has been increasing at the regional scale towards a threshold which can be expected to change aquatic ecosystems (Kaushal et al. 2005). Due to the large concentrations in late fall and winter the contributions of salt from water softeners and septic tank effluents was determined to be minimal (Kaushal et al. 2005).

In the Mohawk River basin estimated concentrations of Ca, Mg and K during the 1990s were similar to estimates from the 1950s with all three showing a modest increase of around 10%. Na and Cl on the other hand increased by 130 to 243%, respectively, from 1950 to 1990. Compared to 1970 levels all ions showed a decrease by 1990, except Na and Cl, which displayed increases of 34 and 40%, respectively (Godwin et al. 2003). The only plausible source of Na and Cl which could account for the large mean daily yields was concluded to be road salt (Godwin et al. 2003).

Three rivers and creeks in the area of Toronto, Canada, were studied extensively for chloride (Williams et al. 2000): (1) Highland Creek, located largely in a heavily urbanized metropolitan area of Toronto, (2) the Rouge River, located in a less densely populated area, and (3) Dufflin Creek in a catchment that consists largely of forests, woodland/grassland and farmland. Concentrations of chloride were highest in Highland Creek (mean concentration of 316 mg/L) and lowest in Dufflin Creek (mean concentration of 107 mg/L). Peak concentrations of Cl were measured in Highland Creek and the Rouge River in January and February coinciding with peak snowfall and affiliated road salting (Williams et al. 2000).



**Figure 3: Chloride concentrations in Battle Creek (2.2 miles from outlet into Mississippi River) which drains portions of East St. Paul and empties into the Mississippi River (Metropolitan Council data).**

In the state of Minnesota data are available showing high concentrations of chloride traveling through streams and storm sewers during the winter months (Figure. 3). During a TMDL (Total Maximum Daily Load) study of Shingle Creek in the Minneapolis/St. Paul Twin Cities Metropolitan Area (TCMA), the highest recorded concentration of chloride reached 12,000 mg/l in the winter (Wenck Associates 2006). Median concentrations at the same locations were 150 mg/l and minimum concentrations were 64 mg/l during the summer months. In the same study chloride concentrations in grab samples of storm sewer effluents reached 35,000 mg/l during the winter. In storm sewers emptying into the Mississippi River, concentrations of chloride reached 900 mg/l during January while the maximum concentrations in the summer months were less than 130 mg/l (MWWMO 2006). In time series of chloride concentrations in streams of the TCMA peaks can be seen in the winter months corresponding with road salt applications (Figure 3) (MPCA 2007). Median chloride concentrations in urban streams throughout the Upper Mississippi River basin, including the Twin Cities metropolitan area, were substantially greater than most urban streams located across the United States (Stark et al. 2000). The highest Cl concentrations in these 29 urban areas were found in the Northern United States where deicing salts are used (Stark et al. 2000).

High concentrations of chloride in streams are strongly correlated with the size of impervious surfaces in the watershed and urbanization (Smith et al. 1987, Talmage et al. 1999, Williams et al. 2000, Rhodes et al. 2001, Kaushal et al. 2005). In one study the concentration of chloride in the streams increased logarithmically with the relative amount of impervious surfaces in the watershed (Kaushal et al. 2005). In another nationwide study chloride level increased by 30 % from 1974 to 1981 were moderately correlated with population increases, but more significantly associated with increasing rates of highway deicing salt use, and not at all correlated with changes in irrigation water use (Smith et al. 1987). A linear relationship between impervious surfaces and chloride and sodium concentrations (R-value of 0.88 and 0.82 for chloride and sodium, respectively) was found for streams in the Twin Cities area (Talmage et al. 1999). These

studies show conclusively the influence of road salt application on the chloride concentration in streams.

### **1.5 Groundwater**

Groundwater in urban areas has been contaminated by sodium and chloride. Some consider road deicing salts as one of the most invasive and damaging chemicals polluting groundwater in the snowbelt countries (Williams et al. 2000, Oberts 2003). Numerical simulations of a well field in southwestern Ontario found that well contamination due to deicing salts could be delayed due to storage of chloride in the subsurface (Bester et al. 2006). Concentrations in the aquifer were substantially higher than concentrations in the actual well water which benefits from dilution (Bester et al. 2006). Due to the high concentrations in the aquifer, groundwater contamination of wells may be more of a long term quality issue since even with complete elimination of deicing salt applications removal of the residual chloride will take years or even decades. Under a continuous salt application scenario, on the order of 100 years may be required to reach equilibrium concentrations in well water (Bester et al. 2006). Regional studies in Southern Ontario determined that natural chemical process contribute very little chloride to waters with background concentrations in the range of 15 to 20 mg/L (Howard and Beck 1993). This suggests strongly that most of the sources of chloride are anthropogenic.

Many urban areas have already reported chloride contamination in the groundwater. Wells located around Madison, WI, have shown increasing chloride concentrations from 1975 to 2001 (Madison Department of Health 2000). Wells in the outermost counties of the metropolitan Chicago area have experienced increases in chloride concentrations; more than 50% of the wells have increases greater than  $1\text{ mg L}^{-1}\text{ yr}^{-1}$ , and approximately 13% have increases greater than  $4\text{ mg L}^{-1}\text{ yr}^{-1}$  (Kelly and Wilson 2002). In Toronto, Canada chloride concentrations in groundwater are strongly related to urbanization with concentrations in urban areas of Toronto 10 to 60 times higher than baseline concentrations of 20 mg/L (Williams et al. 2000). In the Don Valley area of Toronto chloride levels in the range of 2000 – 14000 mg/L were found at sites adjacent to roads; some of the highest values occurred at depths of 4.5 m, less than 3 m above the water table (Howard and Beck 1993). In a study of groundwater in urban areas of the glaciated parts of the United States groundwater chloride concentrations have been seen as high as 800 mg/L with a median of 46 mg/L while concentrations in selected forested areas are typically less than 10 mg/L (Mullaney 2005). In a study conducted in southern Ontario, Canada, wells contaminated with elevated chloride concentrations were closely aligned with paved roads that receive NaCl road de-icing salt in winter. Wells located down-gradient of paved roads were also more frequently contaminated than wells on the up-gradient side (Howard and Beck 1993). This relationship has also been found in the Twin Cities area with chloride concentrations significantly greater in groundwater wells immediately down-gradient from major highways (Andrews et al. 1997, Andrews et al. 2005).

Concentration of chloride in groundwater under urban areas of the Twin Cities metropolitan area were much higher than in groundwater below other parts of the state of Minnesota (Andrews et al. 1997, Fong 2000). Median ground water concentrations were an order of a magnitude higher in 30 urban land use wells than samples from 992 wells throughout the upper Mississippi River watershed area with concentrations of 46 mg/L and 5.8 mg/L, respectively (Andrews et al. 1997). Differences have also been seen in the state of Minnesota between surficial sand and gravel aquifers located under agricultural, urban and forested land. Concentrations of sodium and chloride were the highest in the urban areas of the Twin Cities and lowest in the forested area. Chloride concentrations were found to exceed the USEPA secondary standard of 250 mg/L in 3% of the water samples taken in the Twin Cities. The highest value recorded was 330 mg/L (Fong 2000). None of the sampling stations had a concentration over this mark in either the agricultural or forested areas. Median chloride values were 46 mg/L in urban areas, 17 mg/L in agricultural areas, and 1.2 mg/L in forested areas, and similar patterns were seen with sodium (Fong 2000).

## **1.6 Changes in Soil Chemistry**

The addition of road deicing salt (NaCl) influences the chemistry of the soils into which it infiltrates. Chloride is a conservative substance and has little effect on the soil chemistry, but sodium takes part in chemical processes changing the soil properties and affecting the fertility of the soil. The clay materials and organic compounds have a particular structure which allow for the presence of a net negative charge on the molecules.

Two phenomena are responsible for the net negative charge: (1) isomorphic substitution of Al by Mg or Fe or Si by Al resulting in a permanent change on the clay particles (Amphlett 1969) and (2) organic matter functional groups such as carboxyls, and or surface hydroxyls of inorganic material resulting in a variable change dependent on pH and ionic strength of the soil solution (Tabatabai and Sparks 2005). Isomorphic substitution is the replacement of an atom by another atom of similar size in the clay structure. In the case of Al being substituted by Mg, the sizes of the atoms are similar but the charges are different. Al has a net charge of +3 and Mg has a net positive charge of +2 resulting in a net negative charge on the clay particle after substitution. The variable charge forms by the donation of protons from the organic matter functional groups or surface hydroxyls. When the pH of the soil environment increases the weak acid functional groups donate a hydrogen proton resulting in a net negative charge.

The net negative charge on the soil particles is balanced by the adsorption of cations consisting mostly of Ca, Mg, Na and K but also H, Fe, and Al. Typically Ca and Mg are preferred over Na due to the smaller size of the ions and the divalent charge, but when water with high concentrations of sodium infiltrates the soils, sodium becomes preferred inducing ion exchange between the sodium and primarily calcium and magnesium (Shanley 1994, Mason et al. 1999, Lofgren 2001, Norrstrom and Bergstedt 2001, Oberts 2003). The process increases the concentration of calcium and magnesium in surface and groundwater and decreases the Na/Cl ratio.

In a study on Mirror Lake, NH, the Na/Cl ratio was 1.01 from 1970 to 1975. After the construction of an interstate highway in the watershed, highway deicing salts caused a fourteen fold increase in Cl and a decrease in the Na/Cl ratio to 0.68 (Rosenberry et al. 1999). In some cases ion exchange can increase the mobility of hydrogen ions as well decreasing the pH of the water in the process (Lofgren 2001, Oberts 2003).

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). Consequentially, 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 been 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).

The adsorption of the sodium ions onto the clay particles influences the properties of the soils. Due to the relatively large size, single electrical charge and hydration status of sodium ions, when sodium replaces calcium and magnesium the forces binding the soils particles are disrupted causing separation, dispersion and swelling (Warrence et al. 2003). Soil dispersion hardens soils and blocks water infiltration by causing clay particles to plug soil pores reducing soil permeability. Soil dispersion also reduces the hydraulic conductivity of the soil, i.e. the rate at which water flows through the soil (Warrence et al. 2003). In general, clays containing mostly Na-ions are sticky and impervious while clays containing mostly Ca-ions are easily worked and readily permeable (Krauskopf and Bird 1995). Sodium can change the permeability of the soils to the point that in some situations brines are used in reservoirs to convert calcium clays to sodium clays in order to make the bottom sediments less permeable (Krauskopf and Bird 1995).

### **1.7 Effects on Biota**

Chloride and sodium levels can influence terrestrial and aquatic biota. Salinity levels of 1000 mg/L can have lethal and sub-lethal effects on aquatic plants and invertebrates (Environment Canada Health Canada 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 (Environment Canada Health Canada 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 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).

## **2 STUDY AREA AND LAKE SELECTION**

We conducted a study of salinity in 13 urban lakes in the Minneapolis/St. Paul Twin cities Metropolitan Area (TCMA). The TCMA is an urbanized area with a population of 2.7 Million that contains many watercourses and lakes. Located in the north-central U.S., the TCMA experiences cold climate in the winter and hence significant NaCl applications for winter road maintenance is used. 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.

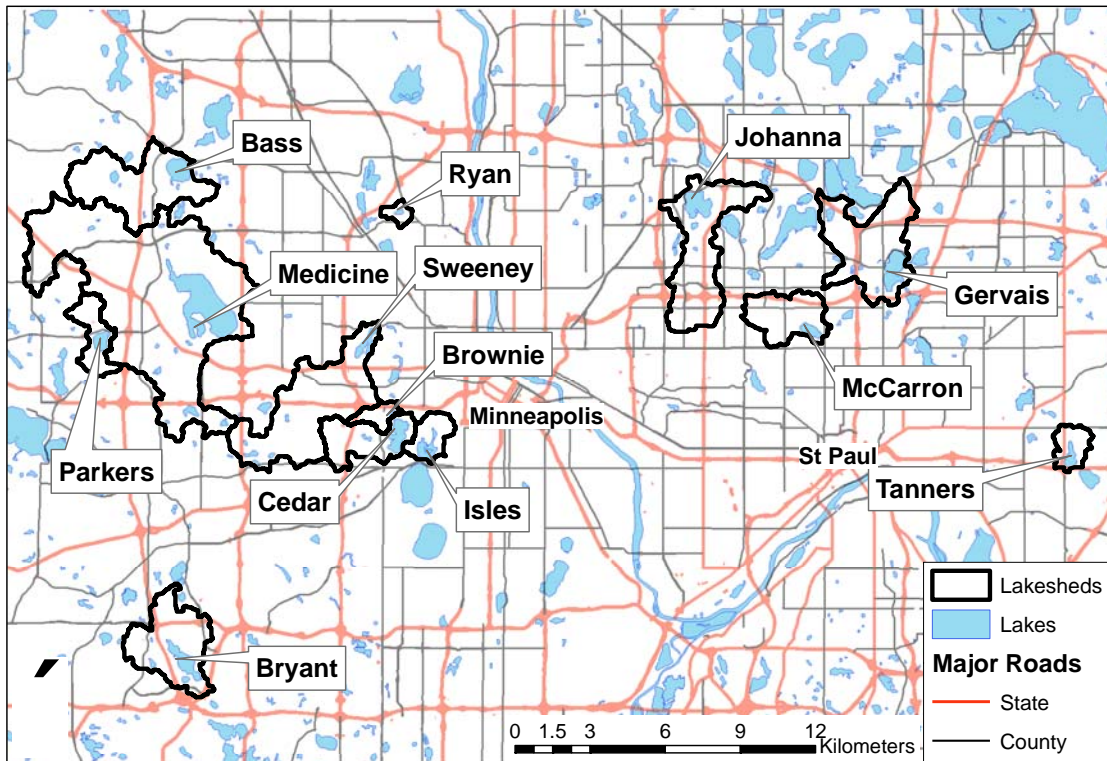
The seven-county Minneapolis/St. Paul Twin Cities Metropolitan Area (TCMA) has over 950 lakes (Metropolitan Council) and uses over 349,000 tons of road salt annually (Sander et al. 2007). With an expanding population and road system, more and more lakes in the TC area are susceptible to pollution from storm water and snowmelt runoff. We collected data in 13 lakes from February 2004 to April 2005 and January 2006 to November 2007. The set of lakes was somewhat different but overlapped for the two periods (Table 1).

