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Predictors of Summer Chloride Concentrations in Urban Aquatic Ecosystems

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Abstract

Urban aquatic ecosystems are highly threatened by excess concentrations of chloride (Cl⁻), which can negatively impact the biodiversity and functioning of aquatic ecosystems. High Cl⁻ concentrations in most northern cities come primarily from road salt use for de-icing, in the form of NaCl. Specific pathways of runoff and hydrology of waterbodies will regulate Cl⁻ concentrations in the months after the snowmelt season. This study attempted to understand the hydrologic controls on Cl⁻ concentrations and identify how the hydrology of urban ecosystems may impact exposure to chloride in streams. To accomplish this, stream sites around the Twin Cities Metro Area in Minnesota were sampled for Cl⁻ as well as several biogeochemical tracers to indicate groundwater inputs, including oxygen isotope ratios of water (δ¹⁸O) and dissolved inorganic carbon (DIC), and landcover information, including road density and percentage developed of the various site watersheds. Trends between Cl⁻ and the landcover showed a positive linear relationship, signifying how winter road salt application can have an ongoing effect on ecosystems in the more productive summer months. There was a surprising lack of correlation between the groundwater tracers and Cl⁻, possibly explained by the unusual water year Minnesota had faced at the time of sampling, which likely diminished the correlation between water source and Cl⁻ concentration. This study highlights the variety of factors that shape seasonal variations in Cl⁻ and underscores the need to understand these factors to inform future environmental management and monitoring.
Introduction

Almost every northern urban area in the United States faces problems with chloride concentration and pollution in waterways (Mullaney et al., 2009). Excess concentrations of chloride in the environment can negatively impact diversity within aquatic ecosystems, reduce drinking water quality, and increase corrosivity of surface water (Richburg et al., 2001; Stets et al., 2018). High chloride concentrations in most northern cities come primarily from road salt used for de-icing, in the form of NaCl, but can also arrive in the environment by way of wastewater and fertilizer (Overbo et al., 2021). Road salt application is highly concentrated in winter months and is primarily applied to impervious surfaces that readily shed water, such as roads, but some proportion infiltrates to groundwater.

Even minor concentrations of chloride can be harmful to aquatic life. Many studies have found both direct effects of chloride on taxa and pronounced indirect effects on food web structure and interactions, even at low levels of chloride (Collins & Russell, 2009; Sanzo & Hecnar, 2006; Van Meter et al., 2011). A Toronto study found significant changes in the benthic macroinvertebrate community with chloride levels as low as 50 to 90 mg/L (Wallace & Biastoch, 2016). This is much lower than most official water quality standards for chloride. In Minnesota, the Chronic Standard, meaning the highest concentration in water or fish tissue for which aquatic life, wildlife, or humans can be exposed to long-term without causing chronic toxicity is set at 230 mg/L for both cold and warm water (Minnesota Pollution Control Agency, 2023). The Canadian government holds a slightly higher standard, setting the guideline for protection of aquatic life at 120 mg/L Cl⁻ long term and 640 mg/L for short-term exposure (CCME, 2024). These standards are still much higher than the concentration of chloride that has been shown to impact these aquatic ecosystems.
Surface runoff is largely responsible for the chloride carried into the environment during winters, while groundwater is the major source during summers. Therefore, specific pathways of runoff to streams, whether surface runoff, shallow soils (quickflow), or groundwater, will regulate chloride concentrations in the months after the spring runoff season, and understanding these hydrologic controls is critical to predicting the effects of chloride on the environment.

Much research has investigated the effects of chloride (Hintz & Relyea, 2019; Novotny & Stefan, 2012), but still more needs to be done to conceptualize how and in what quantities chloride enters the environment, and how that changes over the course of the year.

