Documentation and Prediction of Increasing Groundwater Chloride in the Twin Cities, Minnesota

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Abstract
We provide a comprehensive overview of historic chloride concentrations in the groundwater of the Twin Cities metropolitan area (TCMA) in Minnesota, in order to define the extent of chloride contamination, due primarily to the seasonal application of deicing salt to roadways. Data collected from 1278 wells between 1965 and 2020 are representative of the major aquifers underlying the TCMA and establish a regional natural background chloride concentration of less than 10 mg/L. However, 55% of all measurements (1616 of 2943) are above 10 mg/L, with the highest concentrations found within the uppermost Quaternary aquifers. Chloride concentrations in underlying bedrock aquifers are negatively correlated with the thickness and clay composition of overlying materials. Most chloride measurements (92%) remain below chronic exposure limits set by state and federal authorities. Historical trends indicate that, if the current imbalance between chloride inputs and outflows persists, chloride concentrations in TCMA aquifers will surpass regulatory thresholds by midcentury as surface waters and Quaternary aquifer waters migrate into underlying bedrock aquifers. Most wells in this study are monitored annually, making it impossible to detect important sub-annual fluctuations of chloride concentration that can exceed 40%.

Introduction
Among the many environmental contaminants common to urban areas, chloride is particularly concerning for the Twin Cities Metropolitan Area (TCMA) of Minnesota and many other cities in cold climates due to the extensive use of rock salt in road and sidewalk deicers. In the TCMA, chloride concentrations are known to be increasing in regional lakes and streams (Novotny et al. 2008, 2009) and many residential wells in Quaternary sediments are starting to show upward trends in chloride concentration (Kroening and Ferrey 2013; Demuth and Scott 2020). Similar trends are seen in urban areas elsewhere in the United States (Kelly 2008; Ophori et al. 2019), Canada (Bester et al. 2006; Howard and Maier 2007), the United Kingdom (Rivett et al. 2016), Italy (Rogora et al. 2015), and even Iran (Jamshidi et al. 2020). High chloride concentrations harm freshwater ecosystems, limit water usability, and increase corrosion of built infrastructure.
While TCMA groundwater chloride concentrations are not yet at the point where expensive remediation systems are necessary, it is critical to protect and monitor the region’s groundwater resources to ensure they do not reach those concentrations.

Current groundwater monitoring practices used by state agencies provide detailed data on many chemical species, but only from a small minority of wells per year. The resulting time series data are sparse geographically, uneven in the aquifer units that are sampled, and limited to roughly annual sampling frequency at best. Given that chloride concentration can vary significantly due to sub-annual climatic controls (e.g., Rivers 2011; Kasahara 2016), and spatially as a result of geologic heterogeneities (e.g., Tipping 2012), hand-testing individual wells limits the ability to fully understand important processes such as chloride transport to the deeper aquifers that are used as sources of drinking water. New monitoring strategies are needed to bring these processes into focus.

This study combines historical data with local hydrogeology to examine three key questions: (1) How are chloride concentrations changing over time within Quaternary and bedrock aquifers in the TCMA? (2) How do chloride concentrations vary spatially within the region’s bedrock aquifers? (3) What are the timescales for chloride migration within and between aquifer units? Here we demonstrate chloride buildup across multiple Quaternary and bedrock aquifers and also present a simple empirical model for predicting future chloride concentrations based on historical data.

**Hydrogeologic Context**

The geologic setting for the TCMA is Paleozoic sedimentary bedrock deposited as part of an expansive shallow marine shelf, overlain by variable thicknesses of much more recent, unconsolidated sediment related to Quaternary glacial processes (Figure 1a). Quaternary deposits are heterogeneous, with sand and gravel units serving as aquifers, and diamictons (“till”) and lacustrine clay-rich units serving as aquitards. The western TCMA is characterized by extensive and thick clay-rich tills of the Des Moines lobe, whereas the eastern TCMA has generally thinner, patchier, and sandier tills (Figure 1b). The sedimentary bedrock that hosts the most heavily used regional aquifers is Cambrian and Ordovician in age (about 505 to 450 million years old). Most individual formations are subhorizontal layers dominated by sandstone, shale, and/or carbonate from 15 to 60 m thick. The hydrogeologic framework delineates six major regional bedrock aquifers (Figure 1a; Runkel et al. 2003). Aquifer layers are dominated by fine- to coarse-grained sandstone or pervasively fractured and karstified carbonate rock. Designated aquitards are composed of finer-grained sandstone, siltstone, and shale as well as carbonate rock lacking through-going fractures.

