UNIVERSITY OF MINNESOTA

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A Salt (Chloride) Balance for the Minneapolis/St. Paul Metropolitan Area Environment

by

Eric Novotny, Andrew Sander, Omid Mohseni and Heinz Stefan

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Abstract

There are no natural sources of NaCl in the geology of the Twin Cities Metropolitan Area (TCMA) of Minnesota. Salinity in surface water or groundwater of the TCMA must therefore be of anthropogenic origin. The largest salt uses in the TCMA are for water softening and for road de-icing. Water softening occurs in individual households, and in commercial and industrial establishments. Backwash is typically disposed of in sanitary sewers and discharged from wastewater treatment plants to major rivers. Road salt is used for public safety on winter roads. Road salt is a solute in snowmelt water, which runs into storm sewers, small streams, rivers, lakes and wetlands. In the TCMA watershed analyzed, approximately 267,000 short tons (242,000 metric tonnes) of road salt (NaCl) are applied annually for road de-icing. Within the political boundaries of the seven county TCMA, the numbers are 350,000 short tons (315,000 metric tonnes). It is important to understand how these applications influence the environment.

Salt balances for the entire TCMA and for 10 smaller sub-watersheds reveal that a large portion of the local road salt applied in the TCMA is not carried away in the Mississippi River water. Streamflow and bi-weekly concentration measurements from 2000 to 2007 indicate that the Minnesota and Mississippi Rivers import 235,000 tonnes of chloride annually from upstream into the Twin Cities Metropolitan Area and 355,000 tonnes are exported by the Mississippi River downstream. 120,000 tonnes are being added to the rivers as they travel through the Twin Cities. Of these 120,000 tonnes, approximately 87,000 tonnes come from wastewater treatment plants as determined from flowrate and biweekly concentration measurements in 2007/2008. The remaining 33,000 tonnes are attributed to road salt, and represents 22% of the total of 148,000 tonnes of chloride that are applied to the roads in the TCMA watershed every year. The latter figure was obtained from a detailed survey and inventory of road salt uses from 2000 to 2006. Roughly, 78% of the road salt applied is staying in the watershed. From chloride balances in 10 small sub-watersheds, slightly lower values of 65 - 73% were calculated.

Although salt export from the TCMA by wind (in the form of dust), and export in commercial and other products are not included in the chloride budget, it is fair to conclude that much of the road salt imported and applied annually in the TCMA, remains in the area, most likely dissolved in surface water of lakes and wetlands, and in groundwater. Rising trends in the salinity of these water bodies have been documented.

Units

In this report metric units have been used preferentially.

Area in ha or km^2

Concentration in mg/L

Flow in streams or rivers in m^3/s

Mass or weight in metric tonnes = 1000 kg = 2205 lb,

compared to short tons = 2000 lb = 907.2 kg

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1. 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, Smith et al. 1999).

It has been reported that 23 million short tons of roadsalt were used in the US in 2005 (USGS 2007). In the Twin Cities Metropolitan Area (TCMA) of Minneapolis/St.Paul in Minnesota an estimated 350,000 short tons (315,000 metric tonnes) of road salt are used annually for road de-icing to improve driving safety. The question arises, what happens to all this salt after it has fulfilled its purpose as a road deicer. To address this question several studies have been conducted under the sponsorship of the Local Roads Research Board (LRRB) of the Minnesota Department of Transportation (Mn/DOT). Two reports on these studies have already been issued (Sander et al. 2007; Novotny et al. 2007), and this is the third report. This report will deal with a chloride (Cl) budget for the TCMA.

Sodium and chloride are used for many purposes in the United States. NaCl is used in agriculture, by industrial and commercial producers of chemicals, for road deicing, foods, metals, paper, petroleum, textiles and dying, and for water softening (Kostick 2004). Sodium and chloride are also found naturally. The natural sources of chloride and sodium are mineral sodium chloride deposits, weathering of geological formations and wet deposition from ocean evaporation (Jackson and Jobbagy 2005). Sources of NaCl used by humans are salt mines and solar ponds. The ultimate sinks of NaCl are commercial products and natural water bodies, especially the oceans, because NaCl is highly soluble and fairly conservative.

When NaCl is applied to the roads it accumulates in the snowpack or is transported with the melt water. 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 along 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 designated as base flow (Novotny, Smith et al. 1999). On pathway (1) both chloride and sodium act as a conservative material, i.e. equal ionic equivalents of sodium and chloride are delivered to a lake or river that receives the direct runoff. If the snowmelt water is transported through the soil, following pathways (2) and (3), more chloride will be delivered than sodium. Sodium does not act as conservatively in soils as chloride. The sodium exchanges with other cations adsorbed to soil particles, causing an increase in calcium, magnesium, potassium and hydrogen ions by cation exchange (Mason et al. 1999). The chloride ions are conservative in the soil and will pass readily into the surface water and groundwater (ECHC 1999), although retention in the soil capillary water results in a residence time for Cl that exceeds that of water (Mason et al. 1999).

Salt applied to a road during the winter eventually finds its way into the soil, streams and rivers, lakes, wetlands and the groundwater. According to Canadian studies, water bodies that are most affected 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 salt applications are common (ECHC 1999). Not only can the salt be transported into or through each of these water bodies, but also each of the pathways create opportunities for NaCl to accumulate in the watershed. In pathway (1) the runoff can flow into a lake or wetland, which have longer residence times than streams. In pathways 2 and 3, NaCl can accumulate in the shallow groundwater before flowing into streams and rivers. The purpose of this report is to estimate how much of the 315,000 metric tonnes of road salt applied annually in the TCMA is staying in either the ground or surface water storage, and how much is being transported out of the metropolitan watershed through the Mississippi River and other outflows.

2. STUDY AREA AND CONTROL VOLUME

In this report we examine the transport of sodium and chloride through the Twin Cities Metropolitan Area (TCMA) urban environment by creating a budget for the chloride ion in a watershed or control volume that covers more or less the TCMA. Figure 1 displays the 7-county TCMA and the control volume used for the chloride budget. The TCMA is located inside the watersheds of two major rivers, the Minnesota and the Mississippi Rivers, therefore the boundaries of these two rivers were used to delineate the control volume in Figure 1. Also shown in this figure are the locations of the data collection points. To develop a chloride budget, flow data and chloride concentration data were needed. The locations where these data were collected are show in relation to the borders of the watershed. Also displayed are the locations of the four wastewater treatment plants (WWTPs) which discharge inside of the watershed. Impervious surfaces represent population centers and level of urbanization in relation to the watershed boundaries.