**Table 1: Lakes studied and sampling periods.**

	<b>Max Depth</b> (m)	<b>Lake Area</b> (ha)	<b>Watershed Area</b> (ha)	<b>Volume</b> (m <sup>3</sup> )	<b>Percent Impervious</b> (%)	<b>Watershed District</b>	<b>Sampling Period</b> (year/year)
Ryan	11.0	7.6	77	295,222	34	Shingle Creek	04/07
Gervais	12.5	94.7	1144	4,822,960	30	Ramsey Washington Metro	06/07
McCarron	17.4	27.6	549	2,150,795	24	Capitol Region	04/07
Johanna	13.1	86.2	1188	4,274,367	39	Rice Creek	04/05
Tanners	14.0	28.3	214	1,847,756	33	Ramsey Washington Metro	06/07
Medicine	14.9	358.6	4380	18,589,074	29	Basset Creek	04/05
Parkers	11.3	36.9	340	1,413,903	27	Basset Creek	06/07
Bass	9.4	70.4	1131	672,715	21	Shingle Creek	04/05
Sweeney	7.6	26.7	1512	951,751	37	Basset Creek	06/07
Cedar	15.5	68.4	537	4,432,514	28	Minnehaha Creek	04/07
Brownie	14.3	5.0	136	199,866	33	Minnehaha Creek	04/07
Bryant	13.7	65.2	901	3,245,083	24	Nine Mile Creek	06/07
Lake of the Isles	9.4	44.1	252	1,119,547	29	Minnehaha Creek	04/05

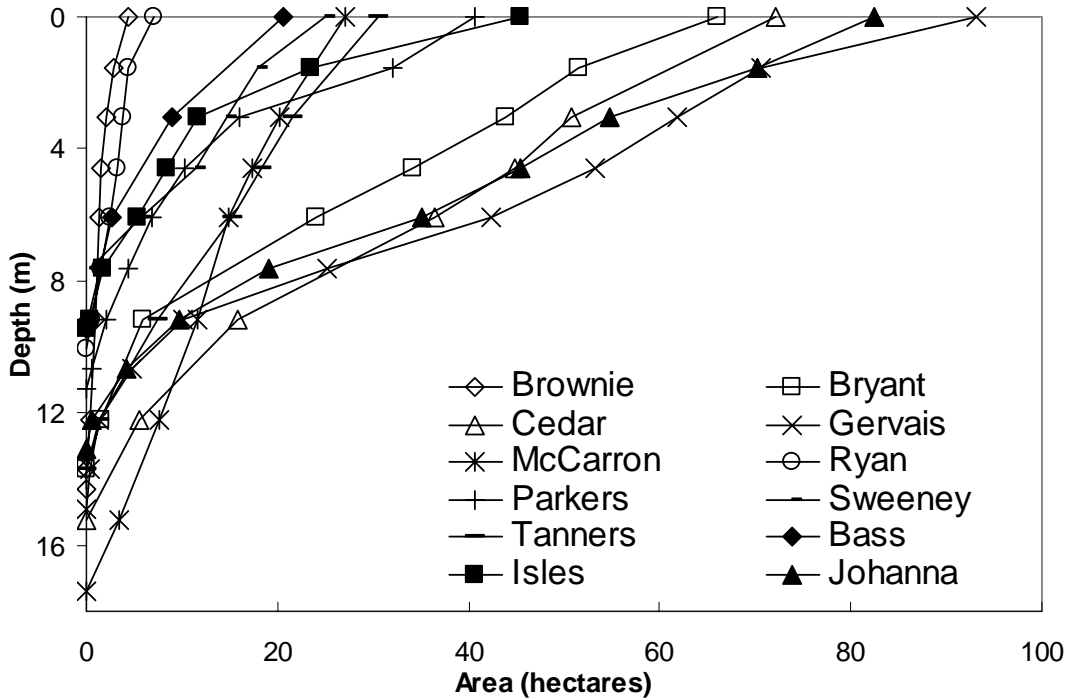
To be selected a lake had to meet four criteria: 1) receive runoff from a major highway or roadway through storm sewers, streams or overland flow. 2) have a maximum depth large enough so that stratification by a thermocline and/or chemocline could form, 3) have previously been monitored by a public agency, e.g. by the Metropolitan Council, Minnesota Pollution Control Agency (MPCA) or area watershed district, so that long term unbiased information is available. 4) have data on bathymetry and watershed available.

From 2004 to 2005 eight lakes were sampled: Bass, Cedar, Lake of the Isles, Johanna, McCarron, Medicine, Ryan and Brownie. From 2006 to 2007 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.



**Figure 4. Locations of the study lakes and their watersheds in the Minneapolis-St. Paul Metropolitan Area (TCMA).**

Locations of the selected lakes and their watersheds in the TCMA are shown in Figure 4. Lakes are listed in Table 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 5: Area vs. depth profiles for 12 of the 13 study lakes. Medicine Lake with a surface area of 358 hectares is not included.**

### 3 METHODS

Water temperature and specific conductance profiles were measured in all lakes at 4 to 8 week intervals. Water samples were extracted from 9 study lakes in February 2007 (winter) near the water surface and near the deepest point of the lake and analyzed for ionic composition. The results were used to establish a relationship between specific conductance of the water and ionic concentration of the solutes. These relationships were used to compute chloride concentrations from the specific conductance measurements. From these data seasonal variations in chloride concentration profiles and total NaCl content of the sample lakes were determined

Lake sediment cores were extracted from the deepest portions of two lakes, and ionic concentrations in the pore water of the lake sediments were measured to determine if sodium and chloride are penetrating into lake sediments from where they may leach into the groundwater.

#### 3.1 Water sampling and analysis of ionic composition

Water samples were taken 1 m below the water surface and 1 m above the bottom of 9 lakes at approximately the deepest location in the winter (22 February 2007).

Samples were analyzed for major ion concentrations in the laboratory of Geology and Geophysics at the University of Minnesota- Twin Cities by ICS-2000 Chromatograph. Historical ionic composition data were obtained from online databases available through the Minnesota Pollution Control Agency (MPCA 2007) and the Metropolitan Council (MCES 2007a). The MPCA database contains data for chloride concentrations and specific conductance collected by watershed districts, consulting companies, and the MPCA. Most of the data are for the ice-free months (May-October). Metropolitan Council Environmental Services (MCES) has water quality data for all major ions in rivers and streams of the seven county TCMA, typically at two week intervals throughout the year. A relationship was then calculated between specific conductance and chloride concentrations to be used with profile measurements of field conductivity, in units of micro Siemens per centimeter ( $\mu\text{S}/\text{cm}$ ), and temperature, in units of degrees Celsius ( $^{\circ}\text{C}$ ). These measurements were taken using an YSI Model 63 probe and taken as a function of vertical distance in the water column every 0.5 meters at approximately the deepest location in each lake.

Specific conductance ( $SC$ ) was calculated from measured field conductivity and temperature using the following equation:

$$SC (\mu\text{S}/\text{cm} @ 25 ^{\circ}\text{C}) = \frac{\text{Conductivity}}{1 + TC(T - 25)} \quad (1)$$

Where  $TC$  is a temperature coefficient,  $T$  is the measured temperature ( $^{\circ}\text{C}$ ), and  $Conductivity$  is the measured field conductivity ( $\mu\text{S}/\text{cm}$ ). A temperature coefficient  $TC = 0.0191$  was used (YSI 1999). Conductance, chloride concentrations, and temperature profiles were also obtained from the Minnesota Pollution Control Agency's Environmental Data access website.

### 3.2 Determining lake salt/chloride content and seasonal cycling

Chloride concentration profiles were converted to an average chloride concentration obtained for each field survey using a volume-weighted average. The depth area profiles (Figure 5) were linearly interpolated to obtain horizontal lake area values at every half-meter depth and then a lake volume was determined using equation 2.

$$V = \sum_{i=1}^{n-1} \frac{A_i + A_{i+1}}{2} * (d_i - d_{i+1}) \quad (2)$$

The volumetric average concentration was then calculated by equation 3.

$$[Cl^-]_{ave} = \frac{\sum_{i=1}^{n-1} \frac{A_i + A_{i+1}}{2} * (d_i - d_{i+1}) * \frac{[Cl^-]_i - [Cl^-]_{i+1}}{2}}{V} \quad (3)$$

Where  $V$  = volume,  $A$  is the area for a particular depth,  $d$  is the depth,  $n$  is the number of area points and  $[Cl^-]$  is the chloride concentration.

### **3.3 Collection of sediment cores and pore water analysis**

Sediment cores were extracted from two lakes, McCarron and Tanners Lake, and pore water samples analyzed for major ion concentrations. One 1.2 m long sediment core was extracted from each lake at the deepest part of the lake. The cores were separated into 4-centimeter sections and the pore water was extracted using a centrifuge and filtered with a standard 0.45  $\mu$ m filter.

### **3.4 Calculating trends of ionic composition in TCMA lakes**

Historical lake water quality data for the TCMA were obtained from the MPCA environmental data access website (MPCA 2007). Specific conductivity data profiles were retrieved for 72 lakes in the 7 county TCMA. The majority of the profiles had been taken at 2-week intervals during the summer months (May – October). An average specific conductivity value for the top 3 meters and for the bottom 3 meters was calculated for each lake and date of survey. Annual averages of specific conductivity were then calculated for each of the two layers in each lake. The time series of these annual values for each lake were then normalized by the average annual concentrations from 2001-2005. The normalized annual data for all lakes with more than 10 years of data (39 lakes) were averaged to obtain one representative normalized specific conductivity value for all 39 lakes in the TCMA.

## **4 RESULTS OF THE FIELD STUDY**

### **4.1 Ionic composition of solutes in the TCMA study lakes**

The chemical analysis of 18 water samples from 9 urban TCMA lakes yielded the results summarized in Table 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 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.

The TCMA has no natural sources of chloride. Consequently, under natural conditions  $Cl^-$  concentrations would be expected to be very low compared to current concentrations. 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 (based on the interquartile 25<sup>th</sup> – 75<sup>th</sup> percentile) values found in the North Central Hardwood Forests

ecoregion of Minnesota which includes the TWMA (MPCA 2004). That sodium and chloride concentrations in TCMA urban lakes (Table 2) have increased well above expected background concentrations must therefore be related to human salt uses.

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

Ion	Median all	Min all	Max all	Median top	Stdev top	Median bottom	Stdev Bottom
Cl-	140.85	79.48	614.80	132.00	38.32	186.00	160.87
Na+	80.85	48.82	366.90	73.14	21.05	104.80	99.40
SO <sub>4</sub> <sup>2-</sup>	13.80	1.72	56.73	13.50	17.09	15.68	17.37
NH <sub>4</sub> <sup>+</sup>	0.91	0.26	36.22	0.79	1.18	1.98	11.56
K+	3.43	2.63	9.99	3.40	0.52	3.43	2.21
Mg <sup>++</sup>	16.82	4.69	37.58	16.73	9.40	17.57	8.77
Ca <sup>++</sup>	49.66	20.61	108.80	47.62	24.28	50.90	19.90
NO <sub>3</sub> <sup>-</sup>	0.14	0.01	0.43	0.22	0.11	0.09	0.13

#### **Comparison of ionic composition with other North American freshwater bodies**

Ionic concentrations in the 9 TCMA urban lakes are summarized in Table 2. For reference, ionic concentrations in other North American and regional freshwaters are summarized in Table 3. Values in Table 3 are 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. A comparison of Table 2 and Table 3 reveals noticeable differences.