Secondary pore networks are common and play an important role in both siliciclastic and carbonate bedrock aquifers (e.g., Alexander Jr and Lively 1995; Muldoon et al. 2001; Runkel et al. 2003, 2006; Swanson et al. 2006; Tipping et al. 2006; Meyer et al. 2008; Anderson et al. 2011; Green et al. 2012; Runkel et al. 2018). These fractures and solution features allow water to move rapidly within the bedrock aquifers, particularly within the karstic Prairie du Chien Group. In some areas of the eastern TCMA where the cover of unconsolidated sediment is thin and sandy, such as in parts of Washington and Dakota counties, infiltrating surface water can rapidly migrate through the underlying unconfined bedrock aquifers via these secondary pore networks. Vertical hydraulic head gradients are downward in most places, and horizontal gradients show a general flow direction towards the major river valleys (Figure 2; Delin and Woodward 1984). In addition to discharge along valleys, locally significant discharge occurs via pumping for municipal water supply, industrial use, and agricultural irrigation purposes.

The heterogeneities in the glacial deposits and secondary pore systems in the bedrock are important controls on transport from the land surface to aquifers at depth (Runkel et al. 2018). These hydrologic considerations are not unique to the TCMA, and analogous conduit flow systems are likely to give rise to heterogeneous groundwater behavior in other communities, even across a diversity of geologic settings.

**TCMA Groundwater Management**

In Minnesota, statutory responsibility for monitoring groundwater is shared across four entities: the Minnesota Pollution Control Agency (MPCA), the Minnesota Department of Health (MDH), the Minnesota Department of Agriculture (MDA) and the Minnesota Department of Natural Resources (MDNR). In their individual purviews, water quality monitoring is carried out by staff or partners of these agencies by physically visiting wells and springs, conducting a suite of on-site tests, and obtaining samples for extensive laboratory characterization. The availability of human and financial resources is a constraint for all agencies on the number of wells that can be sampled in any given year and any particular well might be tested once per calendar year, at best.

**Prior Research on Chloride in Minnesota**

Water samples from Minnesota aquifers show generally low natural chloride concentrations with isolated areas of elevated concentrations (Maclay et al. 1972; Winter 1974; Wolf et al. 1983; Lass 1990; Strobel and Haffield 1995; Kroening and Ferrey 2013). Using an analysis of chloride to bromide ratios (Davis et al. 1998; Panno et al. 2006) to differentiate between natural and anthropogenic sources of chloride, Kroening and Ferrey (2013) found that groundwater in the state which were unaffected by anthropogenic sources tended to have chloride concentrations less than 7 mg/L. This estimate is consistent with the earliest known measurement of chloride concentration in TCMA groundwater of 4.5 mg/L at Coldwater Spring (Maguire 1880).
More recently, the uppermost aquifers in the unconsolidated sediments of the TCMA were found to be significantly impacted by anthropogenic chloride (MPCA 2016). In some areas, chloride concentrations are well above the chronic and acute environmental water quality standards set by the state (230 and 860 mg/L, respectively), as well as the U.S. Environmental Protection Agency’s (EPA) Secondary Maximum Contaminant Level of 250 mg/L (Kroening and Ferrey 2013; EPA 2020). (For information about these water quality standards, see Text S1). In their sample of approximately 200 Quaternary sand and gravel aquifer wells, Kroening and Ferrey (2013) found the median chloride concentration was five times higher inside the TCMA than outside (86 vs. 17 mg/L) and the proportion of wells with samples exceeding a chloride concentration of 250 mg/L was 27% inside the TCMA but only 1% outside (Kroening and Ferrey 2013; MPCA 2016). Novotny et al. (2009) reported some shallow groundwater wells in the TCMA region having concentrations as high as 2000 mg/L.