A recent study of sources of chloride in the environment in Minnesota (Overbo et al., 2021) shows that road salt is the highest source of chloride in the environment. The Minnesota Department of Transportation found accumulation and transport of road salt through the Lake McCarrons Watershed in the Minneapolis-St. Paul area (Herb et al., 2017). Recent work has also documented impacts of summer chloride concentrations on aquatic species in a different northern urban area - Toronto, Canada (Lawson & Jackson, 2021). Here, I expand on that research, using biogeochemical tracers and geospatial analysis to understand the factors that influence summer chloride concentrations in urban aquatic ecosystems. Biogeochemical tracers are used in this study to identify groundwater sources. The two tracers used in this study are dissolved inorganic carbon (DIC) and oxygen isotope ratios of water (δ¹⁸O). DIC is generally found in higher concentrations in ground water than surface water because it is a weathering product (Chmiel et al., 2015; Li et al., 2022; Worrall & Lancaster, 2005). δ¹⁸O of water is more negative in groundwater because snowmelt is a major source of groundwater, and snow tends to have a lighter isotopic signature (O’Driscoll et al., 2005; Reddy et al., 2006; Sharp, 2017).
This project aims to fill gaps in current knowledge surrounding the controls of chloride concentrations during summers, and how the hydrology of urban ecosystems may impact their exposure to chloride. Specifically, I will test the hypothesis that (1) summer chloride is higher in urban areas because of road salt application, and (2) catchments with higher groundwater inputs will have disproportionately higher chloride levels during summer baseflow. I predict that DIC will be higher and δ¹⁸O lower where chloride is higher because these factors coincide with chloride infiltration in groundwater.

**Methods**

*Study Area*

![Figure 1. Map of the seven-county Twin Cities Metro Area, with site locations and mappable watersheds labeled and streams and lakes visualized.](image)
The Twin Cities Metro Area (TCMA) encompasses an area of nearly 3,000 square miles, with 7 counties and a population of over 3 million (Minnesota Pollution Control Agency, 2022) (Figure 1). Yearly precipitation is 31.62 inches, on average, with average annual temperatures of 55.4°F (Minnesota DNR, 2020). The center of the region is largely urbanized, transitioning into agriculture and pasture towards the edges of the region. The area has a wealth of water, with an estimated 950 lakes and three major river systems: the St. Croix, the Minnesota, and the Mississippi rivers (Thrive MSP, 2014). Groundwater from three main aquifers in the region is also a crucial resource, providing approximately two-thirds of the water in the region: 1.12 million m³ d⁻¹ out of a total 1.68 million m³ d⁻¹ of ground and surface water use (Peterson et al., 2012).

At the time of sampling in July of 2023, the area was experiencing a very unusual water year. Normal winter precipitation (from a 1991-2020 average) is 4.61 inches (Dec-March), and 16.89 inches in summer (May-Aug). In 2023, winter precipitation was 9.17 inches – double the normal precipitation. In contrast, the summer was unusually dry – only 7.41 inches of precipitation in summer 2023, less than half the usual amount (Minnesota DNR, 2020, 2024; National Climate Data Center, n.d.). The heavy precipitation in the winter meant a large snowpack and associated salt application, but one that had melted off quickly and gave way to a hot, dry summer.
**Study Design**

I sampled 36 stream sites chosen to represent a diversity of natural through urban stream types and locations across the Twin Cities area. All sites were sampled between July 11th and 27th, 2023, with baseflow conditions at the time of sampling. Sites were scouted with Google Maps ahead of time, but upon arrival some sites could not be accessed safely or without crossing into private land, making the site choosing process slightly more difficult than anticipated. What’s more, despite the dry summer in Minneapolis the few storms that rolled through happened to coincide with sampling days, which meant I had to change the location or reschedule a few days, until streamflow data for the area showed a return to normal conditions, to ensure that samples were truly taken at baseflow conditions.

**Field Measurements**

At each site I used a Hach HQ40d conductivity probe to measure the conductivity and temperature of the water. The conductivity measurement gave a rough idea of the chloride concentration at each site. We collected three samples with two replicates each, for a total of six samples at each site. Four samples were collected in polyethylene 20 mL scintillation vials by filtering water through 0.7 µm GF/F Whatman syringe filters, leaving headspace in the vial. These samples were designated for dissolved inorganic carbon (DIC) and ion analysis, with two replicates per analysis type. The other two samples, designated for water isotope analysis.
(primarily $\delta^{18}$O), were collected in glass 20 mL scintillation vials with cone-lined caps. These samples were not filtered, and no headspace was left in the vials. These three analyses primarily served to identify chloride concentrations and different compounds (DIC and $\delta^{18}$O) that serve as biogeochemical tracers to indicate whether groundwater or surface water dominated in each site. As summer groundwater is more likely to reflect winter inputs of chloride, the tracers were intended to explain the variation in chloride concentrations between sites. Once we transported the samples back to the lab, the water isotope and DIC samples were refrigerated, and the ion samples were frozen until analysis could be performed.