First, the concentrations of all ions are much higher in the urban lakes than in other freshwater bodies except for the Minnesota River. Second, ionic concentrations in the urban lake water are similar to those in Mississippi River water, 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 ionic composition of the lakes in the TCMA and other freshwater systems is the dominance of chloride over other anions in the lake. 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).

**Table 3. Ionic composition (mg/L) of reference surface waters in North America.**

	Continental Rain <sup>a</sup>	Pristine Wisconsin Lake <sup>b</sup>	Minnesota Type III lakes <sup>d</sup>	North American River waters <sup>a</sup>	Mississippi River (847.7) <sup>c</sup>	Minnesota River (39.4) <sup>c</sup>
Ca ++	0.2 - 4	12.6	29.3	21	50.3	103.1
Mg ++	0.05 - 0.5	3.3	15.5	5	17.1	47.1
Na +	0.2 - 1	1.6	5.5	9	11.6	31.6
K +	0.1 - 0.5	--	3.2	1.4	2.8	5.2
NH <sub>4</sub> +	0.1 - 0.5	--	--	--	--	--
SO <sub>4</sub> <sup>2-</sup>	1 - 3	--	13.5	20	17	161.8
Cl -	0.2 - 2	0.3	4.3	8	17.2	34.0
NO <sub>3</sub> <sup>-</sup>	0.4 - 1.3	--	--	1	0.8	5.6

a: from Wetzel (2001)

b: from Long Term Ecological Research (LTER) site (North Temperate Lakes (Crystal Lake) Region)

c: averages (2000-2007) from Metropolitan Council Database. Mile marker in ().

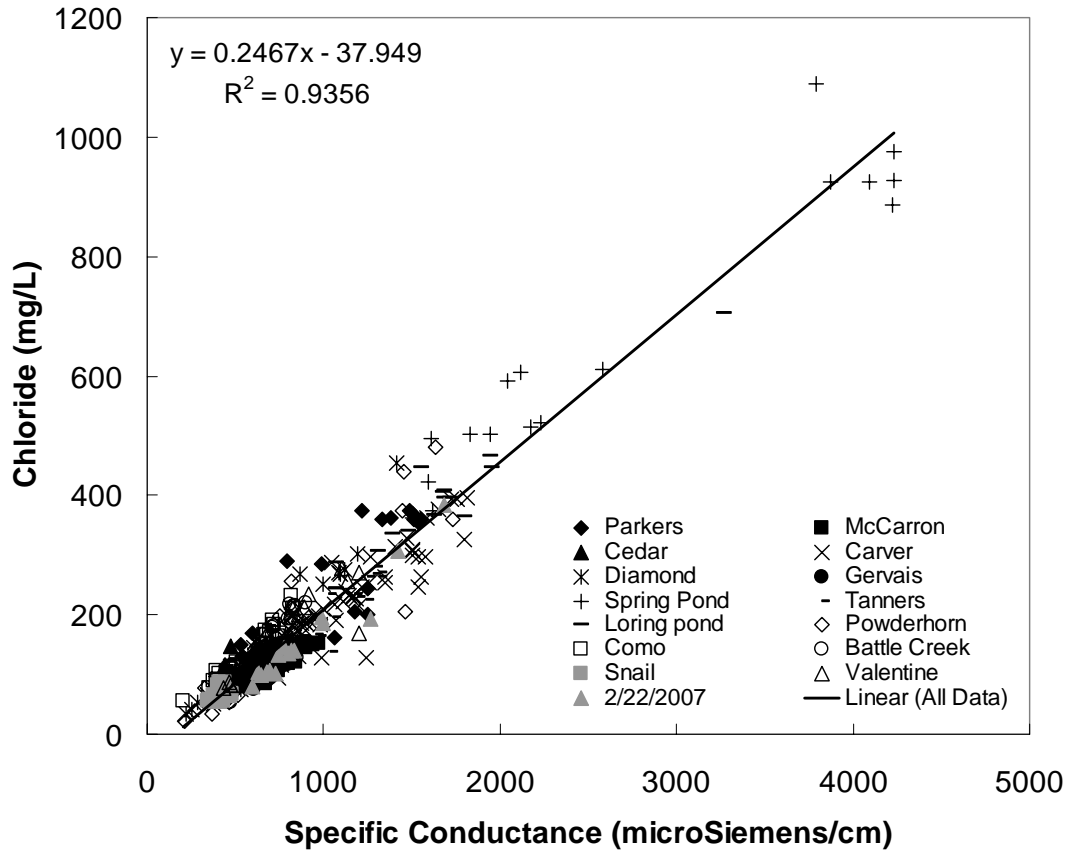
d: Averages from Type III lakes in Minnesota (Gorham Dean et al 1982).

Fourth, ion concentrations in lakes of the same geographic regions are either similar (e.g. Mg<sup>2+</sup>, K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>) or dissimilar (e.g. Cl<sup>-</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>). Chloride and sodium concentrations in lakes of the TCMA show a much larger variability than any other ions when compared to lakes throughout the state. The ranges are 4.3 mg/L to 132 mg/L for chloride and 5.5 to 73 mg/L for sodium. Lakes located in the state of Minnesota (91 lakes overall) with specific conductance values between 141 and 501 us/cm (Type III lakes as defined by (Gorham et al. 1982)) were used for the comparison. Excluded were 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. The gypsum and pyrite minerals in western Minnesota are also the source of high sulfate concentrations in the Minnesota River.

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.



#### 4.2 Relationship of specific conductance to chloride concentration



**Figure 6. Relationship between specific conductance and chloride concentration in TCMA lakes. Data from 14 lakes in the MPCA Environmental Data Access (listed by names), and the authors' water samples from 9 TCMA lakes (2/22/2007).**

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<sup>-</sup> and Na<sup>+</sup> concentrations exists, specific conductance profiles can be measured to determine profiles of chloride concentrations in the TCMA lakes. In other words, a relationship between chloride and other ionic concentrations and specific conductance in TCMA lakes was needed (Figure 6). Lake water quality data were available from the MPCA Environmental Data Access (2002-2006) and from our own water samples (2006/2007) to establish the relationship for TCMA lakes. Both chloride and specific conductance data from different lake depths and times throughout the year were available. The data plot (Figure 6) shows a linear relationship between specific conductance and chloride concentrations. As the concentration of chloride increases, so does the specific conductance of the water. Equation (4a) is fitted to the data ( $R^2 = 0.96$ ).

$$[\text{Cl}^-] = 0.2467 * \text{SC} - 37.949 \quad (4a)$$

where [Cl<sup>-</sup>] is the chloride concentration in mg/L and SC is the specific conductance in  $\mu\text{S}/\text{cm}$ . This equation was used to convert specific conductance measurements to chloride concentrations.

If Cl<sup>-</sup> is derived solely from salt (NaCl), then the molar concentrations of Cl<sup>-</sup> and Na<sup>+</sup> should match one to one and a relationship similar to equation (4a) should hold for Na<sup>+</sup>. It was found that the molar ratio of Cl<sup>-</sup> to Na<sup>+</sup> was 1.08 : 1, and an equation fitted to the Na<sup>+</sup> data ( $R^2 = 0.95$ ) is

$$[\text{Na}^+] = 0.26 * \text{SC} - 68.7 \quad (4b)$$

It is speculated that the molar relationship is different from 1;1 because Na<sup>+</sup> is known to be adsorbed onto soil particles whereas Cl<sup>-</sup> is not (Shanley 1994, Mason et al. 1999, Lofgren 2001, Norrstrom and Bergstedt 2001, Oberts 2003).

#### 4.3 Relationship of specific conductance to other ion concentrations.

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 (Table 4). The concentrations of these ions were low.

**Table 4. Correlation coefficient between specific conductance and seven different ion concentrations in TCMA lake water samples.**

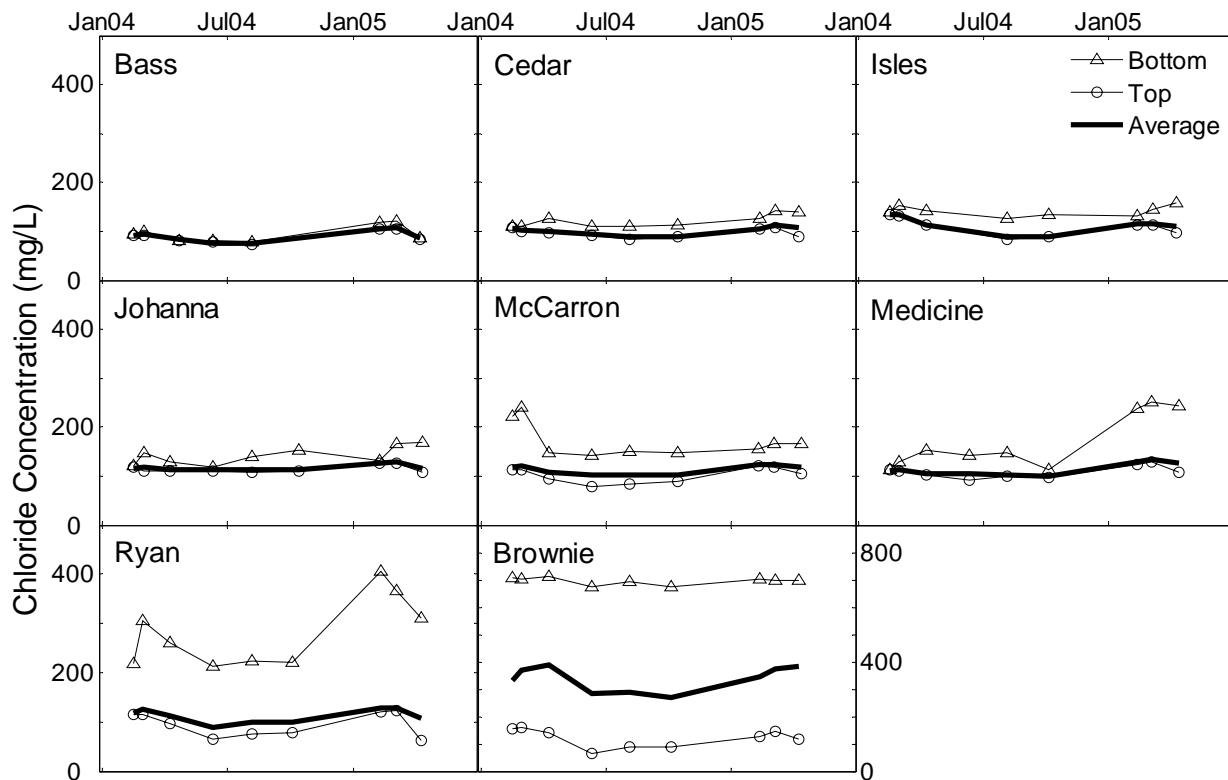
<b>Ion</b>	<b>Correlation with SC</b>	<b>Median (moles/L)</b>	<b>Min (moles/L)</b>	<b>Max (moles/L)</b>
Cl <sup>-</sup>	0.96	3.97	2.24	17.32
Na <sup>+</sup>	0.95	3.73	2.12	15.95
SO <sub>4</sub> <sup>2-</sup>	0.28	0.15	0.02	0.59
NH <sub>4</sub> <sup>+</sup>	-0.02	0.06	0.01	2.01
K <sup>+</sup>	0.59	0.09	0.07	0.26
Mg <sup>++</sup>	0.27	0.69	0.19	1.55
Ca <sup>++</sup>	0.37	1.22	0.51	2.71

The relationship between chloride or sodium and specific conductance is high - with correlation coefficients above 0.95 for both ions. Other major ions such as calcium, sulfate, ammonium, potassium and magnesium do not have a clear relationship with specific conductance. The high median values in moles/L for sodium and chloride coupled with the high correlations with specific conductance justify the conclusion that sodium and chloride are the dominant ions in the urban lakes analyzed. They represent the highest concentrations even in waters with low specific conductance. Our study shows increases in chloride concentrations as well as an increase in the dominance of chloride in the water systems with increases in specific conductance. These findings and

the lack of natural chloride sources lead to the conclusion that the increases in chloride and sodium in the lakes of the Minneapolis/St. Paul Twin Cities Metropolitan area are not due to natural processes.