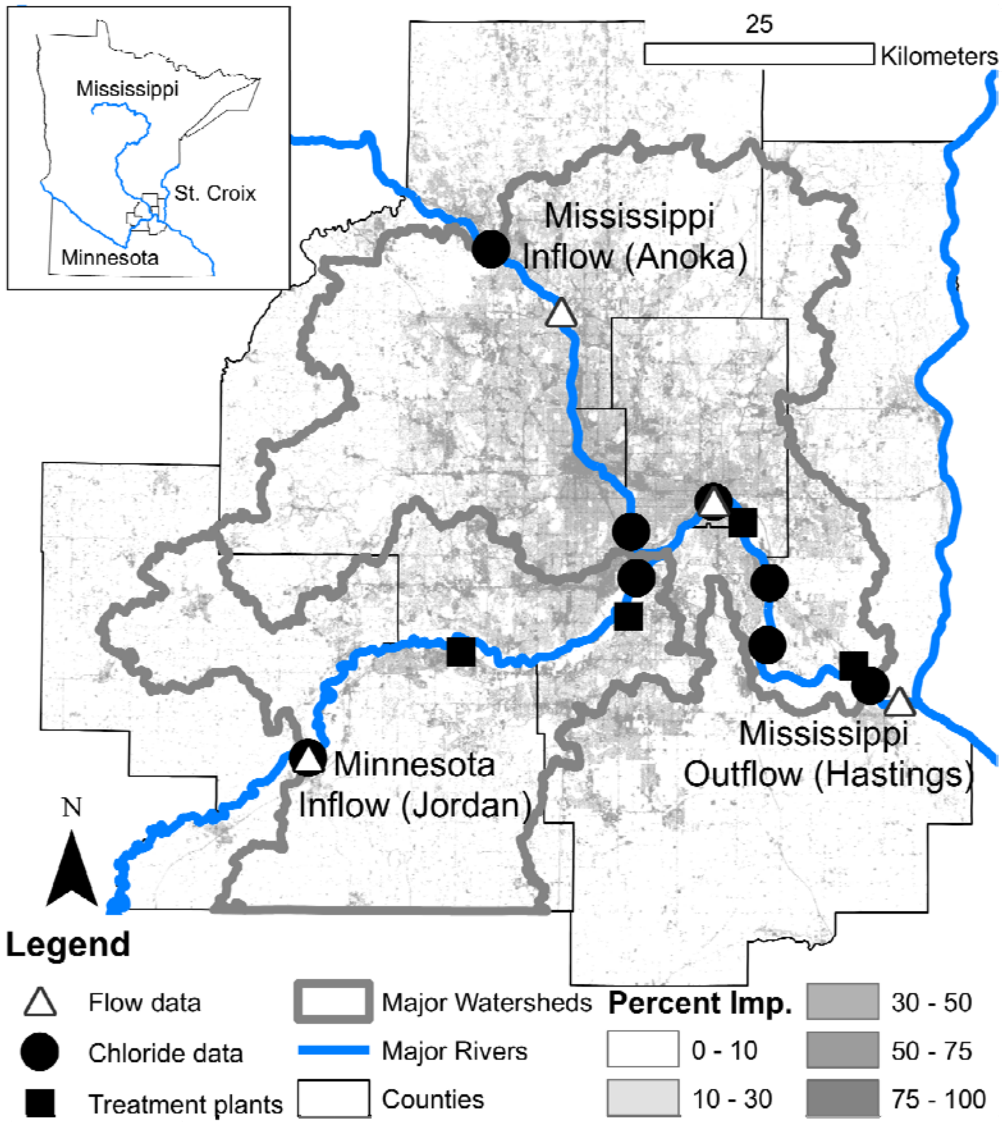


Figure 1: Boundaries of the control volume used for the Cl^- - mass balance. Watershed boundaries shown by bold gray lines are within the political boundaries of the 7-county TCMA shown by finer gray lines. Levels of urbanization are given by gray shades representing percent imperviousness of the surface area (from Metropolitan Council GIS database).

3. METHODS

3.1 Chloride mass balance

The chloride balance of the TCMA watershed can be stated as follows: The total mass (rate) of chloride in the inflows to the TCMA watershed plus the total mass (rate) of chloride applied within the watershed minus the chloride mass (rate) leaving the system is the amount (rate) that stays behind in the watershed. This amount (rate) will therefore accumulate somewhere within the watershed. Since chloride is highly soluble, and does not interact significantly with soils, potential accumulation in groundwater, lakes, wetlands and plants inside the watershed is likely.

A very detailed study of a salt budget for Olmsted County, Minnesota, was recently conducted by Wilson (2008). In that study the control volume was delineated by the boundaries of Olmsted County, and all inputs and exports were measured in great detail. In our study we did not use the political boundary of the TCMA, but a sub-watershed that covers most of the TCMA, because most of the NaCl transport in the environment is in aqueous form and therefore in streams and rivers. Our chloride balance considers surface inflows and outflows only.

The following transport mechanisms into and out of the TCMA watershed were considered:

INFLOWS/EXTERNAL LOADING OF NaCl INTO THE WATERSHED (Inflow):

1) Mississippi River ($Miss_{in}$)

2) Minnesota River ($Minn_{in}$)

3) Atmospheric (dry and wet) deposition (Atm)

4) Natural Deposits (Nat)

APPLICATIONS, USES AND SOURCES OF NaCl IN THE WATERSHED (Loads):

1) Road salt applications (RS)

2) Industrial sources (IS)

3) Domestic uses/water softening (WS)

4) Foods and agricultural products (F)

5) Fertilizers (Fert)

EXPORTS OF NACL FROM THE WATERSHED (Outflow):

1) Mississippi River ($Miss_{out}$)

2) Air-borne (dry) particles (Air)

In summary, our chloride budget of the TCMA watershed can be expressed by the following mass balance equation:

$$(Miss_{in} + Minn_{in} + Atm + Nat + RS + IS + WS + F + Fert) - (Miss_{out} + Air) = S \qquad (1)$$

where the symbols have been identified in the listing above.

Note that chloride content of goods imported or exported from the TCMA has not been explicitly listed. These amounts either balance each other or are considered small relative to others.

3.2 Inflows and outflows

In order to determine how much salt is being stored in the system the amounts of salt entering and exiting the watershed must be estimated. The principal hydrologic input of chloride to the control volume (TCMA watershed) is through the Mississippi and Minnesota Rivers; they are the two principal natural inflows into the system. Deposition of chloride by rainfall or dry deposition, e.g. as salt dust are ignored. Salt import in foods is captured in WWTP effluents. Chloride import to the TCMA in other goods is ignored, and so is chloride export in goods manufactured in the TCMA. The natural export of salt from the CMA watershed can occur through a number of pathways including surface runoff that leads to the Mississippi River and airborne particulate spreading (Blomqvist and Johansson 1999). Export by surface runoff will be captured in stream measurements at the outflow of the Mississippi River from the watershed. Airborne spreading of roadsalt is usually over short distances. Between 20-63% of the total salt applied to a major roadway in Sweden was transported by air, with 90% deposited within 20 m of the road (Blomqvist and Johansson 1999). If the majority of the salt transported by air is deposited near the roadways it is unlikely that a significant amount of salt is exported out of the watershed by wind. Road salt is also removed with the removal of snow pack by trucks and by plowing, but due to the size of the watershed it is unlikely that these practices would remove a significant amount of salt from the control volume. The inflow and outflow of the Minnesota and Mississippi Rivers are therefore the major import and export pathways of salt from the metropolitan watershed control volume.

Information on sodium and chloride concentrations and water flow rates in the two major rivers that drain the watershed area were obtained from sampling points on both the Mississippi and Minnesota Rivers throughout the metro area and at the inflow and outflow points of the control volume (Figure 1). The Metropolitan Council has collected sodium and chloride data since at least 2000. Grab samples were taken at six locations along the Mississippi River and two locations on the Minnesota River two to five times per month throughout the year.

River flow data have been collected by the United States Geological Survey (USGS). The daily average, and monthly average river flow rates were obtained for the period 2000 -2007. River flow data were available for four locations: on the Minnesota River at Jordan and on the Mississippi River in Anoka, Downtown Saint Paul, and Hastings. The location on the Minnesota River matched the Metropolitan Council concentration sampling location, but the flow and concentration locations on the Mississippi River did not. The flow rates and the chloride concentrations of the Mississippi River inflow to the TCMA watershed control volume were measured at two different positions. The Mississippi River watershed area upstream from the grab sampling position is 48,900 km^2, while the watershed area upstream from the flow measurement position is 49,500 km^2. Since the difference in watershed area is only 1.2%, and no major tributaries come in between the two points, it is likely that there is only a small change in flowrate. The flowrate at Anoka was therefore used as the inflow into the control volume.

Likewise, at the outflow from the metro watershed area, the grab samples and flowrates were not measured at the same locations. Two gauging stations are located near the grab sampling location, one station upstream in downtown St. Paul, and the other downstream at Prescott, WI. The Prescott gauging station is downstream from the confluence of the St Croix River with the Mississippi River. The St. Croix River is a large river with a watershed area of 20,000 km. No flow data exists for this river right before it enters the Mississippi River. Therefore flow data from this gauging station were not used. The upstream flow gauging station in St. Paul is located 38 km upstream from the grab sample location, but the watershed areas for these two locations are 95,300 km^2 at St. Paul and 95,900 km^2 at the grab sample location, for a difference of 0.6%. The only major inflow between these two points is the Metro wastewater treatment plant, which has an average flowrate of 8.6 m^3/s. The river flow rates used with the outflow concentrations were therefore taken as the flow rate at the gauging station in St. Paul plus to the outflow from the Metro WWTP.

Using the daily flow data and grab sample data from 2000-2007 flow weighted monthly average chloride concentrations were calculated. Each grab sample concentration was multiplied by its corresponding flow, and the results were used to obtain a flow weighted monthly average chloride concentration. Each of these flow weighted monthly average chloride concentrations was then multiplied by the mean monthly flowrate obtained from daily measurements at the selected stream gauging station to get the total mass of chloride entering and exiting the watershed each month.

3.3 Uses, discharges, releases and sources of NaCl inside the watershed area

The next step was to calculate the loads or strengths of the chloride sources from salt uses inside the TCMA watershed. Major sources of chloride inside the watershed are effluents from wastewater treatments plants containing water softening salt, snowmelt runoff containing road salt, industrial effluents, food and agricultural products, fertilizer applications and natural deposition.

Natural deposition: Natural sources of chloride in the Twin Cities area are negligible. Lake chloride concentrations before settlement were determined to be 3 mg/L in the TCMA (Ramstack et al. 2004) meaning weathering of minerals and possible groundwater sources in the area are minimal. Contribution from rainwater is small as well. According to the National Atmospheric Deposition Program (NADP) the maximum annual average concentration of chloride in rainwater at a site in Anoka County from 2000-2007 was 0.08 mg/L. With a total watershed area of 415,000 ha and annual rainfall of around 747 mm in the TCMA, the chloride contribution from natural deposition is only approximately 230 metric tonnes/year.

Fertilizers: Farming in the outskirts of the TCMA is limited to 22% of the total land use area in the watershed. This percentage was calculated using land use data for 2005 provided by the Metropolitan Council. If all of this agricultural land (77,000 ha) was used for the production of corn, which according to the Minnesota Department of Agriculture requires 36 kg/ha of potassium chloride (Wilson 2008), the total input of chloride by fertilizers would only equal 2,800 short tonnes/year. Since not all of the land would be used to grow corn and likewise not all of the land designated for farming is currently used for farming the actual value is lower. A value of 49.9 kg/ha per year was used in a study of fertilizer and manure contributions to streams in Sweden (Thunquist 2004).