There has been far less data published on chloride contamination in the underlying bedrock aquifers. Kroening and Ferrey (2013) reported data from about 65 bedrock aquifer wells located in SE Minnesota, only some of which were from the TCMA. They found chloride concentrations that modestly exceeded the presumed natural background concentration (median of 18 mg/L), but few measurements exceeded state water quality standards. However, bedrock aquifers do display locally elevated chloride concentrations, especially where they are close to the land surface and are not protected by overlying low-permeability Quaternary sediments. For example, there was sufficient data to calculate Cl/Br ratios in water from 34 wells in the MPCA network, all of which are used for drinking water. Of these, 31 samples had results that can only be explained with anthropogenic contamination.

The primary anthropogenic sources of chloride in the TCMA are rock salt used in road and sidewalk deicing and brines from water softeners (MPCA 2016). Water softener brines are transported via household drains into septic systems (about 22%) or municipal sewers (about 78%) (Overbo et al. 2019). While the small fraction that passes through septic systems can leach directly into shallow groundwater aquifers, the majority of household...
wastewater passes through water treatment plants and then into the region’s rivers. Since most Minnesota rivers serve as discharge zones for groundwater, there is likely little migration of chloride from the rivers into the groundwater. In contrast, an estimated 385,000 tons of NaCl are used each winter to deice roads in the TCMA (MPCA 2022a). Because the road salt is dispersed directly into the outdoor environment, chloride from road salt is carried into nearby lakes and aquifers. Novotny et al. (2008) demonstrated a strong temporal correlation between the salinity of 38 TCMA lakes and the amount of rock salt purchased by the state of Minnesota. It has also been shown that less than 30% of the salt spread in the TCMA annually leaves the watershed via the Mississippi, Minnesota, and St. Croix Rivers with the rest (more than 70% or approximately 270,000 tons) retained in the region’s lakes, soils, and groundwater (Novotny et al. 2009; Novotny and Stefan 2010).

One of the only studies documenting sub-annual variation in groundwater chloride concentrations in the TCMA was conducted by Kasahara (2016) at Coldwater Spring on the bluffs of the Mississippi River near the Minneapolis-St. Paul International Airport. Weekly/biweekly chloride measurements demonstrated dramatic spikes during spring runoff amounting to 40% variations within a single year (Figure 3). This pattern would not be visible under annual sampling. (See Text S2 for additional details about Coldwater Spring.)

Figure 2. Interpreted potentiometric surface contours for the combined Prairie du Chien and Jordan aquifers in the TCMA. Flow directions indicated by arrows. Aquifers not present in unshaded areas. Based on individual county geologic atlas publications from the MN Geologic Survey and MN Department of Natural Resources (Balaban and McSwiggen 1982; Balaban 1989; Balaban and Hobbs 1990; Swanson and Meyer 1990; Meyer and Swanson 1992; Peterson 2014; Berg 2016).

Figure 3. Chloride concentrations at Coldwater Spring from early 2013 to late 2014. Data from Kasahara 2016.

Methods

Data Sources

The chloride data in this study were obtained from the MPCA, MDNR, and MDH and encompass well water samples collected throughout the TCMA between July 1965 and November 2020. (Data inside the TCMA were not available from the MDA.) Additional data on the thickness and composition of Quaternary deposits at each well site were obtained from the Minnesota Well Index (MDH 2022). Wells were assigned to aquifers using the
Minnesota Well Index Coding System (MGS 2022) and encompass 37 separate aquifer units (full list in Text S3). More than half of the data comes from just three aquifer units: the Quaternary Water Table Aquifer (QWTA), the Prairie du Chien Group (OPDC), and the Jordan Sandstone (CJDN). Most (20/37) other units are represented by fewer than 10 wells. Wells tagged with the INDT (“indeterminate”) and MTPL (“multiple”) codes were excluded from our analysis because of the aquifer ambiguity. A number of wells span two aquifer units (e.g., OPCJ, CSLT, CTCW). These wells have been included since the provenance of the water is more constrained. The final data set consists of 2943 measurements from 1278 wells across 33 aquifer codes (McDaris et al. 2021; Figure 4).

Data coverage varies over time (Figure 5). The oldest records come from the MDH and span the late 1960s to 1980s. There is a data gap until 2004, when data from all three agencies are available. This does not mean that water monitoring ceased during that period. Data from 1986 to 2004 are presently not available to the public as paper records from state agencies await digitization. MPCA and MDH data are more consistent, resulting from regular monitoring work, while the MDNR data is episodic, representing periods of work on County Geologic Atlas projects for counties inside the TCMA.