#### 4.4 Seasonal salinity cycles

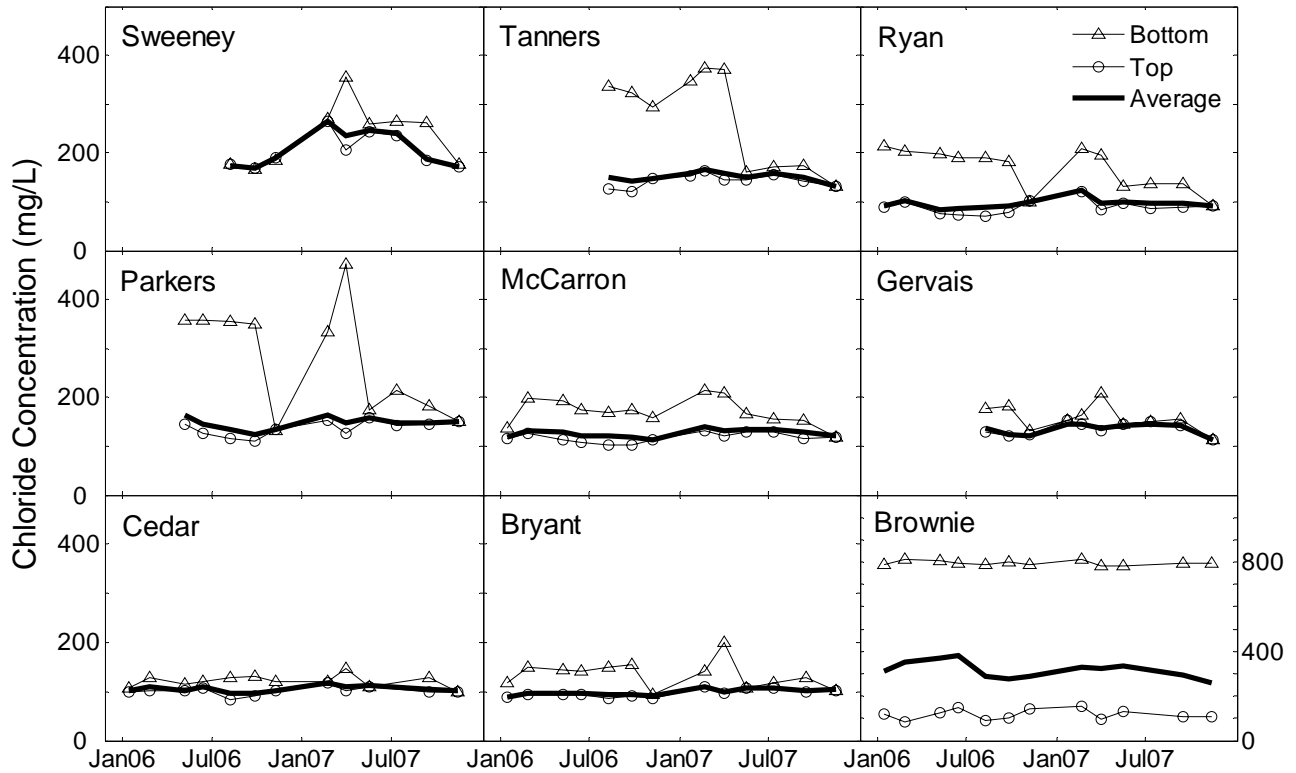
In total, 173 specific conductivity/temperature profiles were measured in 13 lakes over a 42-month period. The transition from specific conductivity measurements to chloride concentrations can be made with equation (4a). The specific conductivity profiles measured at different times of the year, allow 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, and all the lakes have surface water outflows throughout the year. Lakes that receive salt-laden snowmelt runoff in winter and spring, and rainfall runoff without road salt content in summer and fall would therefore be expected to have a seasonal salinity cycle regardless of how often they stratify and mix throughout the open water season. Seasonal variations in salinity for an entire lake should be detectable in volume-weighted average concentrations. These values were therefore calculated for each individual lake and plotted against time in Figures 7 and 8.



**Figure 7. Chloride concentrations 0.5 m below the surface and 0.5 m above the bottom of a lake, 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 (1 meter below the waters surface) and near the bottom (1 meters above the lake bottom) of each lake, as is also shown in Figures 7 and 8. 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.

Results for the lakes sampled from 2004 to 2005 are presented in Figure 7. 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 in the 2006 to 2007 period (Figure 8).



**Figure 8. Chloride concentrations 0.5 m below the surface and 0.5 m above the bottom of a lake, and average chloride concentrations in each lake sampled from Jan 2006 to Sept 2007.**

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 (Figure 7 and 8). 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 2007 as seen from 2004 to 2005 (Figure 7 and 8).

Sweeney Lake is an artificially mixed lake and the measured salinity profile is therefore not natural. High concentrations of salt can be observed in the lake, but the lake is fully mixed during the summer. This is due to an aeration system installed in Sweeney Lake to reduce the effects of eutrophication on the lake. In April 2007 this system was shut off for the purpose of conducting a phosphorus TMDL study, resulting in the formation of chemical stratification during the winter months with chloride concentration reaching 400 mg/l near the bottom of the lake (Figure 8).

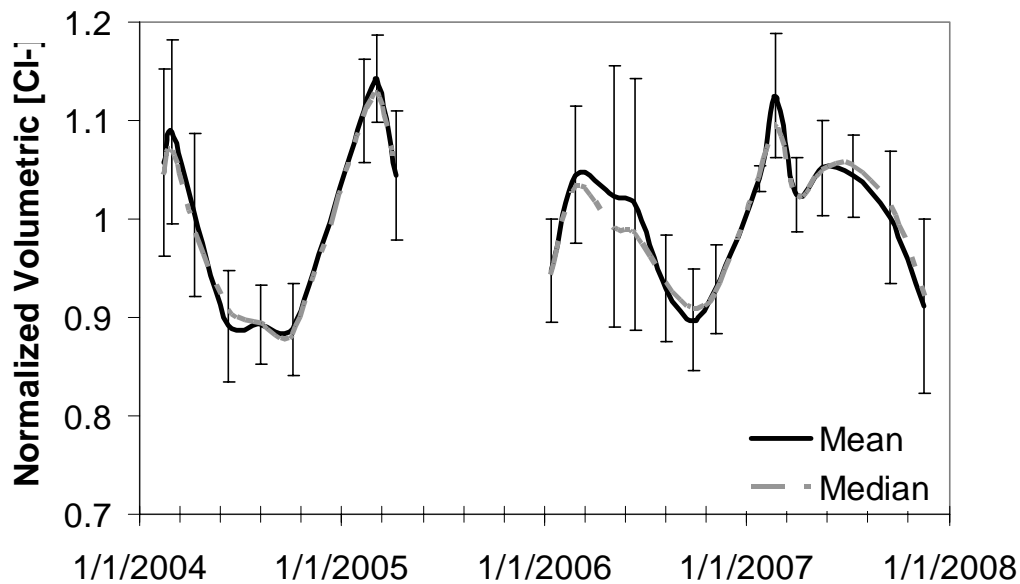
For a more comprehensive view of the salinity cycles in the lakes, the volume-weighted average concentrations for each survey date were normalized. For the set of lakes in Figure 8 the average concentration from Sept 2006 to August 2007 was used as the reference for normalization; for the set of lakes in Figure 7, 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 9). 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 were present in all the lakes studied. Seasonal salinity cycles are more pronounced in some of the lakes than others. 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 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 following results regarding the strength of the seasonal salinity cycle: (Table 5).

**Table 5: Salinity 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
<b>Sweeney</b>	--	--	--	--	--	--	172	266	<b>55</b>
<b>Tanners</b>	--	--	--	--	--	--	131	167	<b>27</b>
<b>Ryan</b>	88	128	<b>45</b>	85	103	<b>21</b>	92	123	<b>34</b>
<b>Parkers</b>	--	--	--	--	--	--	147	163	<b>11</b>
<b>McCarron</b>	102	123	<b>21</b>	113	132	<b>17</b>	121	139	<b>15</b>
<b>Gervais</b>	--	--	--	--	--	--	113	146	<b>29</b>
<b>Cedar</b>	88	106	<b>20</b>	96	109	<b>14</b>	101	118	<b>17</b>
<b>Bryant</b>	--	--	--	89	97	<b>9</b>	100	110	<b>10</b>
<b>Brownie</b>	270	386	<b>43</b>	279	381	<b>36</b>	256	338	<b>32</b>
<b>bass</b>	76	94	<b>24</b>	--	--	--	--	--	--
<b>Isles</b>	88	135	<b>54</b>	--	--	--	--	--	--
<b>Johanna</b>	112	127	<b>14</b>	--	--	--	--	--	--
<b>Medicine</b>	101	128	<b>27</b>	--	--	--	--	--	--

The max concentrations all occurred within the three months of January – March except for Brownie lake where larger concentrations could be seen later in the year. This could probably be due to saline water being upwelled from below the chemocline from high winds or other mixing events. The minimum concentration in all of the lakes including Brownie Lake were all seen in the last profile taken in the late fall (November).



**Figure 9: Seasonal salinity (Cl<sup>-</sup>) cycles illustrated by normalized (volume-weighted) average chloride concentrations, averaged 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 smaller in surface area. This would allow for a larger flushing effect and smaller resonance times. For Brownie Lake since the bottom layer is so saline the changes in salinity due to snowmelt runoff only influences the top 6 meters allowing for rainwater to remove more of the road salt containing runoff then if it were to penetrate into the lower depths of the lake. The highest salinity cycle is seen in Sweeney Lake, which drains a large portion of interstate 394 and highway 100, both high traffic highways in the Minneapolis area. Sweeney Lake is also a shallow lake with aerators that allow for complete mixing throughout the year. This results in a larger flushing effect of the lake with rainwater.

Two of the four lakes analyzed for the entire sampling period (2004-2007) show increases in the annual minimum concentration from year to year. Both Cedar Lake and Lake McCarron both display higher minimum and maximum concentrations each year representing an accumulation of road salt into the lake. Bryant Lake also displays this same pattern, but has only been studied for two years. These patterns show the likely presence of salt accumulation in some lake throughout the area.

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 were highest in the winter and spring and lower in the summer and fall. This 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.

#### **4.5 Salinity and temperature stratification profiles**

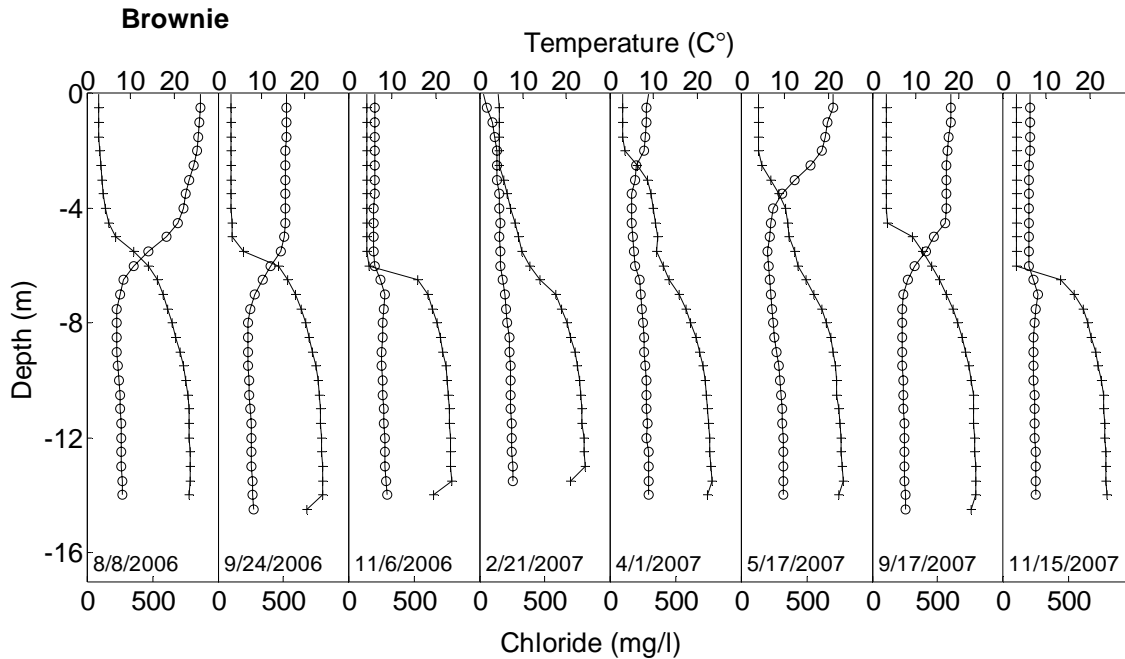
The salinity dynamics in the surface and the bottom layer of each lake have already been illustrated (Figure 7 and 8) and discussed. In this section we want to consider the complete measured temperature and salinity profiles, and discuss chemoclines and thermoclines.

Examples of measured temperature and salinity profiles from the 2006-2007 surveys are shown in Figures 10 to 18. They are for the lake with the strongest chemocline (Brownie) that can resist full vertical mixing in the spring; Tanners lake with a strong chemocline in spring that can nevertheless mix fully in the summer; and Lake McCarron with a weak chemocline, which can mix regularly in spring and fall. These profiles illustrate the seasonal salinity stratification cycle in more detail than Figures 7 and 8. .