**Analysis**

A Thermo Scientific Integration High Pressure Ion Chromatography system was used to quantify chloride, fluoride, bromide, nitrate, nitrite, sulfate, and phosphate by ion chromatography. This analysis took place in the Research Analytical Laboratory at the University of Minnesota. The water isotope samples were analyzed for ratios of oxygen and hydrogen isotopes using a Picarro L-2130-i Isotope and Gas Concentration Analyzer at the Large Lakes Observatory at the University of Minnesota Duluth. DIC concentrations were determined in the lab of Dr. Jacques Finlay at the University of Minnesota with a Shimadzu TOC-L.

For nineteen of the sites where watershed boundaries could be reliably defined, I used Model My Watershed (a website developed by Stroud Water Research Center) to determine watershed area and summarize land use within each watershed. I then used the watershed boundaries from Model My Watershed in ArcGIS Pro to determine road density using a raster dataset from the MSP LTER depicting road surface area in the TCMA as 1-meter rasters (Marek-Spartz, 2023). I imported the watershed layers as shapefiles from Model My Watershed, clipped
the road layers to the individual watersheds, and summarized the sum of the pixels within each watershed. Since each pixel represented 1m$^2$ on the ground, the sum of pixels within the watershed boundary represents the total area of road surface within each watershed in m$^2$. From there, I converted those values to km$^2$ and divided by the total area of the watershed to get the final road density (road km$^2$/watershed km$^2$) within each watershed.

I used R Studio to plot chloride concentrations against the biogeochemical tracers, as well as the percentage of the watershed that was characterized as “developed” land use (excluding “open developed,” which included parks and golf courses), and road density. I then ran a linear regression analysis to determine the relationship between chloride concentrations and each of the four factors. I also compared chloride values amongst groundwater dominated and surface water dominated sites and created a correlation matrix to analyze the relationship between the variables.

**Results**

*Landcover Indicators*

Figure 3. Chloride against percent developed within the watershed (left) and road density (right, as road area per watershed area). Sites are colored based on $\delta^{18}$O (O18) value, with purple indicating more groundwater dominate sites (more negative $\delta^{18}$O) and orange indicating more surface water dominated (more positive $\delta^{18}$O values).
Both land use indicators had a positive relationship with chloride concentrations, although the percent developed of the watershed certainly had a stronger relationship (Figure 3). For every increase in the percentage of developed land within the watershed, chloride concentrations were shown to increase by 4.3 mg/L ($R^2 = 0.38$, $p = 0.0053$). Road density was not a significant predictor of chloride ($R^2 = 0.053$, $p = 0.343$). However, there was one significant outlier in the data, Bridal Veil Falls (Cl = 657.8 mg/L). When that outlier was removed, both land use indicators had much stronger relationships with chloride concentration. Chloride concentrations increased by 2.48 mg/L without the outlier included for every percent increase in developed land in the watershed ($R^2 = 0.51$, $p = 0.00089$). Road density now had a significant relationship with chloride, with an 8.2 mg/L increase in Cl concentration for every 0.01 increase in road area ($R^2 = 0.31$, $p = 0.016$).

Groundwater Indicators

![Figure 4. Oxygen isotope ratios (δ¹⁸O) and dissolved inorganic carbon (DIC) at each site against chloride concentrations. δ¹⁸O values are generally higher in surface water supplied by summer runoff and DIC is normally found in higher concentrations in groundwater.](image)

The relationship between the biogeochemical tracers and chloride were much weaker than the landcover indicators and showed much fine scale heterogeneity (Figure 4). Oxygen
isotope ratios ($\delta^{18}O$) showed an inverse relationship with chloride as predicted, but the trend was not significant ($R^2 = 0.085, p = 0.0996$). DIC trends with Cl$^-$ showed the opposite of the predicted behavior, with lower Cl$^-$ values at higher DIC, and this relationship exhibited even less significance ($R^2 = 0.0063, p = 0.66$). Overall, both groundwater indicators showed no significant relationship to Cl$^-$ concentrations, with a lot of variance within the data, and a few outliers.

*Residuals Analysis*

![Residual analysis](image)

**Figure 5.** Residuals for the chloride-landcover metrics relationship plotted against the groundwater metrics. Percentage developed for the watershed and chloride residuals on the left (orange trendline) and road density and chloride residuals on the right (blue trendline). Residuals are plotted against DIC (top) and $\delta^{18}O$ (bottom).