Wastewater treatment plants (WWTP): Effluents from WWTPs are a significant source of chloride from domestic salt uses in foods and water softening, and from industrial and commercial uses. One of the main sources of NaCl in the watershed is water softening. Large amounts of NaCl are used in water softeners, which are connected to either private septic systems or sanitary sewers and wastewater treatment plants. The vast majority of the population in the TCMA uses a sewer system, as opposed to septic systems. The majority of the population is connected to four wastewater treatment plants (Figure 2). Due to the extensive coverage of the sewer systems in the TCMA, only effluents from the WWTP were considered to determine the impact of water softeners on the chloride budget. Following our request, grab samples were collected by the Metropolitan Council Environmental Services (MCES) from 6/2007 – 6/2008 every two weeks at the effluent of the four wastewater treatment plants. Chloride concentrations in the grab samples and daily flow data provided by MCES were used to find the total mass of chloride in the monthly and annual effluents of the four WWTPs by applying the same method of analysis as for the Minnesota and Mississippi River data. Around one third of the water used in the TCMA comes from surface water sources and two thirds comes from groundwater sources (Metropolitan Council 2007). Since the groundwater sources are from deep aquifers and only one third is coming from surface water sources the background chloride concentration is assumed to be insignificant.

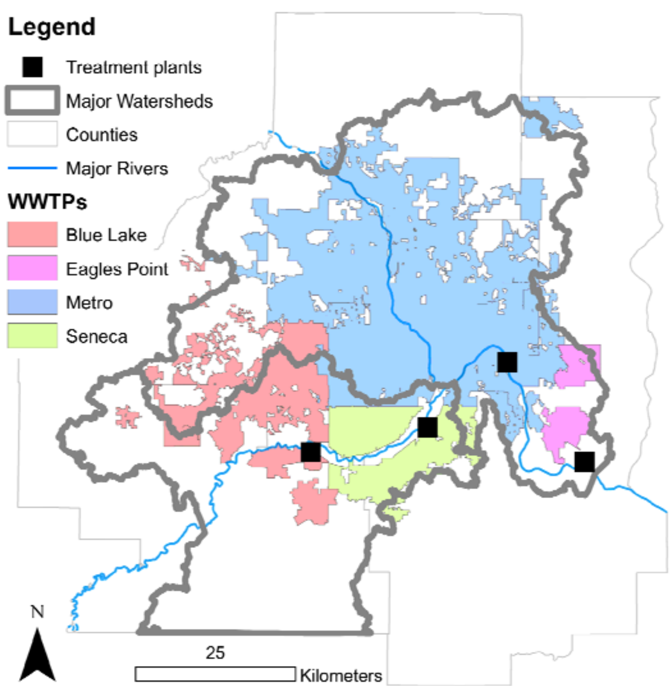


Figure 2: Coverage of the four MCES waste water treatment plants in the TCMA watershed. Data layers obtained from the Metropolitan Council GIS database

Industrial Sources: Industrial sources such as salt water used in pickling, cheese processing and tanning factories - along with other industries – were considered as sources of chloride. Since the majority of these industries discharge their water to sanitary sewers their contribution of salt is covered in the effluent of the WWTPs.

Road Salt: The amount of road salt applied to the roads within the seven-county TCMA was determined using values obtained for city, county, and state applications rates in the TCMA as defined and summarized by Sanders et al. (2007). It was estimated that approximately 350,000 short tons of road salt are applied in the TCMA annually. This translates to around 317,000 metric tonnes. Since the watershed boundaries in Figure 1 do not coincide with the political (TCMA) boundaries, the 317,000 tonnes/year had to be adjusted to give the amount applied inside the watershed area. Road miles were used to make the adjustment. City, county and state road data were obtained from the GIS database of the Metropolitan Council. Road lengths were divided by government entity into total lane kilometers of city roads for each city, of county roads for each county and state roads. Fractions (percent) of road lengths inside the watershed vs. the total roads inside a municipality, county, or state jurisdiction were then determined. These percentages were then multiplied by the total amount of road salt that each city, county or state agency applied to get an estimate of the amount of salt applied in the watershed by government entity. In addition, 24% of the total amount of road salt applied is estimated to come from private and commercial uses on parking lots, sidewalks etc. (Sander et al. 2007). The fraction of 24% was chosen from several options as discussed by Sander et al (2007). Therefore, the amount of road salt applied by government entities was increased by a factor (1 + 24/76 = 1.32) to determine the total amount of NaCl applied to all roads, parking lots, sidewalks and other surfaces with traffic in the TCMA watershed.

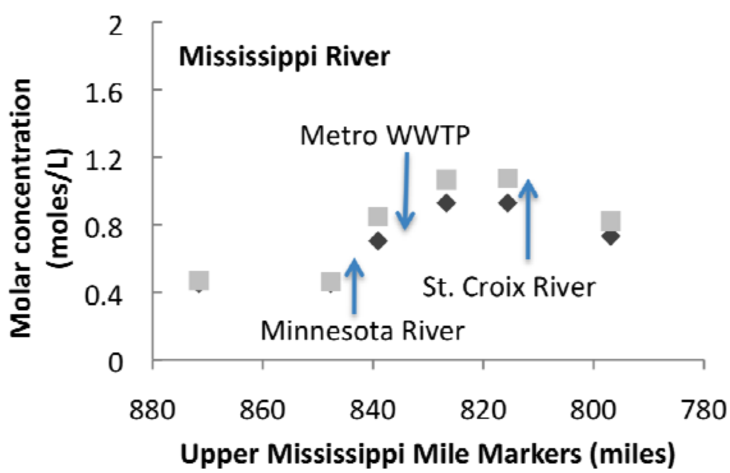
3.4 Small watershed study

In addition to the TCMA watershed, the above methodology was also applied to 10 watersheds of small streams in the TCMA. The amounts of NaCl (Cl^-) applied to each watershed and leaving each watershed were determined. The locations of these streams are shown later in Figure 11. Since the watersheds of these streams are entirely within the TCMA, no inflows had to be studied. Outflow concentrations of NaCl and flow rates in the streams were obtained from the Metropolitan Council (MCES), and amounts of road salt applied to the roads were determined as explained above. The amounts of NaCl staying behind in individual watersheds were estimated and related to watershed characteristics such as salt application per unit watershed area, percentage of the watershed covered by impervious surfaces, flow rates, and average chloride concentrations in the streams.

4. RESULTS OF THE STUDY

4.1 Spatial distribution of chloride and sodium concentrations in the major rivers of the TCMA

Three major rivers travel through the TCMA: the Mississippi River, the Minnesota River, and the St. Croix River. Chloride molar concentration measurements in these rivers were plotted against distance to see changes as the rivers flows through the populated TCMA (Figure 3). Increases in Na^+ and Cl^- concentrations are most pronounced in the Mississippi River downstream from the confluence with the Minnesota River and with the Metropolitan WWTP. The Minnesota River arrives in the TCMA with higher concentrations than the Mississippi River. After the Minnesota River receives the effluents from the Blue Lake WWTP and the Seneca WWTP, and runoff from more populated areas, the chloride concentrations increase further from about 0.85 moles/L to about 1.18 moles/L (30 mg/L to 42 mg/L). Sodium and chloride concentrations follow similar distributions with distance. When the concentrations are expressed in moles/L the concentration distributions collapse but sodium appears to be larger in the Minnesota River and increases faster in the Mississippi River after the Minnesota River and the metro WWTP converge with the Mississippi River. The St. Croix River has much lower Na^+ and Cl^- concentrations than the other two major rivers. The St. Croix River watershed is a largely undeveloped watershed, although some small cities (Afton, Hudson, Stillwater, Taylors Falls, and St.Croix Falls) discharge wastewater from their WWTPs into the St. Croix River. Chloride concentrations are around 0.14 moles/L (5 mg/L) at both locations. The inflow of the St. Croix River causes a decrease of the chloride concentrations in the Mississippi River. After the St. Croix joins the Mississippi River a decrease in the chloride concentrations is observed. In the Mississippi River chloride concentrations increase from 0.45 moles/L (16 mg/L) at the inflow to 0.93 moles/L (33 mg/L) after the Metro WWTP.