The stratification dynamics seen in Figures 10 to 18 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.

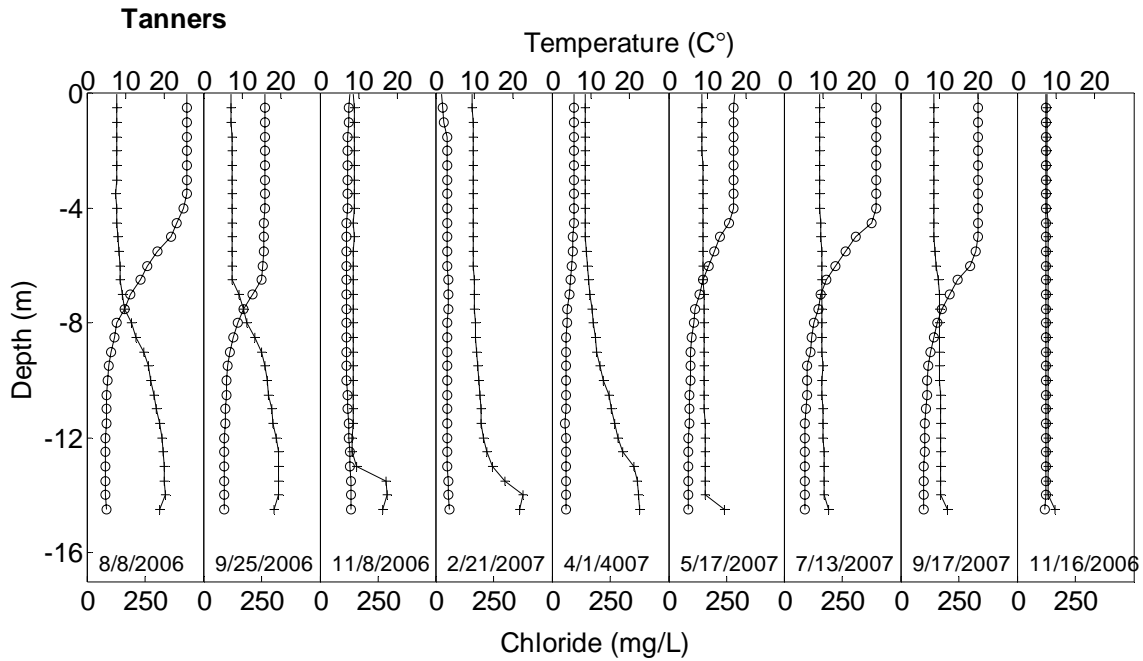
Brownie Lake (Figure 10) is the only meromictic lake analyzed. The water above the chemocline in Brownie Lake behaves like water in any other lake. A pattern of spring and fall overturns occurs in this lake only above the chemocline. The chemical stratification in the lake is so strong and the salinity 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.



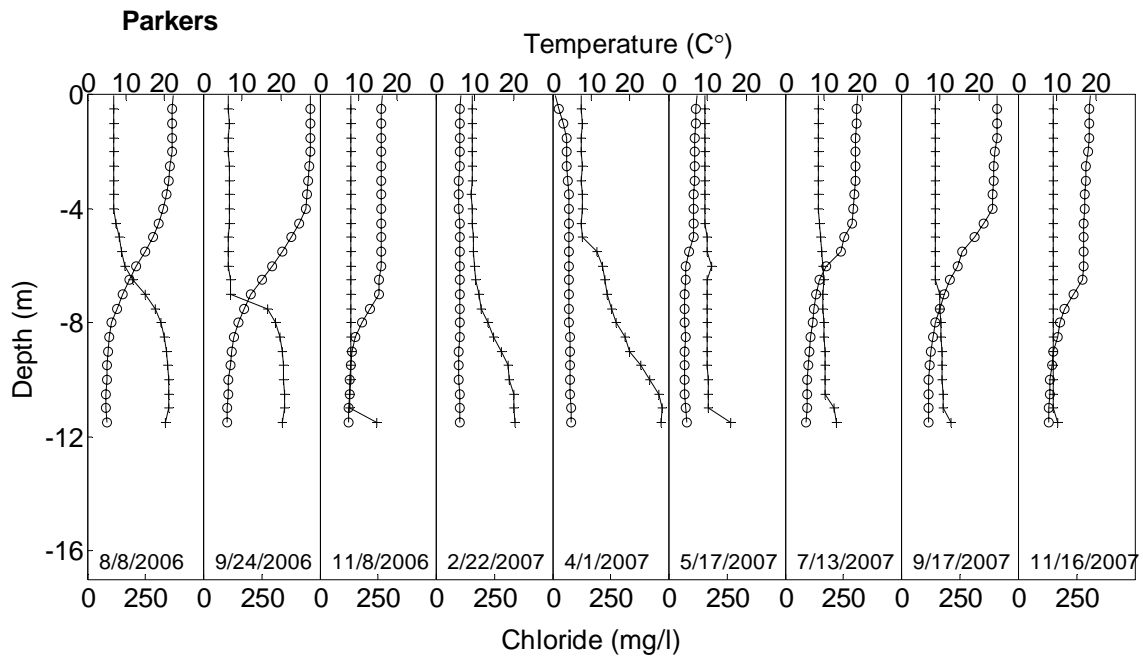


**Figure 10: Conductivity and Temperature profiles for Brownie Lake**

Tanners Lake (Figure 11) does not appear to be meromictic, but monomictic at times, and possibly heading to meromixis. During the summer months 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 almost becomes almost fully mixed except for a small saline layer at the bottom of the lake. During the winter months the chemocline reforms 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 patterns are seen in Parkers Lake (Figure 12) except that full mixing occurred as late as November 2006.



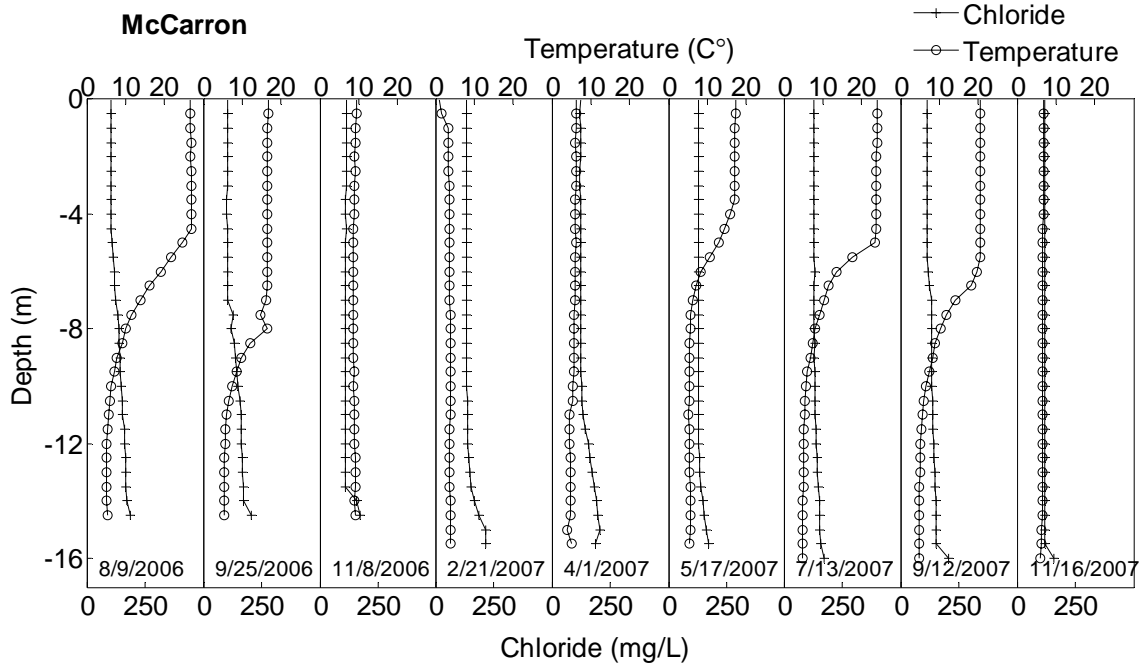
**Figure 11: Conductivity and Temperature profiles for Tanners Lake**



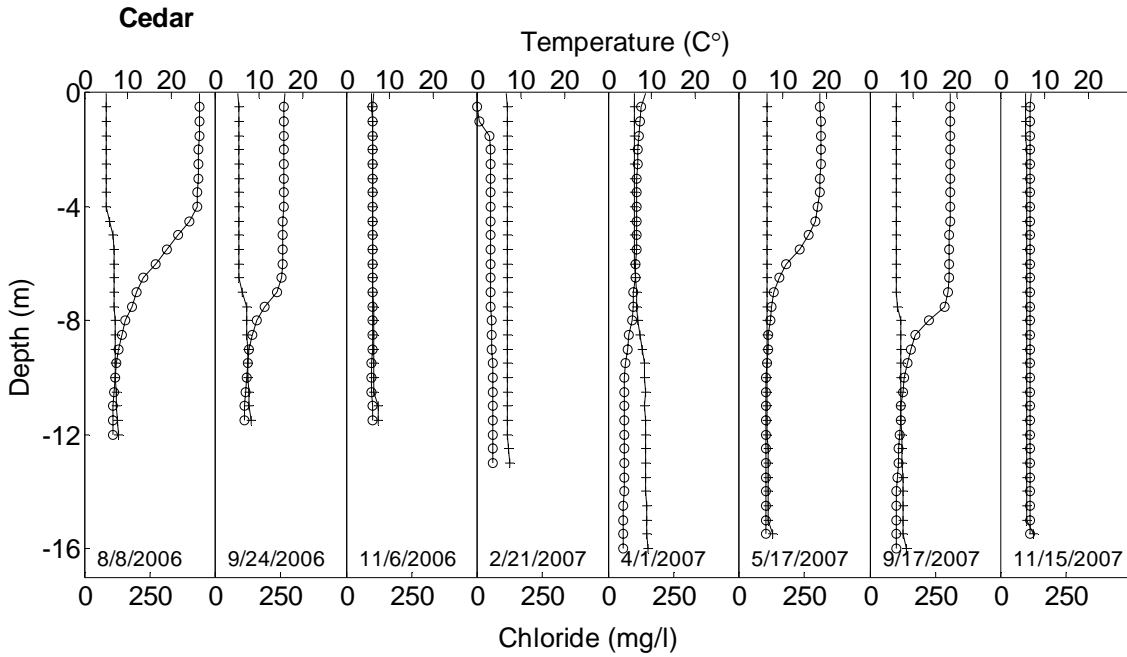
**Figure 12: Conductivity and Temperature profiles for Parkers Lake**

Lake McCarron (Figure 13) 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

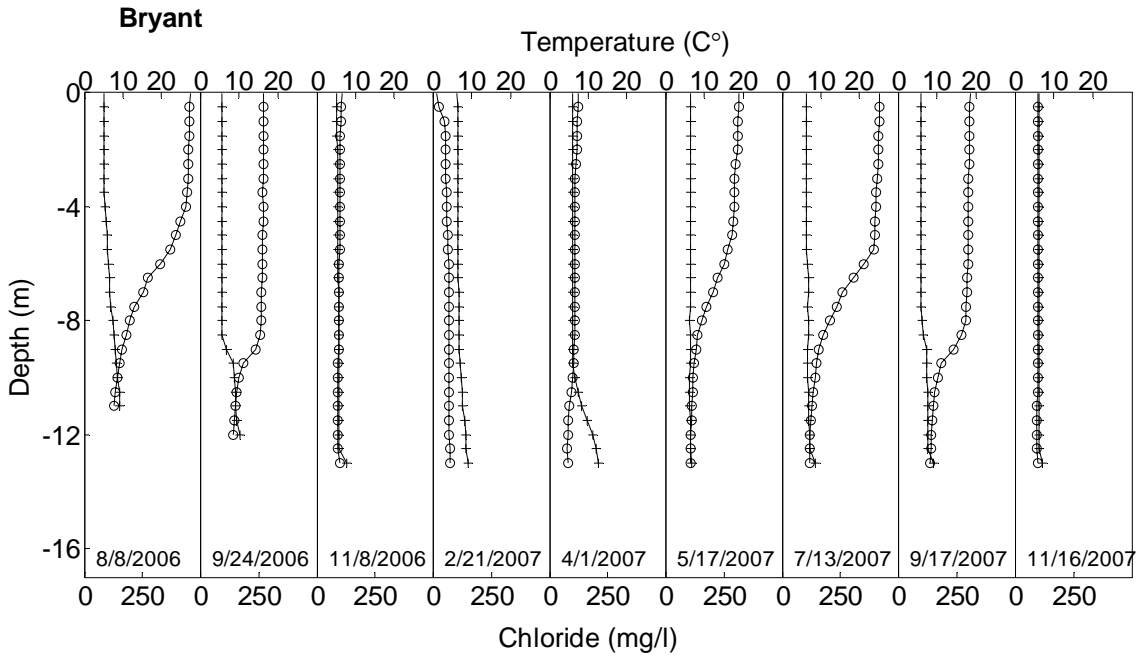
similar to those in Cedar, Bryant, Ryan and Gervais (Figures 14-17). In all of these lakes inflows of high density salt water can be seen to enter the lakes during the winter causing chemical stratification. This chemical stratification is not as strong as in Tanners Lake and Parkers Lake; therefore full mixing still occurred during the spring and fall. McCarron and Ryan Lake formed stronger chemoclines than Gervais, Bryant and Cedar Lake.