Computation and Analysis

Since the chloride concentration data available from any single well are not normally distributed in time, the nonparametric Mann-Kendall statistical test (Kendall 1975) was used to determine if any wells exhibited a statistically significant trend in chloride concentration as a function of time (α < 0.05). The test was performed on the data from wells with eight or more measurements during the study period and, for those exhibiting significant trends, Sen’s Slope (Sen 1968) was calculated to estimate the magnitude of the trend. Standard linear regressions were also computed for each well for comparison and in many cases the results were similar (as seen in Figure 8a). However, the two
methods did produce slightly different sets of wells with statistically significant trends. Given the nature of the data distribution, the nonparametric significance and test statistics were used for the analysis.

Spatial analyses of the data were conducted using QGIS. Well locations were defined using the latitude and longitude associated with each well in the Minnesota Well Index. These coordinates are available to seven significant figures which equates to sub-meter precision for the well locations. Land cover information indicating the percentage of impervious ground cover (i.e., roads, sidewalks, parking lots, and building rooftops) was obtained from the University of Minnesota Data Repository (Rampi et al. 2016) at 15 m resolution. This raster image was overlaid on the base map in QGIS to sample the pixel at each well location.

**Results and Discussion**

**Unit Statistics**

Table 1 provides a statistical overview of chloride concentration in aquifers represented by at least 30 measurements in the data set over the study period. Near-surface aquifers generally have higher chloride concentrations than lower strata, as one would expect with chloride loading from the surface. Noticeable deviations from that pattern are the QBAA and CMTS units.

QBAA is the Quaternary Buried Artesian Aquifer. Because these sand and gravel deposits are covered by fine-textured aquitards, they are poorly connected to the larger groundwater system and are relatively well-protected from contamination (MPCA 1999), resulting in lower chloride concentrations than the other Quaternary units. The majority of wells from the QBAA have chloride concentrations less than 10 mg/L, which is consistent with natural background chloride concentrations in the region. The Mount Simon Sandstone (CMTS) is the stratigraphically lowest aquifer in the TCMA and rests directly upon Precambrian bedrock (Figure 1). While the water from this unit has elevated chloride content, it is generally considered to be due primarily to chloride dissolution from the Precambrian bedrock rather than anthropogenic inputs (Berg and Pearson 2012). Data in our study support this conclusion. Three quarters (74/101) of the chloride measurements from this unit have accompanying bromide measurements and the resulting Cl/Br ratios for all but one are below 300, indicating that
Table 1
Chloride Concentration Data for TCMA Aquifers

| Unit    | Minimum [Cl\(^-\)] (mg/L) | Maximum [Cl\(^-\)] (mg/L) | Median [Cl\(^-\)] (mg/L) | Mean [Cl\(^-\)] (mg/L) | Data Points (N) |
|---------|----------------------------|---------------------------|--------------------------|------------------------|-----------------|
| QWTA    | 0.50                       | 8900                      | 48.5                     | 157                    | 686             |
| QBUA    | 0.63                       | 294                       | 25.9                     | 40.0                   | 80              |
| QBAU    | 0.37                       | 352                       | 4.2                      | 22.3                   | 413             |
| OPDC    | 0.50                       | 325                       | 26.2                     | 34.6                   | 284             |
| OPCJ    | 0.02                       | 120                       | 9.8                      | 17.9                   | 229             |
| CJDN    | 0.10                       | 198                       | 9.0                      | 17.2                   | 665             |
| CSLT    | 0.47                       | 176                       | 3.3                      | 10.0                   | 53              |
| CTCLG   | 0.40                       | 120                       | 1.4                      | 8.6                    | 67              |
| CTCW    | 0.50                       | 60                        | 1.0                      | 6.2                    | 116             |
| CTCM    | 0.06                       | 14.3                      | 1.8                      | 3.2                    | 47              |
| CMTS    | 0.56                       | 166                       | 15.7                     | 24.0                   | 101             |

Note: Data for important water sources with more than 30 data points available in the data set are shown. Units are presented in stratigraphic order downward.

**Figure 6.** Cumulative frequency distributions for chloride measurements across the 11 aquifer units in the TCMA with more than 30 measurements. Vertical lines indicate the chronic (230 mg/L) and acute (860 mg/L) water quality thresholds. Note the x-axis is plotted using a log scale.