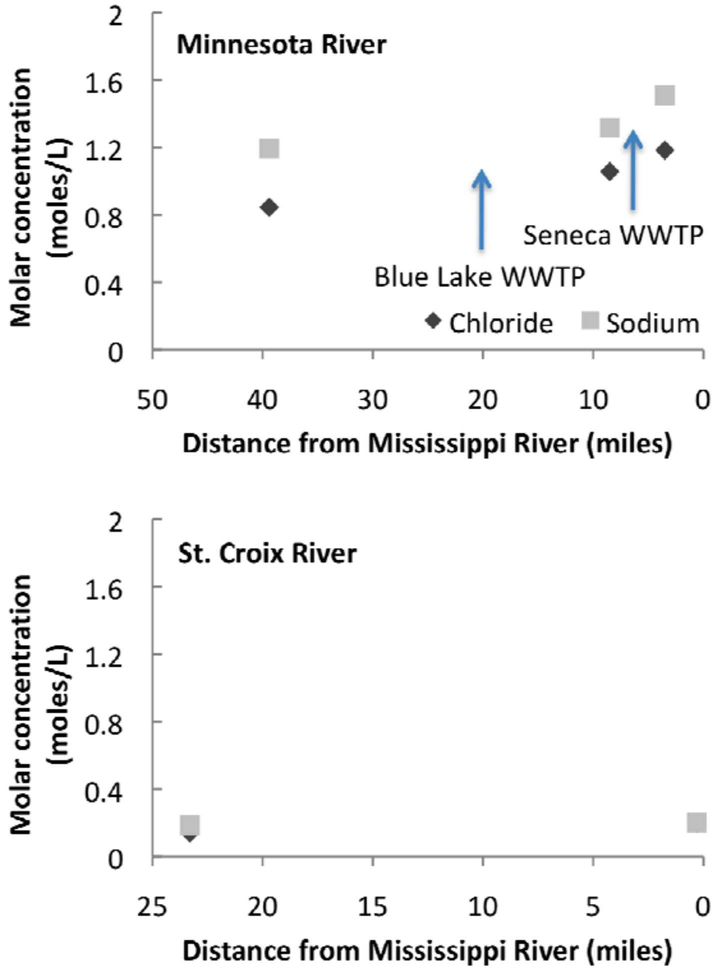


Figure 3: Measured median molar concentrations (2000-2008) of sodium and chloride in the three major rivers of the Twin Cities Metropolitan Area (TCMA).

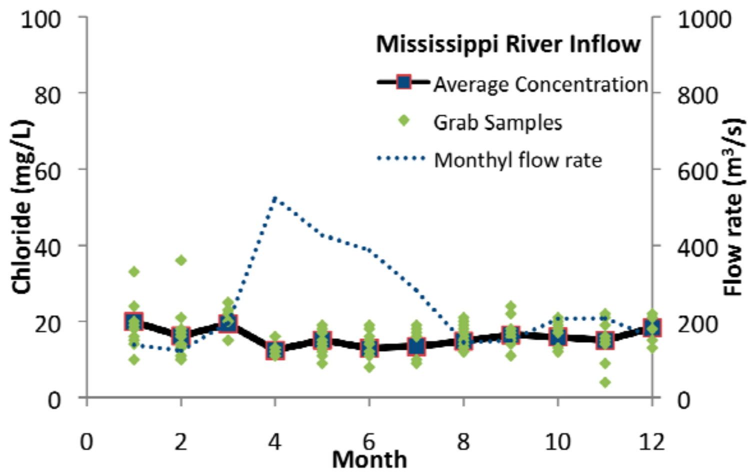
4.2 Chloride transport in the Minnesota and Mississippi Rivers

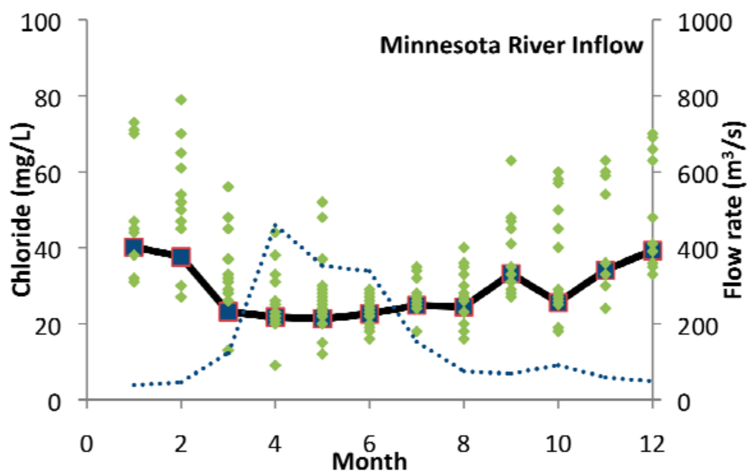
The chloride and flow data collected at both inflows (Minnesota Jordan, Mississippi Anoka) and the single outflow (Mississippi Hastings) of the metropolitan watershed area are shown in Figure 4. Individual grab sample data between 2000-2008 sorted by month are shown with the flow weighted monthly average concentrations and the monthly average flowrates. Where the Mississippi River enters the TCMA, i.e. near Anoka, the flow-weighted mean monthly chloride concentrations are on the order of 10 to 20 mg/L, fairly constant from month to month (Figure 4). Individual grab samples show only small fluctuations from year to year – with the exception of Jan, Feb and Nov.

In the Minnesota River at Jordan, upstream from the TCMA, the chloride concentrations are higher (on the order of 20 to 40mg/L) than in the Mississippi River upstream from the TCMA, and seasonal changes in flow weighted mean monthly concentrations can be clearly seen. Concentrations are highest from Dec. to Feb. and lowest in March to Aug. There is also more variation from year to year for a given month, especially in February. Frequently, when the flow rate is high the chloride concentration is low and vice versa. This can be seen in Figure 4 for the flow-averaged monthly concentrations, but it also applies to the individual grab sample.

In the Mississippi River outflow from the TCMA, i.e. near Hastings, the chloride concentration signature has changed significantly relative to the inflow at Anoka. The flow-weighted mean monthly concentrations now vary from about 20 to 50 mg/L, and the seasonal variations are strong. The high concentrations occur in Jan. to March, and the lows in Apr. to July. Concentrations vary the most from year to year in grab samples from March, and the least from June.

The seasonal patterns in flow-weighted concentrations and the seasonal variability in grab samples can be interpreted as indication of seasonal variations in river flows plus seasonal variability in salt input, i.e. road salt input in the cold months. Other salt uses, e,g, for water softening do not vary a great deal seasonally but could cause concentrations to rise during low flow periods.





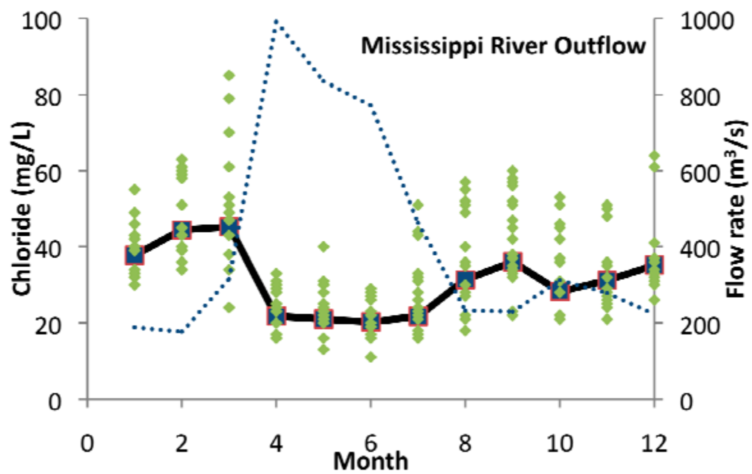


Figure 4: Plots of chloride concentrations and river flows at the inflow (Anoka and Jordan) and outflow (Hastings) stations of the TCMA watershed. Average chloride concentrations are flow-weighted monthly average values. Measurements were taken between the years 2000 and 2007.

Lower flow rates influence the chloride concentrations in the rivers as seen in Figure 4. Another illustration of the dilution effect is obtained by plotting the flow-weighted mean monthly chloride concentration for each of the stations against the average normalized monthly flow rate (normalized flow rate = monthly average flowrate /annual average flow rate) as is shown in Figure 5. As expected, chloride concentrations decrease as the flow rates increase. In the Mississippi River inflow the pattern is not as pronounced as at the other stations. The pattern is broken in the month of March at the Mississippi River outflow station. This pattern could explain the increased chloride concentrations during the late summer months when flow rates are low. During that time period constant sources of chloride such as WWTP effluents can have more influence on the concentrations then during high flow periods. The single exception is for the month of March for the Mississippi River outflow from the TCMA at Hastings: Flow rates and chloride concentrations are both high, most likely due to the addition of road salt in the snowmelt runoff. The other two stations (Jordan and Anoka) are not as influenced by road salt applications and therefore display a decreased concentration in the month of March when flow rates begin to increases due to snowmelt. At the outflow from the TCMA at Hastings, the highest chloride concentrations are observed in March.