Residual analysis showed little pattern within the data (Figure 5). Neither type of residual (chloride values with percentage developed and road density of the watershed, respectively) showed any sort of real pattern with either of the two-groundwater metrics, indicating hydrology is not responsible for the scatter in the chloride versus land metric relationship.
Comparison to Past Data

Figure 6. $\delta^{18}$O values versus chloride concentrations from 2012 data provided by Dr. Jacques Finlay (pink), and data from summer 2023 collection period (blue). Light red line represents chronic standards concentration levels for chloride in Minnesota and dark red line represents Canadian long-term chloride concentration standard for protection of aquatic life.

Comparing the data collected in this project to data collected in 2012 as part of other projects shows a significant difference in the data (Figure 6). Based on precipitation data, 2012 was much more of a “normal” water year than 2023 (Table 1). The 2012 data shows decreased $\delta^{18}$O values where chloride values are higher, with a logarithmic decrease in $\delta^{18}$O values as chloride concentrations increase. The data from the summer of 2023, on the other hand, show more sites with both low $\delta^{18}$O values and low chloride values, as well as more moderate chloride concentrations (~200 mg/L) at sites with relatively high $\delta^{18}$O values of -6 or -7‰. This results in a slight downward slope to the

<table>
<thead>
<tr>
<th>Precipitation Totals (in)</th>
<th>2012</th>
<th>2023</th>
<th>Normals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter (December-March)</td>
<td>4.46</td>
<td>9.17</td>
<td>4.61</td>
</tr>
<tr>
<td>Summer (May - August)</td>
<td>18.19</td>
<td>7.41</td>
<td>16.89</td>
</tr>
</tbody>
</table>

Table 1. Precipitation data in inches from Minneapolis in 2012 and 2023 compared to the 30-year Normals (1991-2020). Data from Minnesota DNR, 2020.
data, rather than a logarithmically decreasing trend. What’s more, more of the 2023 sites seem to have higher chloride values than previous years, with many more approaching the 230 mg/L “Chronic Standards” concentration level.

Variable Correlation

The correlation matrix in [Figure 7](#) shows the relationship between the variables on a scale from -1 to 1, with -1 (purple) indicating perfect negative correlation and 1 (red) indicating perfect positive correlation. Chloride was weakly positively correlated with both sulfate and nitrate at 0.31 and 0.29, respectively, weakly negatively correlated with $\delta^{18}O$ at -0.29, and had almost no correlation with DIC or phosphate. Amongst the other variables, DIC and $\delta^{18}O$ had the highest level of correlation, showing a moderate negative correlation of -0.54.

![Correlation Matrix](#)

**Figure 7.** Correlation between the variables, visualized as a heat map with purple indicative of negative correlation and red indicative of positive correlation.
Discussion

Summer chloride concentrations within the urban aquatic ecosystem depended on a complex interplay of factors, shedding light on the intricate dynamics of chloride transport within these environments. As predicted, urban areas had higher chloride concentrations. Both landcover metrics, watershed developed area and road density, showed significant positive relationships with chloride, reflecting that primary control of urban landcover on chloride applications through road salt and subsequently chloride concentrations in aquatic ecosystems (Figure 3). This finding is consistent with other studies showing positive correlation between stream chloride concentration and chloride applied per watershed, as well as impervious surfaces within the watershed (Kaushal et al., 2005; Novotny et al., 2009).

While landcover metrics act as a primary control on chloride concentrations, flow paths should act as a secondary control dictating the concentration into summer months (Weatherson et al., 2024). The predicted positive relationship between indicators of groundwater and summer chloride concentrations was not reflected in this data, however. The biogeochemical tracers used to determine groundwater presence appeared to work as intended - the negative correlation between DIC and δ¹⁸O shown in the correlation matric (Figure 7) occurs because DIC is normally higher in groundwater, while δ¹⁸O is higher in surface water. Sites with higher DIC should have lower δ¹⁸O and vice versa, because the two variables are indicative of opposite things. The high negative correlation found between DIC and δ¹⁸O confirms that the two variables work as indicators of groundwater.