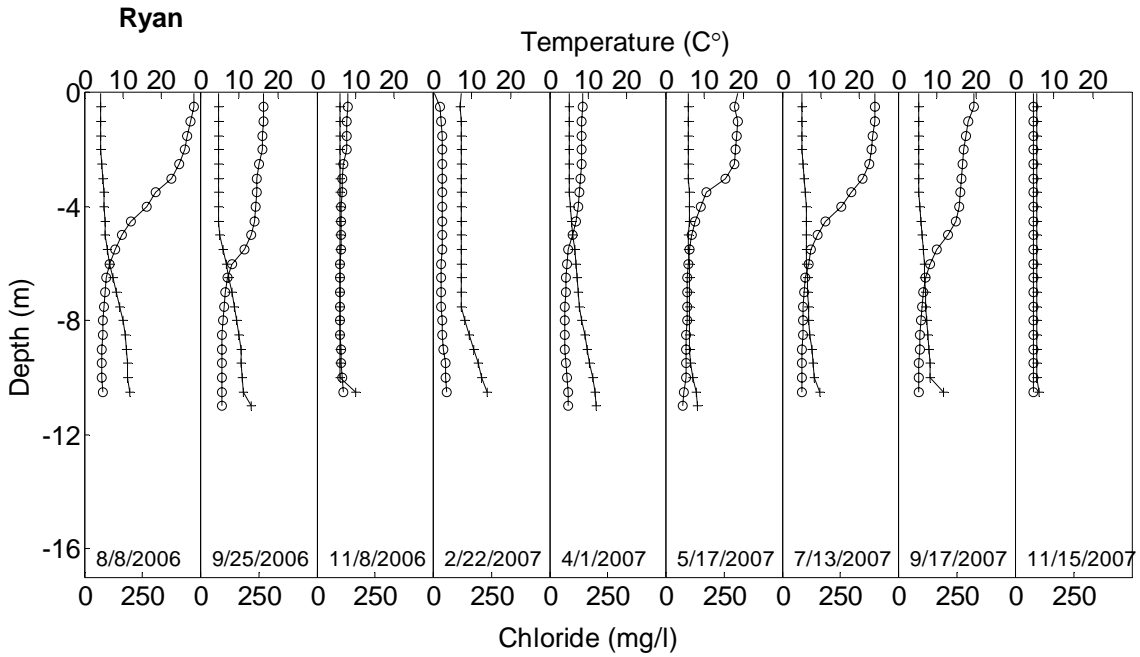
**Figure 13: Conductivity and Temperature profiles for Lake McCarron**



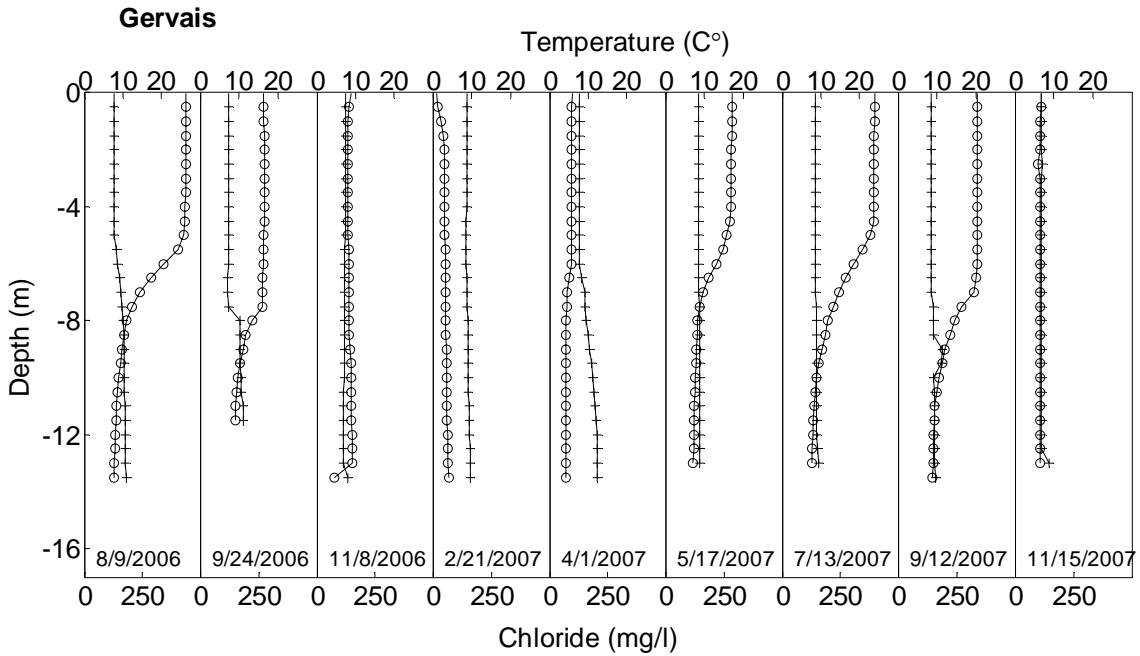
**Figure 14: Conductivity and Temperature profiles for Cedar Lake**



**Figure 15: Conductivity and Temperature profiles for Bryant Lake**



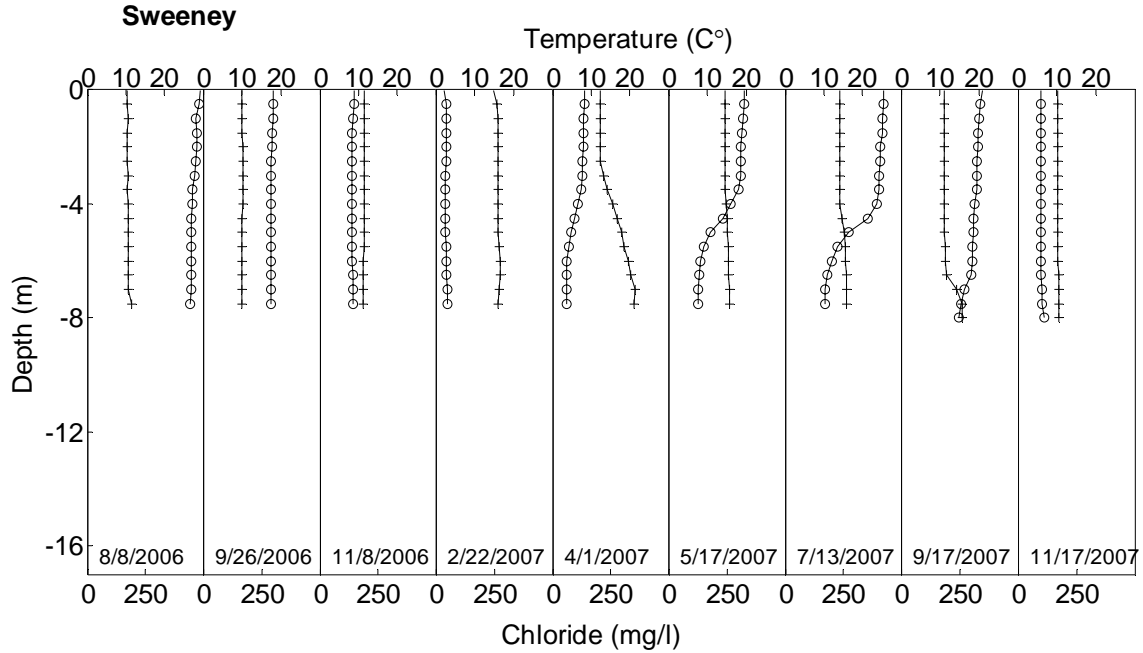
**Figure 16: Conductivity and Temperature profiles for Ryan Lake**



**Figure 17: Conductivity and Temperature profiles for Lake Gervais**

Sweeney Lake has salinity profiles that are different from the other lakes (Figure 18) 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.



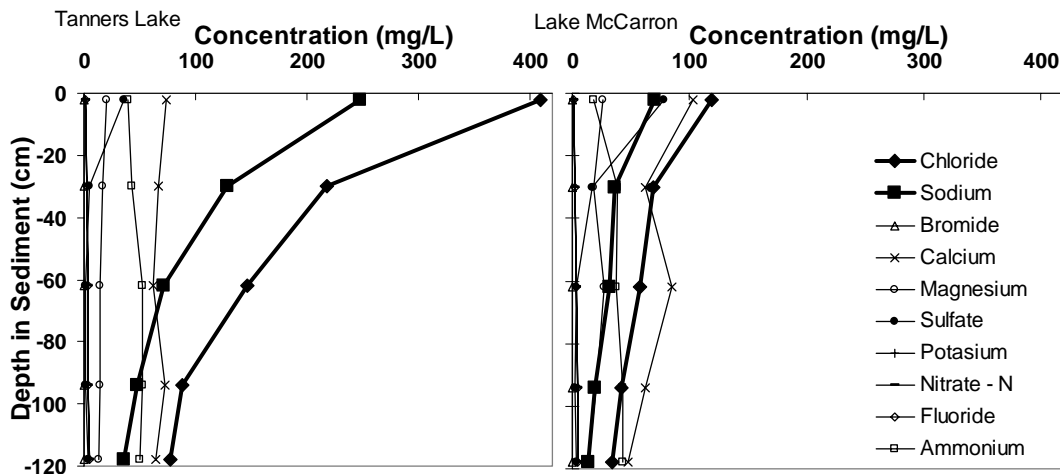
**Figure 18: Conductivity and Temperature profiles for Sweeney Lake**

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 (Figure 2). 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).

## 5 SALINITY IN LAKE SEDIMENT CORES

Leakage of saline water into the sediment can influence the chemical stratification of lakes from year to year. If the density of the water above the sediments is high enough mixing with the sediment pore water by natural convection or so called “viscous fingering” can occur moving water with a lower concentration and density upwards into the water column and moving water with a higher salinity downwards into the sediment pores. The result has to be 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 7 m thick and has concentrations reaching 400 mg/L chloride compared to the maximum concentrations of 240 mg/L chloride in Lake McCarron.



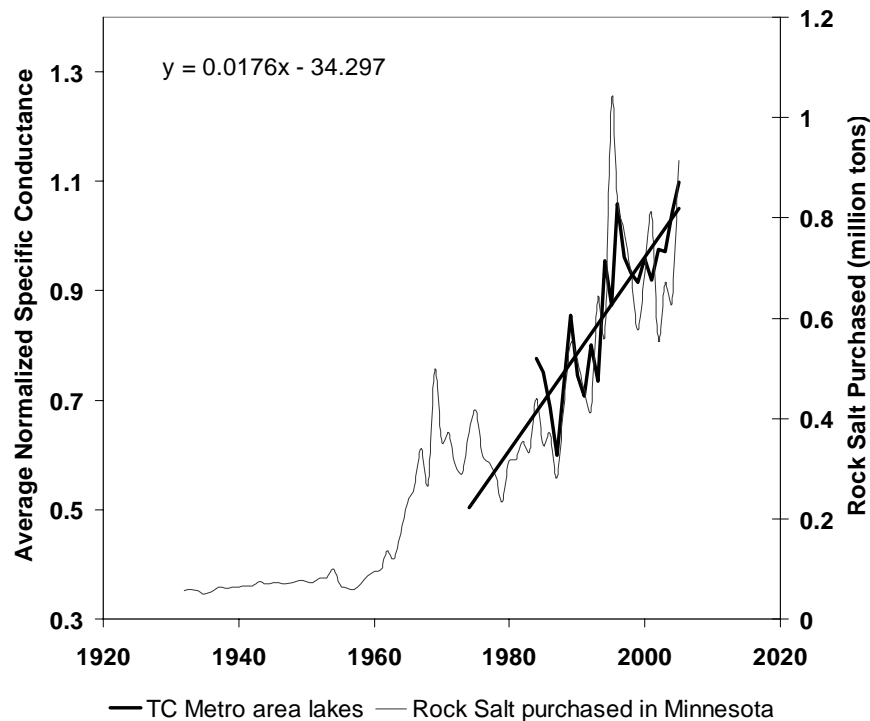
**Figure 19: Ionic composition of pore water from sediment cores extracted at the deepest location of Lake McCarron and of Tanners Lake.**

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 19) 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.