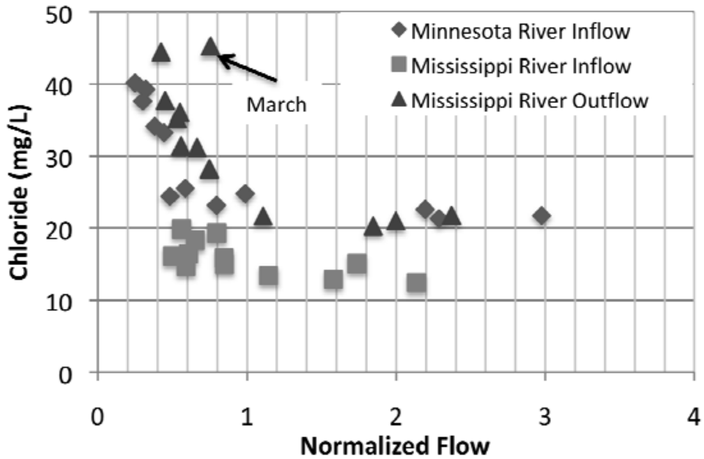


Figure 5: Monthly flow-weighted average chloride concentrations vs. normalized monthly average flow rates for the stations at Jordan, Anoka and Hastings.

Estimates can also be made for the total mass of chloride passing through these three points every month or every year. By using the flow data and the flow-weighted average concentrations the total fluxes of chloride entering the TCMA watershed in the two rivers, and the total fluxes exiting the TCMA through the rivers were calculated. The monthly flux values are displayed in Figure 6. The annual mass fluxes of chloride at the Minnesota and Mississippi River inflow were 119,000 and 116,000 metric tonnes/year respectively. The amount of chloride exiting the watershed at the Mississippi River outflow was found to be 355,000 metric tonnes/year.

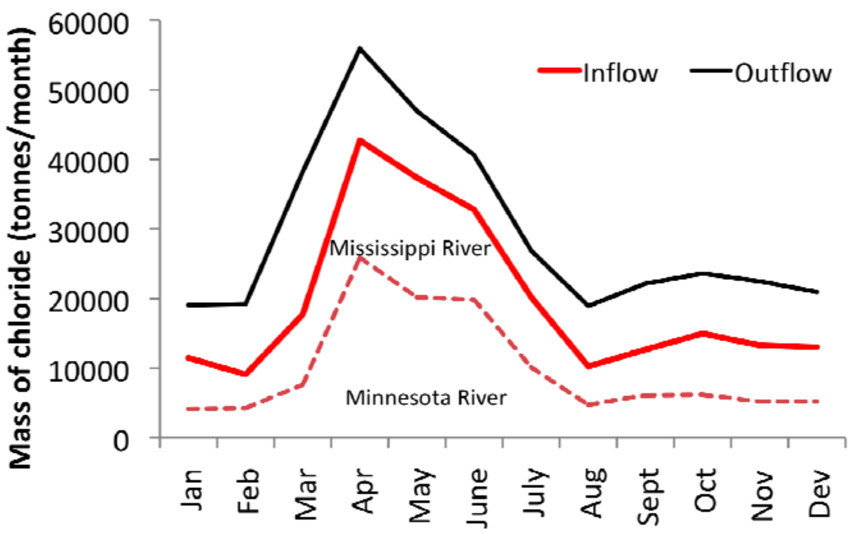


Figure 6: Mass of chloride entering and exiting watershed every month

4.3 Chloride concentrations in wastewater treatment plant (WWTP) effluents

Effluents from wastewater treatment plants (WWTP) are a significant source of chloride from domestic salt uses in foods and water softening, and industrial uses in manufacturing and food and fertilizer processing. The spent water is discharged through sanitary sewers to wastewater treatment plants, which do not remove Cl or Na, but instead discharge it into the Minnesota or Mississippi Rivers. Within the TCMA control volume used for the chloride budget, four major wastewater treatment plants discharge into the two major rivers. The concentrations of chloride exiting the plants along with the flow rates from the plants are shown in Figure 7. Annual averages are given in Table 1. The resulting mass of chloride that enters the river system from the WWTPs is estimated to be 87,000 metric tonnes/year.

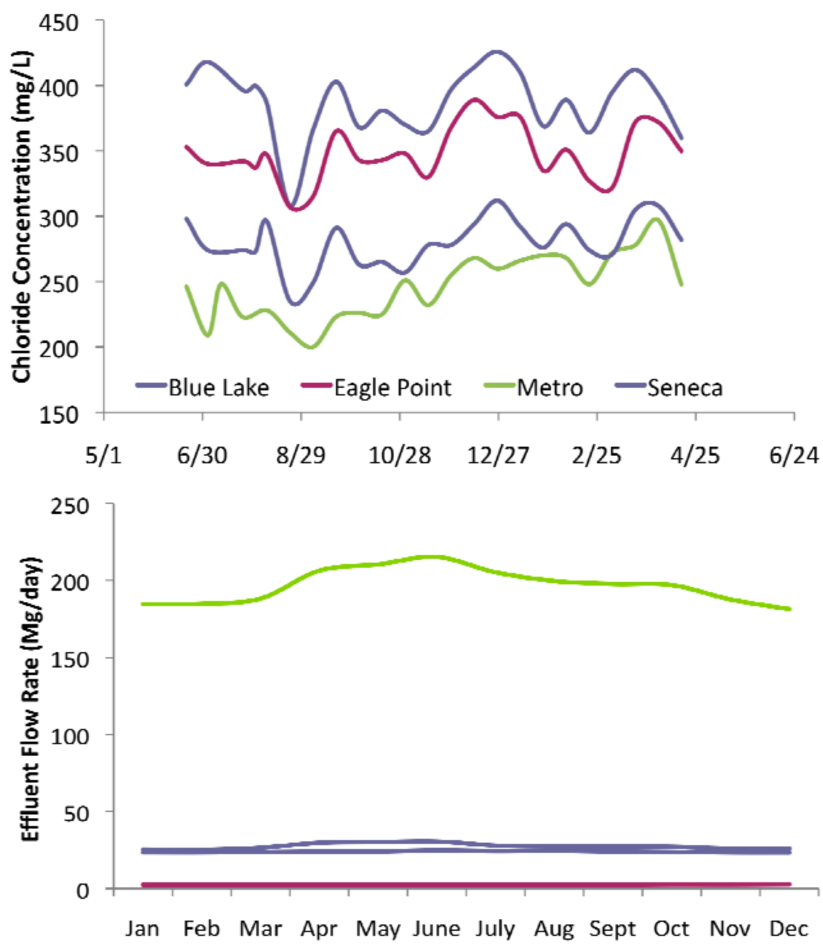


Figure 7: Measured chloride concentrations (top) in the four WWTP effluents, June 2007-May 2008 and monthly average flow rates (bottom).

Table 1: Average chloride concentrations and flow rates, and total amounts of NaCl in effluents from major WWTPs in the TCMA, 2007-2008..

	Chloride (mg/L)	Flow (m^3/s)	Mass (tons/year)
Blue Lake	387	1.18	14447
Eagle Point	348	0.18	1925
Metro	227	8.63	61829
Seneca	280	1.01	8904
		Total	87105

4.4 Chloride concentrations and fluxes from road salt applications

Another major chloride source in the watershed is road salt. The amount of salt applied to the roads in the watershed area was calculated. There are four main appliers of road salt in the TCMA: cities, counties, Mn/DOT and commercial/private appliers. The method used to obtain estimates of the amounts of NaCl applied by each of these entities was described in Section 2. Table 2 summarizes the results of this analysis. Overall 242,000 tonnes of NaCl was estimated to be applied in the watershed defined in Figure 1. This value is converted to just chloride by using the molar mass ratio of 0.6068 grams of chloride for every gram of NaCl. This translates to 148,000 metric tonnes of chloride applied as road salt to the watershed area.

Table 2: Amount of road salt (NaCl) applied in the Twin Cities Metropolitan Area watershed (Figure 1) for which the chloride budget is estimated.

	Total (tonnes)	Watershed (tonnes)
Cities	104,000	89,000
Counties	64,000	38,000
Mn/DOT	73,000	56,000
Commercial	76,000	58,000
Total	317,000	242,000

4.5 Chloride balance for the metropolitan watershed area

Individual chloride flux components presented in the previous sections can be combined in a chloride budget or balance (Equation 1) to estimate how much of the chloride applied to the TCMA watershed area is carried away by the Mississippi River and by air, and how much is staying behind in the TCMA watershed. Since industrial sources were determined to be included in the WWTP values, and fertilizers and natural deposition and airborne transport were found to be negligible these values can be set to zero.

A visual representation of the combined fluxes at both the inflow and outflow of the TCMA watershed can be seen in Figure 8. This figure displays the mean monthly amounts of chloride entering and exiting the TCMA watershed (tonnes/day for each month of the year). The data series for the amount entering was divided into three components: Mississippi River inflow, Minnesota River inflow and WWTP effluents to see how each of these sources contributes to the final chloride flux exiting the watershed. Since the effluent from the WWTPs is discharged directly into either the Mississippi or Minnesota River, it will exit the control volume in the Mississippi River and cannot stay behind in the TCMA watershed, except in a few wetlands and lakes connected to the two rivers and in aquifers, which receive recharge by seepage from the two rivers. One the other hand road salt travels with the snowmelt water and can accumulate in most lakes, wetlands and all of the groundwater aquifers. For this reason road salt amounts were not included as an inflow.