The chloride concentration is unlikely related to human activity (Davis et al. 1998; Panno et al. 2006). The outlier occurs in a well where the CMTS subcrops directly beneath the QWTA and is not deeply buried.

Figure 6 shows the chloride concentration data from the 11 units in Table 1 plotted as cumulative frequency distributions (CFD). The legend has the units listed in descending stratigraphic order. Chloride measurements from each unit are ordered from lowest to greatest and their cumulative frequency is plotted on the vertical. The derivative of CFD would be a histogram of all of the chloride measurements from an aquifer. CFDs with steep slopes indicate a narrow distribution of chloride values, while shallower slopes indicate broader chloride distributions. Such CFDs are useful because they allow resource managers to quickly see, for example, that 17% of all measurements from the QWTA exceed the state’s chronic chloride exposure limit and 5% exceed the acute exposure limit. The median chloride value for each aquifer can be identified as the chloride concentration with a frequency of 0.5, and again, we see the median chloride concentration in each unit decreasing down section with the exception of the QBAU (purple) and CMTS (green). Importantly, abrupt changes in the slope of aquifer CFDs can indicate the presence of water from different sources or deviations through time. For example, the Prairie du Chien Group (OPDC, red in Figure 6), shows a dramatic increase of the slope of the CFD at approximately 10 mg/L suggesting that there are two populations of waters present: one with a lower median chloride concentration and one with a higher median concentration. This change in slope is found at a frequency of only about 0.25, indicating that the population of higher-chloride groundwater is found in about 75% of the aquifer’s measurements. The CFD for QBUA shows a change in slope near 4 mg/L, indicating that just less than half of the measurements exhibit low chloride concentrations, near-background level values, while the other half is influenced by elevated chloride levels. By comparison, the CFDs for QWTA and Jordan (CJDN) both show relatively smooth log-normal distributions, though the distribution of chloride values for the Jordan is narrower and generally lower than that of the QWTA.

CFDs can also provide more subtle observations on chloride concentrations in the TCMA. For example, wells that draw from both the Prairie du Chien and the Jordan (OPCJ) show a distribution that overlaps with the CJDN much more than the OPDC. Wells drawing from both the St. Lawrence Formation and the Tunnel City Group (CSLT) show several stepwise increases in their CFDs. Also, the bend in the CMTS CFD near 20 mg/L suggests a second population of high chloride water comprising 10% to 12% of the data in addition to the higher natural background. The CFDs also highlight round off errors, particularly at 1 mg/L, associated with lower limits of chloride detection within some of the historical data. These lower limits do not compromise the usefulness of CFDs for interpreting chloride concentrations in the TCMA.

These data confirm previous findings (Kroening and Ferrey 2013; Kroening and Vaughn 2019) and also provide
new insights into chloride concentrations in the TCMA. The QWTA aquifer is heavily impacted by anthropogenic chloride with only about 20% of the measurements below 10 mg/L. The OPDC, which supplies a great deal of residential groundwater, is less affected and still half of available chloride measurements are above 10 mg/L. While many of the other bedrock aquifers have median values comparable to a natural background of 7 to 10 mg/L, the shape of their CFDs supports the conclusion that at least a small percentage of samples in each unit contain water bearing non-native chloride.

It is important to acknowledge that Figure 6 lumps together data from geographically distributed wells gathered over the course of five decades. One way to examine how chloride concentrations in some aquifer units have changed with time is to compare measurements from before the 1986 to 2004 data gap with measurements taken in the same units afterward. This comparison is shown in Figure 7 for the Jordan Sandstone (CJDN), which was densely sampled in both time periods. The upper 75% of the CFD is translated to chloride concentrations about 10 times higher in the more recent data.

Increasing Chloride Concentrations with Time

The extensive data record also provides another opportunity to look for long-term trends in chloride concentrations, at the well level rather than at the aquifer level. Of the 1278 wells in the data set, only 231 were densely sampled in both time periods. The upper 75% of available chloride measurements are above 10 mg/L. The CFD is translated to chloride concentrations about 10 times higher in the more recent data.