## 6 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 in section 4.4 but a more comprehensive analysis is needed. To accomplish this specific conductance measurements from the MPCA Environmental Data Access website were analyzed for trends. The average annual conductance in the surface layer (top 3m) of TCMA lakes with more than 10 years of data is plotted in Figure 19. The top 3 meters was used as an estimation of the volumetric average concentration since concentration patterns in the surface of the lakes closely matched the volumetric average concentrations in figures 7 and 8. Values are normalized (referenced) relative to the average for the period 2001-2005. 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 specific conductance (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 normalized conductivity is 0.0176 which means that on average the lakes in the TCMA increased in specific conductivity by 1.76% relative to the average value for the reference period 2001 to 2005. Extending this trend into the future would produce a doubling in specific conductivity and therefore chloride in these lakes in about 56 years. This is unlikely because efforts are under way to reduce road salt use by better application procedures, and a closer inspection of Figure 19 may suggest that the rate of increase has slowed since 1996. Hind-casting at the rate of 1.76% would give zero chloride concentration in about 1950. This agrees with the road salt application values in Figure 1.



**Figure 20: Time series of average normalized specific conductance in 39 TC Metro Area lakes and total rock salt purchases by the State of Minnesota.**



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 in Figure 14 have a correlation coefficient of 0.93.

**Table 6: Average chloride concentrations, trends in chloride concentration, lake and watershed information for lakes in TCMA lakes.**

Lake	Years of data	[Cl-] top 3 meters (mg/L)	Trend (%/year)	[Cl-] average annual max (mg/L)	Lake area (ha)	Depth (m)	Watershed area (ha)	Percent Impervious
Bald Eagle	22	42	0.57	87	513	10.97	2843	9
Beaver	22	90	1.81	117	26	3.35	1446	26
Bennet	22	63	2.23	100	9	2.74	293	36
Brownie	15	105	2.08	798	5	14.33	136	33
Calhoun	18	103	1.17	158	162	24.99	1408	35
Cedar	18	84	0.81	142	68	15.54	537	28
Como	22	89	2.07	166	25	4.57	591	32
Diamond	17	142	2.06	467	47	1.83	268	44
Gervais	22	100	2.38	178	95	12.50	1144	30
Harriet	18	93	1.24	119	136	26.52	737	28
Hiawatha	17	91	1.70	221	22	10.06	2378	45
Independence	12	43	0.13	71	342	17.68	1630	3
Island South	22	44	1.09	77	24	3.35	77	20
Isles	18	87	0.97	134	44	9.45	252	29
Johanna	22	107	2.18	167	86	13.11	1188	39
Josephine	21	48	1.71	81	47	13.41	350	23
Keller	21	87	2.39	113	29	2.44	329	23
Kohlman	22	87	1.73	160	30	2.74	629	27
Long NB	22	99	2.31	202	74	9.14	3781	25
Loring	11	340	2.68	760	3	4.88	144	77
Mccarron	22	85	1.67	189	28	17.37	549	24
Medicine	14	88	1.42	204	359	14.94	4380	30
Nokomis	18	66	1.10	99	83	10.06	1467	36
Otter	18	25	0.55	50	134	6.40	382	7
Owasso	22	44	1.18	81	141	11.28	1047	24
phalen	22	89	2.34	127	80	27.74	580	30
powderhorn	13	86	0.71	361	5	6.71	94	44
Round	22	94	2.39	231	12	2.44	251	29
Snail	22	57	2.44	102	61	9.14	477	22
Spring	10	505	2.97	1018	2	2.13	30	47
Tanners	11	104	1.06	288	28	14.02	214	33
Turtle	22	42	1.23	70	166	8.53	316	12
Valentine	20	117	2.54	208	24	3.96	664	33
Wabasso	22	36	1.25	74	19	20.12	103	32
wakefield	22	97	2.86	178	9	3.05	563	32
Weaver	11	53	0.71	85	60	17.37	203	17
West Silver	21	57	2.20	225	29	14.33	208	30
White Bear Lake	22	31	0.89	43	978	25.30	3059	11

- Top 3 meters is an annual average for the top 3 meters in the lake (2001-2005)

- Trend is based of the annual values for the top 3 meters and normalized with the average annual value between 2001-2005

-Average annual max chloride concentration represents the average value of the max concentration seen in the lake each year from 2001-2005 at any depth.

-Percent Impervious represents the percentage of the watershed covered by impervious surfaces.

Information on these individual lakes were then gathered (Table 6). Overall 39 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. The table gives the number of years of record (maximum 22), average chloride concentration in the surface (3m) layer between 2001 -2005, the trend in % relative to the time series of the annual average chloride concentration in the top 3m in the lake, the average maximum concentration seen in the lake every year from 2001-2005 at any depth, the lakes surface area, depth, watershed area, and the percent of the watershed covered by impervious surfaces. 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. An average maximum concentration all occur during the winter months and are located near the bottom of the lakes. These values range 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.

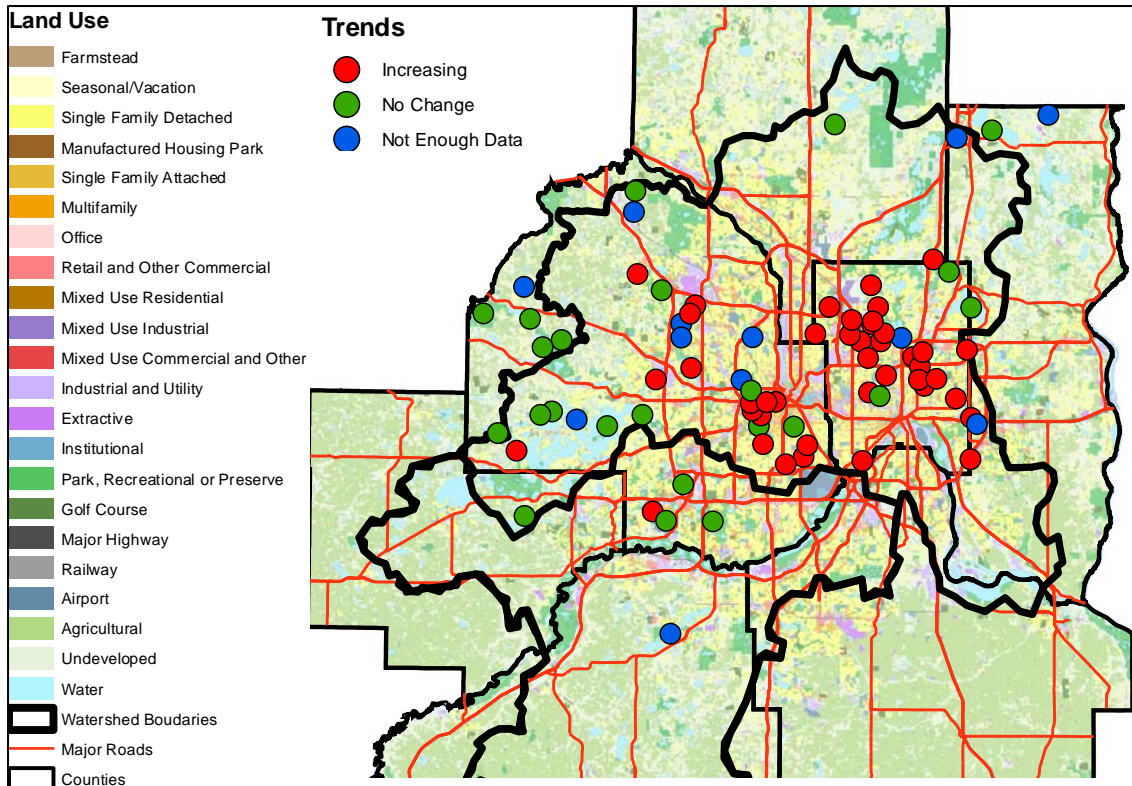
**Table 7: Correlation coefficients between chloride concentrations with lake and watershed information. PI (Percent Impervious), SA (Lake surface area), D (Lake depth).**

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

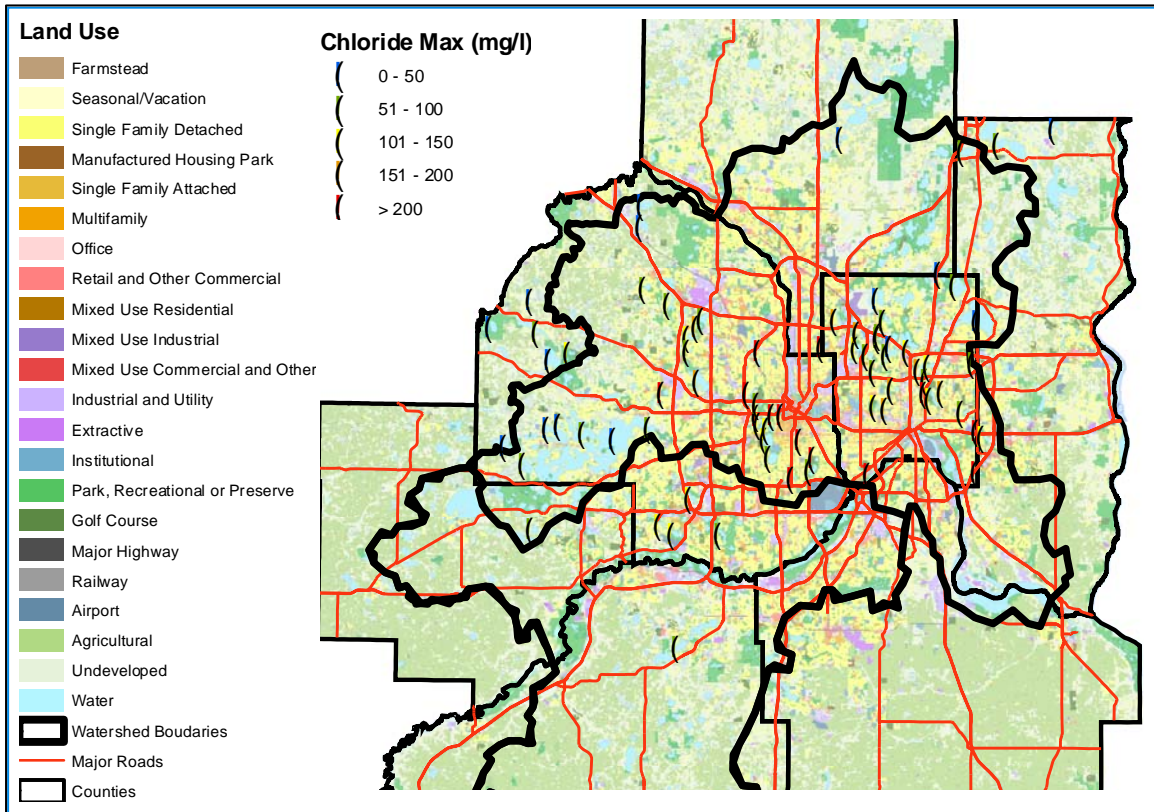
Correlations between these chloride concentration values with lake and watershed parameters can be made (Table 7). With individual lake or watershed parameters all three concentration values correlate the best with the percent impervious surfaces in the watershed. This makes sense since the more impervious surfaces the more likely hood that there is a high concentration of roads and parking lots which would lead to more salt being applied in the watershed. Lake parameters such as area, depth and watershed area have a very low correlation with chloride concentration. When taking the ratio of impervious surfaces to surface area multiplied by the depth the correlation becomes even higher for both the average concentration and the average max concentration. Intuitively this also makes sense because surface area \* depth while not equal to lake volume represent in a comparative sense the volume of each of the lakes. 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 higher the likelihood that storm sewers are present or more surfaces for road salt applications, providing a direct access of the snowmelt runoff into the lake.

The position of these lakes and all 71 lakes where information was available is displayed in figures 21 and 22. These two graphs display spatially where the lakes are located and the average max concentrations seen in those lakes (Figure 22) as well as if

the chloride concentrations have an increasing trend or not (Figure 21). Patterns are present in terms of special orientation of the lakes. For example, lakes located inside the heavily populated areas of the TCMA have higher chloride concentrations and are more likely to have an increasing chloride trends. On the other hand the further away the lakes are from the heavily populated areas the lower the concentrations are.



**Figure 21: Locations of trends for all lakes analyzed.**



**Figure 22: Max concentrations in Lakes studied for the TCMA.**

## 7 A SIMPLE LAKE SALINITY CYCLE MODEL

Some of the results in this paper can be summarized with the creation of a simple lake model. The model assumes the lake is fully mixed and represents the volumetric average chloride concentrations in the lake over time. The model also assumes that a certain mass of chloride is added to the lake over the four month winter period (December – March). Over the rest of the year flushing occurs, washing out some of the salt added to the lake during the winter months. The equations used for this model represent a fully mixed batch reactor with a conservative material (chloride) being added during one phase and flushed out during another.