The time series in Figure 8 show that there is more outflow of chloride from the TCMA watershed than inflow from Jan. to May, and to a minor degree from Aug. to Nov. The differences are shown explicitly in Figure 9. Both of these periods can be linked to road salt applications. A need for road salt applications only arises in winter, typically from Dec. to Mar. It can be expected that snowmelt water reaches streams and rivers with some time lag relative to road salt applications. The pathways 1 and 2 have been mentioned earlier. The Jan. to May values in Figure 9 can be interpreted as the direct impact of snowmelt water routed through soils, systems of small streams and eventually the big rivers. Delays occur because winter is a low flow season, although the routing processes accelerate when snowmelt sets in. In the Aug. to Nov. period a more subtle process, namely the flushing of salinity from lakes and wetlands. Is at work, as documented in the seasonal lake salinity cycles (Novotny et al. 2008).

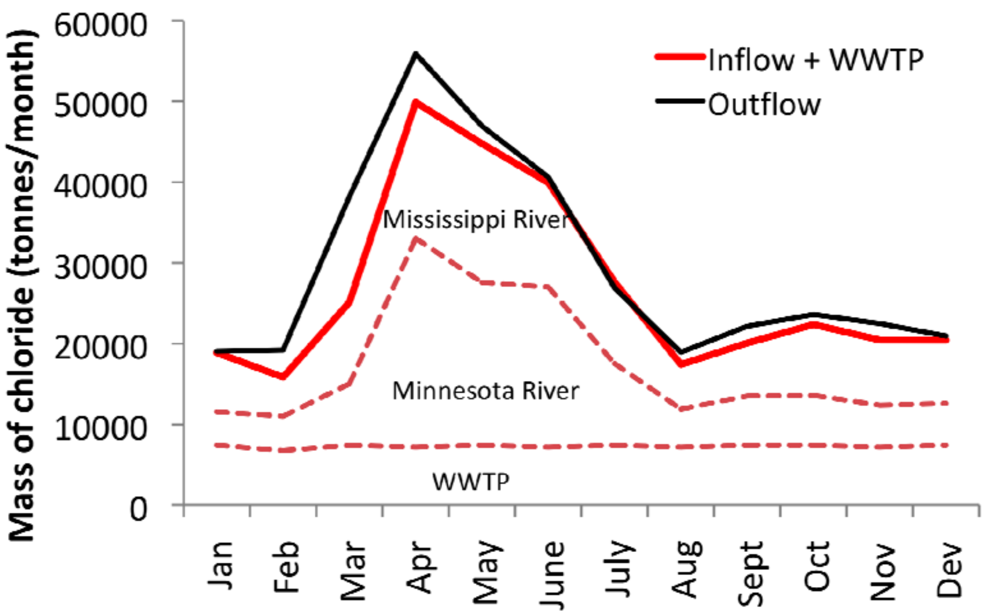


Figure 8: Monthly amounts of chloride coming into or exiting the TCMA watershed. Included in the inflow are the Mississippi River, the Minnesota River and WWTP effluents.

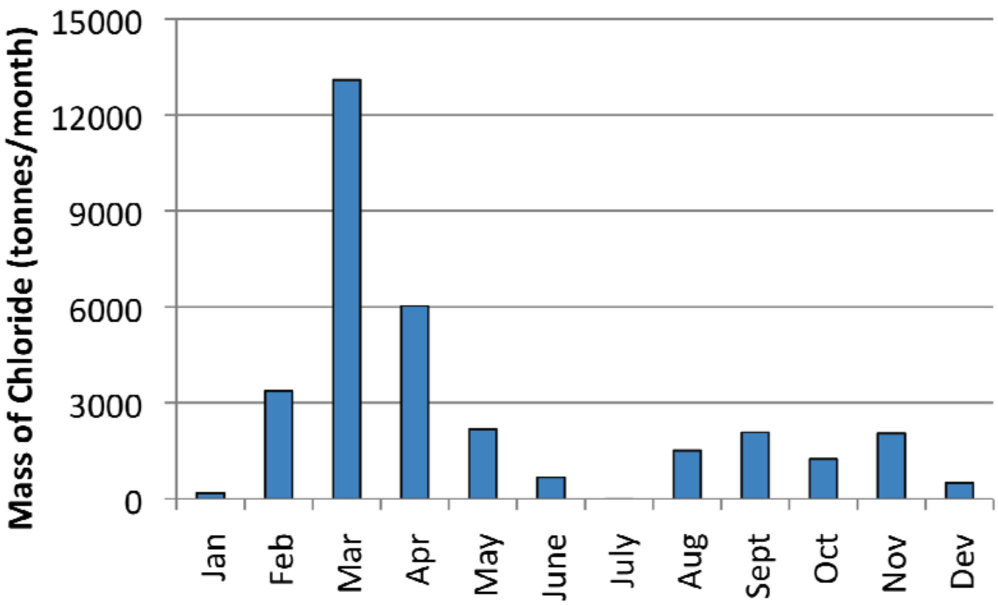


Figure 9: Difference between the monthly amounts of chloride exiting and entering the TCMA watershed by major rivers plus WWTP effluents.

The differences between the monthly (inflow +WWTP) and outflow (Figure 8) are given in Figure 9. The largest difference (about 13,000 tonnes of chloride/mo) occurs in March. By combining all of the months, the total annual difference is found to be 33,000 tonnes of chloride/year. Since road salt application is the only other major source of chloride considered in our chloride balance for the TCMA watershed, it has to be concluded that the extra 33,000 tonnes of chloride/year exiting the watershed are from road salt applications. This value can then be compared to the annual amount of road salt applications in the TCMA. It was estimated earlier that 148,000 tonnes of chloride/year are applied as road salt to the watershed area. If 33,000 tonnes of the 148,000 tonnes of chloride/year are carried away by the Mississippi River, 115,000 tonnes of chloride/year or 78% of the road salt applied stays behind in the TCMA watershed area. This is a crude estimate obtained with many assumptions, discussed earlier. It is nevertheless a result that should cause much concern.

The first question expressing this concern is “Where is this much salt staying?” Most likely in water bodies such as lakes, wetlands and groundwater. In another related study (Novotny et al. 2008) it was determined that 38 urban lakes in the TCMA have risen in salinity by about 1.7 percent/year in the last 20 years. If we assume that lakes and wetlands cover about 8.3% or 34,300 ha of the TCMA watershed (Bauer et al.) and that their average water depth is 5m, their water volume would be 1.715×10^9 m^3, With a median chloride concentration on the order of 87 mg/L obtained from 38 TCMA lakes in the last 7 years (Novotny et al. 2008), the annual increase in chloride content or storage in urban lakes and wetlands would account for only about 2,500 tonnes of chloride/year. This is less than 3% (2,500/115,000) of the chloride content that annually stays behind in the TCMA. Surface waters are therefore most likely not the main sink for road salt that stays behind.

Pathway (3) mentioned earlier in this report suggests that groundwater is another likely sink for road salt left behind in the TCMA. A very crude estimate of the total amount of pore space in the ground under and around the TCMA can be made with a surface area of 414,500 ha, a depth of 1km, and a very low overall effective porosity of 2%. The volume obtained is 80 km^3 or $8*10^{10}$ m^3. If this volume were saturated with water and 115,000 tonnes of chloride were added to it annually, the annual rise in concentration would be 1.43 mg/L. In other words, if deep groundwater were the sink of the chloride left behind in the watershed, a measurable increase in groundwater salinity should be detectable after several decades of road salt applications. We are therefore conducting a separate investigation of ground water salinity.

Another question expressing the concern is “When will the salt retention in the watershed and the resulting trend of water quality degradation stop? The accumulation of salt in the groundwater and surface waters will reach equilibrium when the rate of salt coming into the system is equal to the rate flushed out of the system. Due to the variability in the amount of salt applied to the roads each year and the variability in weather patterns, including rain fall amounts, the point of equilibrium can change. If road salt application rates continue at present levels, concentrations in surface water bodies are likely to increase further for some more years. Concentrations in aquifers are likely to continue to rise much longer because material residence times can be on the order of decades to millennia. Even in application rates are decreased the time lag due to residence time will prevent concentrations from decreasing soon.

4.6 Chloride budgets for small stream watersheds in the TCMA

To verify that a high percentage (estimated 78%) of road salt is staying in the TCMA, chloride balances were established for individual small stream watersheds in the TCMA. Examples of chloride concentration time series measured in grab samples from small streams in the TCMA are given in Figure 10. Substantial chloride concentration spikes occur in spring when snowmelt runoff is common. There is general agreement that the chloride spikes are related to roadsalt applications. It is also noteworthy that base flow chloride concentrations in the summer are significantly higher than zero in all three examples. This suggests that the shallow groundwater that feeds these small urban streams in summer is contaminated by road salt.