Given the role of groundwater in retaining chloride concentrations, the lack of correlation between groundwater presence and chloride concentration is surprising (Cooper et al., 2014; Novotny et al., 2009). Groundwater was simply not a significant driver of chloride
concentrations in the 2023 sampling year. The residuals analysis (Figure 5) also left no indication of a role for groundwater. The lack of any pattern or trend within the relationship between the chloride and landcover metrics residuals and the groundwater indicators suggests that something else is responsible for the variance in the relationship between summer Cl\(^-\) and landcover metrics.

When comparing the 2023 relationship between \(\delta^{18}O\) and chloride to the more “normal” data from 2012, the effects of the unusual water year in 2023 stand out. The logarithmic trend in the previous year’s data, with decreased \(\delta^{18}O\) (meaning more groundwater dominate sites) as chloride increases suggests that chloride is mobilized via groundwater in a normal summer. There is less of a surface water influence in the 2023 data, with significantly fewer sites with \(\delta^{18}O\) less than -6‰, but the data also shows increase in sites with higher chloride and less negative \(\delta^{18}O\) values compared to 2012. The dry spring and summer in the 2023 year may explain this discrepancy – the lack of storm runoff to flush the surface water system likely limited the difference in chloride concentrations between surface water and groundwater dominant sites. The storms experienced over the summer that interrupted sampling days might have also influenced the surface water inputs – while samples were only taken once hydrographs indicated streams had returned to baseflow, new surface water inputs to the system after months of no storms could have had some effect on the data.

Another notable difference between the 2012 and 2023 data lies within the shift of the chloride concentration towards the 230 mg/L threshold defining the Chronic Standard for chloride in Minnesota. This is the highest water concentration or fish tissue concentration of chloride to which aquatic life, humans, or wildlife can be exposed indefinitely without causing chronic toxicity. There are a similar number of sites above that standard in both datasets, but in
the 2023 data many more of the sites, particularly those shown by the higher $\delta^{18}$O values to be more surface water dominated, have moved much closer to that standard line. The lack of storm runoff as a result of the dry season seems to have caused these surface-water dominant sites to retain much higher chloride concentrations, which is especially dangerous to the aquatic ecosystem in the more ecologically productive summer months (Arnott et al., 2020; Tornabene et al., 2020).

Water years like the one Minnesota experienced prior to this sampling period will continue to occur and may only get more frequent as anthropogenic climate change continues (Easterling et al., 2017; Fischer & Knutti, 2015). This study suggests that this may be harmful to aquatic ecosystems, as chloride from winter road salt applications builds up in groundwater and is only slowly flushed out of the system in late spring and summer baseflow. Chloride concentrations collected in this study are similar to summer Cl$^-$ found in previous studies of the TCMA (Novotny et al., 2009), Toronto, Canada (Lawson & Jackson, 2021), and France (Szklarek et al., 2022). More work is needed to continue Cl measurements into the future and gain a greater understanding of seasonal drivers of chloride concentrations in urban ecosystems.

**Conclusion**

Ultimately, these results are slightly contrary to the initial hypothesis, which proposed that urbanization is a primary control of chloride concentrations because of road salt applications and that groundwater flow and retention serves as a secondary control to increase chloride concentrations in the summer. The relationship between the watershed characteristics and chloride concentrations at the sites underscores the impact of land cover on chloride concentrations during the summer. While flow paths may provide a secondary control on
chloride, this study shows that, at least in the conditions present in 2023, groundwater does not have the control over chloride concentrations expected. The possible interaction between sources of chloride in winter and drought conditions in summer underscores the need to understand pathways of chloride in the ecosystem as the climate changes. Water years like the one Minnesota experienced prior to this sampling period will continue to occur and may only get more frequent as anthropogenic climate change continues. This study suggests that certain climate combinations may be harmful to aquatic ecosystems. More work is needed to continue this project on into the future and gain a greater understanding of seasonal drivers of chloride concentrations in urban ecosystems. Many factors beyond direct road salt application and road runoff play pivotal roles in shaping these seasonal variations, and the ability to understand those factors is crucial to future environmental management and monitoring. Reducing chloride in aquatic ecosystems by road salt management, such as switching to deicers with less impact on ecosystems (Terry et al., 2020) or road salt use reduction techniques such as anti-icing and live-edge snowplows (Hintz et al., 2022), is essential in protecting vulnerable aquatic environments and reducing contamination of drinking water.

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