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**Figure 7. Differences in chloride data before and after the gap in available data shown as CFD plots for two aquifers. Blue lines show the distribution of data from before 1990, red lines denote data from after 2000, and black lines denote all data. (a) Jordan Sandstone (CJDN). (b) Combined Prairie du Chien-Jordan aquifer (OPCJ).**

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might undertake to reduce the amount of salt entering the groundwater system. Many efforts are underway to increase spreading efficiency and reduce waste which could alter the future course of chloride concentrations in some aquifers. However, despite these improvements in deicing strategy, data from the MN Department of Transportation shows that the total amount of salt used on state roadways has remained relatively consistent for nearly two decades (MNDOT 2014; 2018; 2021). Until a new equilibrium is reached, we would expect elevated concentrations of chloride to continue to advance through the groundwater system and this model highlights the urgency of the problem posed by chloride contamination.

**Dependence on Overlying Materials**

The distribution of chloride concentrations within an aquifer unit may vary due to several factors. For example, the percentage of impervious land cover is high in the urban core and decreases outward into the suburbs. Such impervious land cover can affect where runoff recharges into Quaternary deposits as well as the size of the catchment supplying water to those recharge sites. Also, a bedrock unit can be overlain by a bedrock aquitard or it may subcrop immediately beneath Quaternary deposits (Figure 1a). Further, in some locations the Quaternary deposits (such as the thick, clay-rich Des Moines Lobe tills in the western part of the TCMA) can act as areally extensive aquitards while others provide less of a barrier to water movement (Tipping 2012). Bedrock aquitards can also slow the downward movement of groundwater, while features such as fractures, dissolution conduits, and poorly grouted well casings can provide faster pathways to deeper units. Extensive groundwater pumping in the TCMA also increases hydraulic head gradients within and between aquifers that can draw more contaminated water into deeper units, regardless of where the recharge areas are located. All of these factors underscore the importance of hydrogeologic context when interpreting groundwater chloride data.

**Effects of Land Cover and Geospatial Patterns**

Areas with a higher percentage of impervious land cover tend to have more paved areas, which require...
deicing. Additionally, impervious surfaces tend to concentrate contaminant-rich runoff towards road ditches, holding ponds, and storm sewer systems where it can percolate into the ground. However, the association of impervious ground cover with roadways is not perfect; rooftops, for example, are impervious, but not subject to rock salt application. Nevertheless, wells drilled in places with more than 50% impervious land cover tend to have higher chloride concentration than wells in less impervious places. Thus, we recognize the limits of what can be concluded from the 15 m resolution land cover data used here.

This study contains 594 measurements from QWTA wells located in areas with up to 50% impervious cover. Of these, five have chloride concentrations above the acute water quality standard (0.8%). There are fewer measurements (90) from areas with greater than 50% impervious cover, but of these, 14 have chloride concentrations above the acute water quality standard (15.5%). Figure 10 shows chloride measurements from QWTA wells as a function of impervious cover. The majority of chloride measurements above the acute water quality standard correspond to the minority of wells with impervious cover greater than 50%. The percentage of wells measuring between the chronic and acute thresholds is higher for those with more impervious land cover (14.1% of wells in ≤50% impermeable locations exceed the chronic standard, while 30% of wells in greater than 50% impermeable localities do). A similar analysis of the land cover surrounding wells in the QBAA, QBUA, and important bedrock aquifers did not indicate a significant correlation.

To investigate spatial patterns of chloride concentration hotspots, we mapped the locations of the 30 highest chloride concentrations (Figure 11). The oldest of these samples dates to 2004 and the most recent is from 2020.
Because some of these measurements were collected from the same well at different times, only 19 points appear in Figure 11. All but one of these hotspots draws water from the QWTA with the one outlier drawing from the Wonewoc Sandstone (CWOC) in an area where that unit subcrops immediately underneath the Quaternary deposits. Thirteen of these hotspots are inside the urban core of the TCMA as delineated by the Interstate 494 to 694 loop. Sixteen of the wells are surrounded by at least 30% impervious land cover, with nine greater than 50% impervious. Two wells were inside parks, and six are within about 200 m of water bodies. All but one are within 100 m of parking lots, residential streets, or at least one major roadway. This distribution highlights the role urban land use plays in chloride contamination of the QWTA.

**Effects of Overlying Geologic Materials**

Data from aquifers with more than 30 chloride measurements were used to assess the effects of overlying bedrock and Quaternary aquitards on chloride concentrations. Data on Quaternary clay thicknesses and the first bedrock encountered were compiled from the Minnesota Well Index (MDH 2022) and are described in Table S1. Chloride data from these wells are shown in Figure S2.