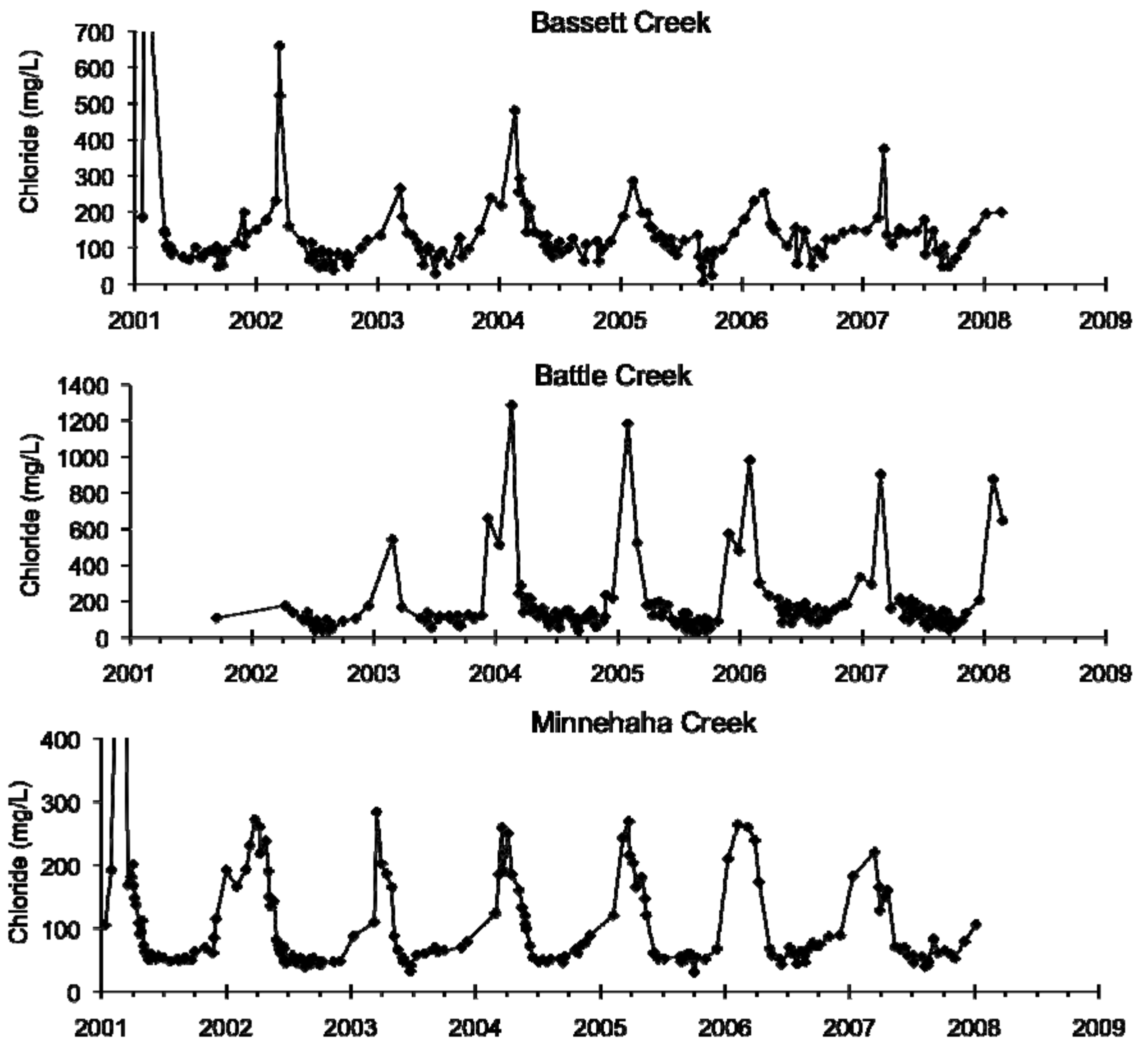


Figure 10: Samples of measured chloride concentration time series data from 3 of the 10 streams studied.

For ten small stream watersheds, located within the TCMA, chloride concentration and flow rate data were available. Measurements were taken at the mouth of each stream (outflow station). Table 3 gives information for each of the streams and Figure 11 displays the stream locations. The flow weighted mean annual chloride concentration in each stream was estimated using the reported flow data and grab sample concentration data from the Metropolitan Council. Average annual chloride concentrations in these streams ranged from 44 mg/L in the Credit River to 185 mg/L in Shingle Creek and annual average flow rates from 0.093 m^3/s in Riley Creek to 1.685 m^3/s in Minnehaha Creek. The percentage of the watershed covered by impervious surfaces and the total watershed area were also calculated (Table 3). Percent impervious surfaces were found using GIS data from the University of Minnesota Remote Sensing and Geospatial Analysis Laboratory (http://land.umn.edu/index.html).

Table 3: Stream watershed information.

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

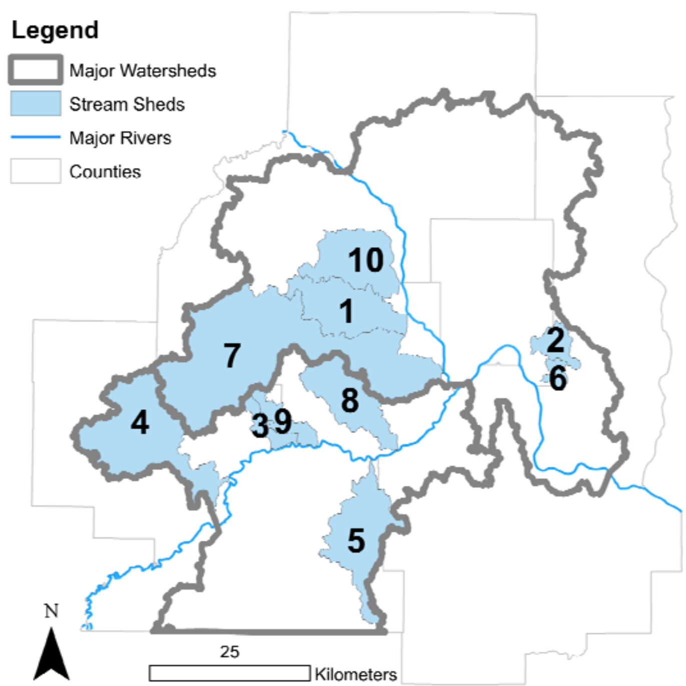


Figure 11: Location of small streams in the TCMA for which chloride budgets were determined.

The amount of road salt and of chloride applied annually was calculated by agency as outlined before. Details and results are given in Table 4. The amount of chloride applied ranged from 0.82 to 0.08 tonnes/ha per year, depending on road lengths.

Table 4: Road Salt applications rates for 10 stream watersheds in the TCMA

	City Salt (tonnes)	State Salt (tonnes)	County Salt (tonnes)	Comm. Salt (tonnes)	Total NaCl applied (tonnes)	Total Cl^- applied (tonnes)	Cl^- applied per area (tonnes/ha)
Bassett	5,013	4,112	1,012	3,201	13,338	8,093	0.73
Battle Creek	1,658	970	420	962	4,010	2,433	0.82
Bluff Creek	221	362	76	208	868	527	0.23
Carver Creek	571	1,041	620	705	2,938	1,783	0.08
Credit River	1,050	169	789	634	2,643	1,604	0.12
Fish Creek	412	262	156	262	1,092	663	0.50
Minnehaha Creek	13,204	5,349	3,746	7,042	29,340	17,804	0.39
Nine Mile Creek	2,762	2,718	882	2,009	8,370	5,079	0.51
Riley Creek	349	366	170	279	1,164	706	0.21
Shingle Creek	4,967	2,118	1,668	2,764	11,518	6,989	0.65
					Total	45,681	

The total mass of chloride exiting the watershed was calculated by multiplying the annual flow rate by the annual average chloride concentrations. Two calculations were made. The first was made without any background chloride concentration, the second used an estimated chloride concentration in groundwater as background. The background estimation was estimated by fitting a straight line to a plot of average chloride concentration in the streams vs. the amount of chloride applied per ha per year. Extrapolation gives a background concentration of 18.7 mg/L when the chloride application rate is set to zero (R^2 0.79). While this number is much higher then concentrations observed in the more pristine St. Croix River is does match concentrations observed in the Mississippi River before it enters the TCMA.

The ratio (percentages) of the amount of chloride staying in a watershed to the amount of road salt applied in the watershed was calculated to be from 36 to 83 % (Table 5). The total amount of chloride applied in the ten watersheds was about 46,000 tonnes per year, and the total amount of chloride leaving with the ten streams, without a background concentration, is about 16,000 tonnes per year or 35 %. The road salt staying in the watershed was therefore, on average, 65% of the total amount of salt applied to the watershed. Using an estimated18.6 mg/L as background concentration, the amount leaving was lowered to about 12,000 mg/L meaning 73% of the salt being applied is staying in the watershed each year. Both of these values are lower than the 78% value obtained for the entire TCMA watershed, but they are comparable.

Table 5: Annual amount of chloride exiting each stream watershed in metric tones/year and as a percentage of the road salt applied. Annual amount retained in the watershed is also given. Results calculated with no background concentration and a background concentration of 18.6 mg/L in each stream.