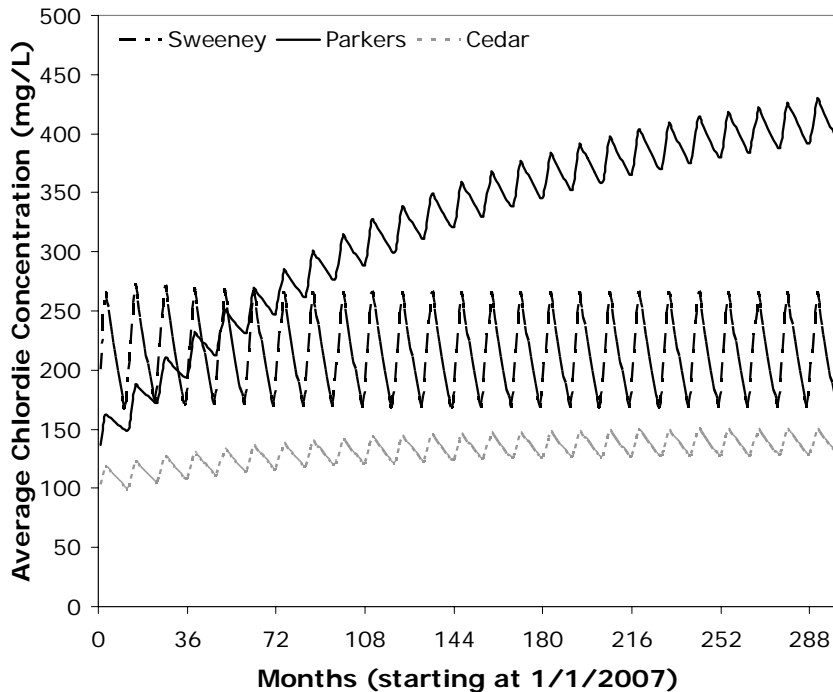
$$\text{Month (December – March)} \quad \frac{dc}{dt} = \frac{(M / 4)}{V} \quad (5a)$$

$$\text{Month (April – November)} \quad \frac{dc}{dt} = -K * C \quad (5b)$$

$$M = (C_{\max} - C_0) * V \quad K = \frac{1}{Tr} = \frac{T}{\ln(C_{\max} - C_e)} \quad (5c)$$

Where  $M$  is the mass of chloride added to the lake in the winter.  $C_{\max}$  is the max concentration seen in the winter.  $C_0$  is the initial minimum concentrations seen in the previous fall before road salt was applied.  $C_e$  is the end concentrations at the end of the following fall after rainfall as washed some of the road salt from the lake.  $V$  is the volume of the lake,  $C$  is the concentration in the lake for a particular month.  $K$  is the first order rate constant defined as 1/residence time.  $Tr$  is the residence time and  $T$  is the number of months where flushing occurs. In this case  $T$  is set to 8 to represent the months of April – November.

The results from this model are limited based on a number of factors. First a limited amount of data is available for the estimation of the mass entering the lake and the residence time. Due to sampling frequency it is unknown if the values obtained are the actual maximum or minimum concentrations seen in the lake. Both total mass and residence time can also be highly variable depending on the amount of salt applied to the watershed, the amount of snowfall in the winter and the amount of rainfall in the summer and spring. The simulations run assume the same conditions seen in the 2006/2007 sampling period will be repeated into the near future. The purpose is to find how each of the lakes would respond. The trend estimates in the previous section assume that a steady state value will not be reached and lake concentrations will continue to increase.



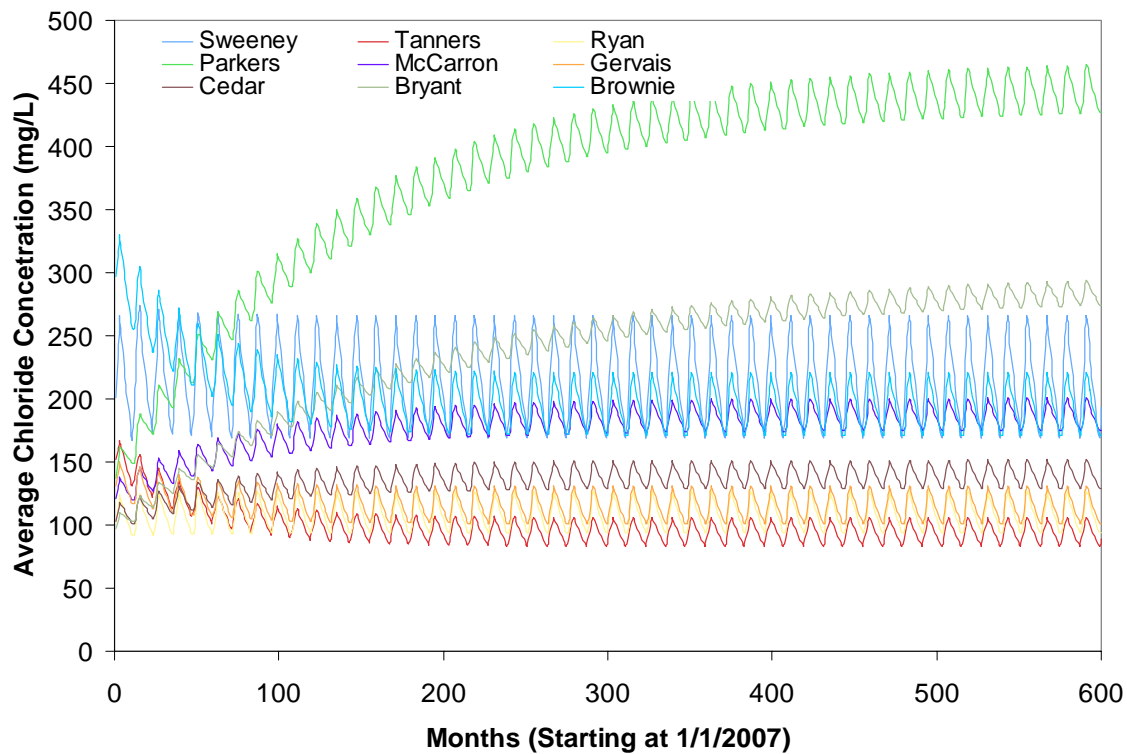
**Figure 23: Steady state calculations for three of the lakes studied.**

Simulations were run for three lakes (Figure 23). These simulations display the differences seen between different types of lakes. Parkers Lake represents a lake receiving high quantities of salt relative to its volume, but also has a high calculated

residence time (94 months). This doesn't allow for a lot of flushing allowing the lake to increase to volumetric average chloride concentrations above 400 mg/L. Sweeney Lake on the other hand has displayed high concentration already. With its calculated residence time of 18 months it also has a high flushing effect. This results in a lake with high fluctuation between winter and fall, but, if similar conditions persisted into the near future, has already reached steady state. Lake McCarron is a final type of lake that has not reached steady state yet, but if it did would not have volumetric average concentrations greater than the 230 mg/L standard for aquatic life. All values obtained represent a fully mixed lake and do not take into account chemical stratification. Values used in the simulation and results from other lakes are available in Table 8 and Figure 24.

**Table 8: Value used for steady state simulations**

	Tr (months)	M (tonnes)	Cmax (mg/L)	Co (mg/L)	Ce (mg/L)
Sweeney	18	93	266	168	172
Tanners	33	42.77	167	144	131
Ryan	27	9.76	123	91	92
Parkers	94	54.42	163	124	148
McCarron	59	55.17	129	113	121
Gervais	32	114.13	146	121	113
Cedar	51	98.41	118	96	101
Bryant	117	64.71	110	90	102
Brownie	32	9.9	329	280	256



**Figure 24: Steady state simulations for all 9 lakes.**

## 8 CONCLUSIONS

Road deicing salt use has increased in the United States from 149,000 tons in 1940 to over 18 million tons in 2003. Road De-icing uses 37% of the total NaCl consumption throughout the United States and around 62% of the total consumption in the state of Minnesota. Natural sources of sodium and chloride in the Minnesota area are low with rain water only containing 0.1 mg/L of chloride and no other significant natural sources of are located in southeastern Minnesota. The pathway the road salt takes to reach a water body can be determined by the ration of sodium and chloride. If the equivalents of sodium and chloride are close to a 1:1 ration then the contamination was from direct runoff. If the ration is less much less than one then the source transported though the soils and/or groundwater. Chloride concentration in lakes, groundwater, and streams were found to be much higher in urban areas when compared to rural and forested areas. Concentrations of chloride in stream throughout the northern United States and Canada have been found to be increasing with concentrations in winter reaching levels that can affect aquatic organisms. Concentration in urban areas in the Upper Mississippi River Basin were found to be substantially greater than in most urban streams sampled throughout the Nation. In the Twin Cities and Baltimore areas stream chloride concentration were well correlated with the percent of impervious surfaces in the watershed. Groundwater chloride concentrations have also been shown to be high in urbanized areas of Toronto, Chicago, Twin Cities, Southern Ontario and Madison WI.

High concentrations of sodium can change soil chemistry causing the soils to become sticky and impervious by adsorbing to the soil particles and displacing calcium and magnesium. Sodium has also been found increase metal mobilization, decrease the pH of the soil, and decrease he fertility of the soils. Salinity levels of 1000 mg/L can have lethal and sub lethal effects on aquatic plants and invertebrates. Continuous levels as low as 250 mg/L can be harmful to aquatic life. Increases in sodium and chloride in aquatic environments have been shown to decrease biodiversity and species richness in some areas affecting the likes of fish, wood frogs and diatoms.

The water quality of urban lakes in the Twin Cities Metropolitan Area (TCMA) of Minnesota has been investigated to identify and quantify impacts of road salt applications. The findings lead to the following conclusions regarding the response of urban lakes to road salt applications in their watersheds.

- 1) In natural fresh surface waters sodium and chloride are typically not the dominant anion and cation. Sodium and chloride are, however, the dominant ions in the TCMA lakes studied. Concentrations in the TCMA lakes are 10 to 100 times larger than background concentrations in natural waters. The one to one stoichiometry of sodium and chloride in the lakes suggests that NaCl is the source of both ions.
- 2) There are no natural sources of NaCl in the geology of the TCMA. The salinity source for the TCMA lakes must, therefore, be man-made. The largest salt uses in the TCMA are for water softening and for road de-icing. Water softening backwash is typically disposed of in sanitary sewers and passes through WWTPs

into the Mississippi River bypassing any lakes. Road salt becomes a solute in snowmelt water which can flow into lakes through storm sewers, ditches, and small streams.

- 3) Chloride concentrations in TCMA lakes have a seasonal cycle, concentrations are highest during the winter and early spring months and lowest during the late summer and fall. This cycle matches road salt applications and snowmelt runoff in winter/spring, and flushing of lakes by rainfall runoff during the summer.
- 4) Concentrations in the lakes studied are highest at the bottom of the lake causing chemical stratification. This stratification can be strong enough to prevent complete vertical lake mixing (turnover) in the spring. In the lakes studied complete vertical lake mixing in the spring was only prevented in a few lakes, and complete vertical mixing in fall occurred in all 13 lakes studied. The notable exception was Brownie Lake which has been continuously salinity stratified for several decades. Seasonal mixing of the other 12 lakes varied from year to year.
- 5) The chronic standard of 230 mg/L chloride required for the protection of aquatic life was exceeded at some point in time in 5 of the 13 lakes studied (Tanners, Parkers, Brownie, Ryan, Sweeney). These elevated concentrations were typically found during the winter and spring months and occurred in the deepest portion of the lakes. Only one lake (Sweeney) displayed chloride concentrations above the standard throughout the entire water column because it was artificially mixed by an aeration system to control eutrophication.
- 6) Chloride concentrations in TCMA lakes have been increasing over several decades. The increases are correlated with increases in rock salt purchased by the state for road de-icing. If current trends continue, the chloride content of TCMA lake waters will continue to rise. Back calculating the trend gives a 0 mg/L chloride concentration in the lakes around 1950, which is also the time when road salt applications in the state of Minnesota started to increase. The continued increase in lake chloride concentrations strongly depends on the hydraulic residence time and the rate of chloride loading entering each individual lake.
- 7) Lake chloride concentrations are correlated with the amount of impervious surface area in the watershed of a lake. The more impervious surfaces in the watershed the higher concentration of chloride seen in the lake. A more accurate correlation is seen with the ratio of impervious surfaces to lake volume.
- 8) Sodium and chloride ions penetrate into the pore water of a lake's sediment by natural convection and diffusion. Lake sediment can act as a sink or a source of sodium and chloride during stratification and mixing periods, respectively. From the sediment pore water, sodium and chloride may be conveyed into the groundwater.

Overall the results show a continued degradation of the water quality of urban lakes due to application of NaCl in their watersheds. Road salt is used to increase driving safety in winter, but road salt application and lake management practices need to be implemented that take into account driving safety but do not impair water quality.



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