There is significant overlap among the chloride values shown in Figure S2. However, examination of median values highlights two important trends. In 6 out of 8 aquifers, median chloride values are higher in wells where the bedrock aquifer is in direct contact with overlying Quaternary deposits than in wells where the bedrock aquifer is below a bedrock aquitard. These aquitards provide resistance to chloride migration into these aquifers. Similarly, in 5 out of 8 aquifers median chloride values are lower in wells that are screened below 15 m or more of clay, than in wells with less than 15 m of overlying clay.

Another demonstration of this effect can be seen by examining chloride measurements from the OPDC that are below the change in slope of the CFD shown in Figure 6. There are 60 OPDC measurements with chloride concentrations less than 11 mg/L. Of these, nearly two-thirds (39) occur in wells where there is greater than 15 m of clay above the screened interval. In addition, another seven...
Conclusions

The TCMA is a case study of the lasting impact that road salt application can have on regional aquifers. Multiple regional aquifers show chloride concentrations elevated above natural background levels, although at this time, most of these measurements remain below chronic exposure limits set by state and federal regulators. Since rock salt will continue to be used for winter driving safety, chloride concentrations will likely continue to increase in all aquifers across the TCMA and the number of water-quality exceedances will also rise. Our results confirm that chloride concentrations in Quaternary deposits tend to be higher in areas with more impervious land cover and that bedrock aquifers protected by low permeability bedrock and Quaternary aquitards tend to exhibit lower chloride concentrations. Our results also provide an empirical relation which offers a statistical estimate of future chloride concentrations based on historical patterns. Additional monitoring will provide ground truth for this model going forward.

The 2943 data points collected from 1965 to 2020 in this study represent the work of many highly dedicated individuals at three state agencies over 55 years. The cooperative, multi-agency groundwater management system in Minnesota is one of the strongest in the nation but the time- and resource-intensive nature of that work places practical limits on the spatial and temporal resolution that is achievable. Given the thousands of wells in the TCMA, it is not feasible to employ the large numbers of geotechnicians needed to physically gather and test samples from any significant fraction of sites with frequency sufficient, for example, to resolve the 40% seasonal oscillations observed at Coldwater Spring. We advocate for the deployment of a sentinel network of in-situ specific conductance sensors across the region that can autonomously provide measurements on short timescales. Specific conductance is easily measured and will be proportional to chloride concentration though the exact relationship will vary between aquifers based on their unique combination of dissolved solids. Taking into consideration the work done to characterize groundwater flow directions and subsurface features such as buried bedrock valleys, monitoring sites can be chosen to maximize the insight into lateral movement of chloride within individual aquifers. In addition, utilizing clusters of wells in the same area that sample different aquifers will help constrain the vertical component of chloride movement. Such a network would greatly enrich the information available to groundwater managers about how chloride concentrations evolve in space and time and provide critical feedback to transportation authorities on the effects of changes to deicing policies.

Acknowledgments

The full data set for this research is available via this in-text data citation reference: McDaris et al. (2021).

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The University of Minnesota is built on the ancestral lands of the Wahpekute band that was ceded to the United States by the Treaty of Traverse des Sioux in July of 1851, in an agreement that was not paid in full and whose underlying aim was the dissolution of the Dakota culture. The University has also benefited from Chippewa and Dakota (Mede-wakanton, Wahpekuta, Wahpeton and Sisseton Bands) land ceded by treaty and given to the University of Minnesota via the Morrill Act. Due to its land-grant status, the infrastructure, financial foundations, and faculty, students, and staff at the University of Minnesota all continue to benefit directly from these ceded lands, and we wish to acknowledge this support in our research.

Authors’ Note

The authors declare no conflicts of interest.

Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article. Supporting Information is generally not peer reviewed.

Text S1: Water quality standards.
Text S2: Coldwater spring case example.
Text S3: Full list of aquifer names and abbreviations found in the data set.

Figure S1: Plot of actual vs. predicted chloride concentrations in wells with less than 8 multiple measurements during the study period based on the power law relation shown in Figure 7.
Figure S2: Box plots of chloride data from aquifers with more than 30 chloride measurements during the study period.
Figure S3: Locations of measurements containing less than 11 mg/L of chloride in the Prairie du Chien (OPDC) Aquifer.

Table S1. Summary of data from wells in bedrock units.

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