	Mass No background (tonnes/year)	Percent Cl^- exported	Percent Cl^- retained	Mass background (tonnes/year)	Percent Cl^- exported	Percent Cl^- retained
Bassett	4196	52	48	3648	45	55
Battle Creek	1024	42	58	896	37	63
Bluff Creek	214	41	59	153	29	71
Carver Creek	1140	64	36	563	32	68
Credit River	689	43	57	395	25	75
Fish Creek	294	44	56	240	36	64
Minnehaha Creek	3605	20	80	2617	15	85
Nine Mile Creek	1647	32	68	1234	24	76
Riley Creek	187	27	73	120	17	83
Shingle Creek	2881	41	59	2584	37	63
Totals	15878	35	65	12451	27	73

5. DISCUSSION

Previous investigations have shown that chloride concentrations in urban aquatic environments in northern climate regions are elevated or increasing, but few studies have attempted to quantify where road salt goes after it has fulfilled its purpose of de-icing roads for safer driving.

Surface waters receive contaminated water from contaminated sources by surface or groundwater flow (Ramakrishna and Viraraghavan 2005). Groundwater can be contaminated with chloride by infiltration; the major factors influencing this transport include soil permeability, vegetation cover, topography, and roadside drainage techniques (Jones and Jeffrey 1992).

Salinity increases in shallow groundwater aquifers have been detected in base flow concentrations of urban streams (Marsalek, 2003). Baseline salinity is increasing in the northeastern part of the United States. During the winter observed chloride concentrations in urban streams are as high as 25% of the concentration in seawater, and 100 times greater than concentrations in non-impacted forested streams during the summer (Kaushal et al. 2005). In the Mohawk River, New York, sodium and chloride concentrations increased by 130 and 243%, respectively, between 1952 and 1998 while other major ions remained the same (Godwin et al. 2003). In the Greater Toronto Area, Ontario, Canada, base flow chloride concentrations increased from 150 mg/L to 250 mg/L between 1972 and 1995 (Bowen and Hinton 1998). In Sweden, regional increases in chloride were observed, and road salt was accountable for more than half of the total chloride load in the Sagan River basin (Thunquist 2004). In another study in Sweden, both the average and maximum chloride concentrations in five catchments were positively correlated with the cumulative use of de-icing salts (Lofgren 2001).

In the TCMA similar observations have been made. The Twin Cities area is covered with over 950 lakes and wetlands. Streams pass through these water bodies before the confluence with two major rivers, the Mississippi and the Minnesota Rivers. This allows for the accumulation of roadsalt dissolved in snowmelt runoff in lakes. Chloride concentrations have been observed to be increasing in TCMA lakes over the past 22 years, following a pattern similar to the amount of road salt the state has purchased (Novotny et al., 2008). Another sink for chlorides in the TCMA is groundwater. In our study chloride concentrations were found to increase in the major rivers as they travel through the Twin Cities Metropolitan Area (Figure 3). Road salt is not the only reason for the increased chloride concentrations. WWTP located along the rivers provide discharges with concentrations over 200 mg/L contributing to the elevated levels of chloride as the rivers travel through the metropolitan area.

As the flow rates in the two major rivers increase the concentrations of chloride in the rivers generally decreases (Figure 4). This can be seen in the Minnesota River inflow to the TCMA at Jordan and the Mississippi River outflow at Hastings. The river flow rates increase during the rainy months of the year providing dilution of chloride concentrations. During the winter and sometimes in late summer/fall river flow rates are lower resulting in elevated chloride concentrations. In the Mississippi River at Hastings the river flow during the late summer/fall is low enough that the metro wastewater treatment plant can have a much larger influence on the chloride concentrations then in the spring and early summer. Information in Figure 5 suggests that from August to February the WWTPs provide around 1/3 to 1/4 of the mass of chloride passing through the in the Mississippi at Hastings; in April the chloride contribution of the WWTPs is decreased to about 1/10. Since the chloride concentrations in WWTP effluents are above 200 mg/L, this effluent can influence the concentrations in the Mississippi River to a much larger extent than during low flow months.

The pattern of higher flow and synoptic lower chloride concentrations is broken only during the month of March in the Mississippi River at Hastings. Located downstream of the TCMA, the chloride concentrations are higher in March than in any other month, but March also has the 5th highest average flow rate. In March the difference between the amount of chloride leaving the TCMA watershed and the amount coming in (including WWTP effluents) is largest. This is attributed to the road salt applications. The month of March is the period when air temperatures start to rise above freezing. This results in the melting of the snowpack and the transport of salt in the snowmelt water to the major rivers producing higher chloride concentrations even though much water is present for dilution.

In groundwater chloride concentrations as high as 330 mg/L have been measured in the northwestern portion of the TCMA; median values have been 46 mg/L (Andrews et al. 1997), much higher then the median value of 5 mg/L found in wells in undeveloped areas of Minnesota and Wisconsin (Stark et al. 1996). Elevated concentrations were found in wells under older urban developments and the highest in a well immediately down gradient of a major highway (Andrews et al. 1997). All studies show that salinity of water is increasing in areas where salt is applied to roads.

Overall, many indicators point towards the retention of road salt within a watershed. Rising concentrations of chloride in urban lakes, and increasing groundwater concentrations point towards the accumulation of salt in a watershed. In this study it was determined that about 2/3 of the road salt applied in the Twin Cities Metropolitan area is staying in the watershed. If a maximum of 78% of road salt applied is retained in the TCMA watershed, 115,000 tonnes/year of chloride are accumulating in the lakes and groundwater of the TCMA. Since chloride is transported as a solute in the water flow, other urban areas will show different results based on their hydrology.

Other studies have shown the retention of road salt in a watershed. Concentrations in streams have been observed to increase even though road salt applications have remained constant in a forested watershed in southeastern New York pointing to a lag effect caused by the accumulation of salt in the soil and groundwater (Kelly et al. 2008). In a catchment of the Greater Toronto area, Canada, it was found that 45% of the road salt applied inside the watershed was transported out of the watershed while 55% was retained in shallow aquifers; a steady-state concentration of these aquifers was projected to reach as high as 426 mg/L (Howard and Haynes 1993). Shallow aquifers throughout much of the greater Toronto have been seriously compromised due to road salt deicing practices (Howard and Maier 2007). Likewise a study in Helsinki, Finland found that 35-50% of the de-icing salt applied to the roads passed through natural streams into the sea (Ruth 2003). In Chicago a much smaller fraction of the applied road salt was found to be retained in the watershed. 55 to 72% of the salt applied to an urban watershed exited the system in the streamflow.

The accumulation of salt in a watershed may not be detected right away since large amounts can be stored in the subsurface before reaching a well. This also implies that if road salt applications were completely stopped, chloride concentrations in wells may continue to increase until the solute migration is completed (Bester et al. 2006).

Lakes and wetlands in the TCMA retain salt from road salt applications for some time, but get flushed in due time. Seepage from lakes, wetlands and streams as well as infiltration from the soil surface conveys salty water into groundwater aquifers. Some stormwater management practices may be adding to conveyance of salt from road salt applications into the groundwater. Stormwater management practices that use detention/retention ponds, infiltration basins, rain gardens and other infiltration-enhancing procedures may be adding to the accumulation of salt in the watershed by promoting retention of surface runoff and/or infiltration into the groundwater.

6. SUMMARY AND CONCLUSIONS

Road salt is used for the de-icing of winter roads to increase public safety. It is important to understand how its application influences the environment.

Chloride concentrations were found to increase in the Minnesota and Mississippi Rivers as they travel through the Twin Cities Metropolitan Area (TCMA). Road salt is not the only source for the increased chloride concentrations. Wastewater treatment plants provide effluents with chloride concentrations over 200 mg/L.

A salt balance for the entire TCMA and separate salt balances for 10 stream watersheds located inside the TCMA watershed reveal that about 2/3 of the road salt applied in the TCMA is not carried away in solution in the Mississippi River. According to a chloride budget 235,000 metric tonnes of chloride are transported annually into the TCMA watershed annually by the Minnesota River at Jordan and the Mississippi Rivers at Anoka, while 355,000 tonnes are leaving the TCMA by the Mississippi River at Hastings. Of the 120,000 metric tonnes of chloride added in the TCMA, approximately 87,000 tonnes come from wastewater treatment plants and 33,000 tonnes from other chloride sources, especially road salt. A total of 148,000 tonnes of chloride are applied to the roads in the TCMA watershed every year. With 33,000 tonnes of chloride leaving the watershed by the Mississippi River, 115,000 tonnes of chloride or 78% of the amount applied in road salt are staying in the watershed or are carried away by other mechanisms. Chloride budgets for smaller stream watersheds in the TCMA indicated that 65 to 73% of the road salts applied were staying in the watersheds.

The main conclusion of the chloride budget analysis of the Twin Cities Metropolitan Area is that a substantial portion of the road salt applied is not leaving the area. With 115,000 metric tonnes of chloride accumulating in the metropolitan area every year, continued increases in chloride concentrations in groundwater, lakes and wetlands are to be expected. Road salt application practices and mitigation measures for salinity reduction in urban water bodies need to be considered.

Acknowledgments

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