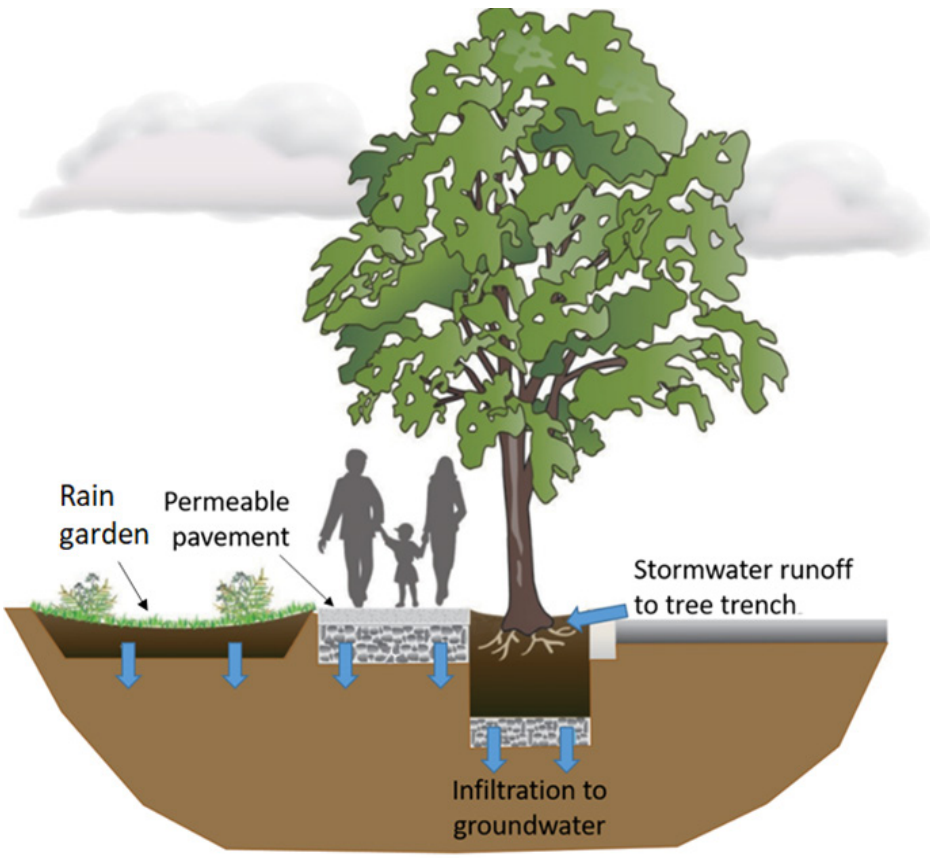
Impacts of Stormwater Infiltration on Chloride in Minnesota Groundwater

MINNESOTA GROUND WATER ASSOCIATION
WHITE PAPER 04

NOVEMBER 2020



Front Cover

The picture on the cover illustrates infiltration of stormwater runoff through three common stormwater control measures (SCM) - permeable pavement, tree trenches, and rain gardens. While most pollutants are filtered in the SCM, chloride is not. Water infiltrating through these practices subsequently migrates to shallow groundwater, thus transporting chloride to shallow groundwater. Source: Philly Watersheds

Cite as:

Minnesota Groundwater Association. (2020, November). Impacts of stormwater infiltration on chloride in Minnesota groundwater. Retrieved from https://www.mgwa.org/documents/whitepapers/impacts_of_stormwater_infiltration_on_chloride_in_minnesota_groundwater.pdf

ACKNOWLEDGEMENTS

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Glossary of Terms and Acronyms

Definitions

Acid—a class of compounds that liberate hydrogen ions in water, are sour and corrosive and have a pH of less than 7.

Adsorption—holding molecules to its surface, causing a thin film to form.

Anion—a negatively charged ion.

Base—a substance capable of combining with an acid to form a salt and water; usually produces hydrogen ions when dissolved in water; pH is greater than 7.

Baseflow—the portion of the streamflow supplied by shallow subsurface flow that sustains streamflow between precipitation events.

Bioinfiltration—a bioretention practice (e.g. rain garden) in which no underdrain is used. All water entering the bioinfiltration practice infiltrates or evapotranspires.

Bioswales—channeled depressions that receive and convey stormwater runoff, contain vegetation, and are designed to treat pollutants through filtration and sedimentation.

Cation—a positively charged ion.

Class 2 Water Quality Standards, chronic and acute—provisions of state, territorial, authorized tribal or federal law approved by EPA that describe the desired condition of a water body and the means by which that condition will be protected or achieved. Class 2 standards are protective of recreation and aquatic life.

Clay dispersion—separation of clay particles from one another in moist soil, resulting in breakdown of soil aggregates and potential clogging of soil pores.

Conductivity (as it relates to chloride concentration)—the transmission of electricity through a solution is increased with increasing salt concentration.

Conservation design—development design that protects the important natural features of the land, such as vegetation and hydrology.

Deicer—a chemical substance used to prevent the formation of ice.

Engineered media—a mixture of sand, fines (silt, clay), and organic matter utilized in stormwater practices, most frequently in bioretention practices. The media is typically designed to have a rapid infiltration rate, attenuate pollutants, and allow for plant growth.

Evaporite—sediment deposited from aqueous solution by evaporation.

Green infrastructure—The U.S. EPA defines green infrastructure as an approach to managing wet weather impacts that reduces and treats stormwater at its source while delivering environmental, social, and economic benefits.

Hard water—water that does not allow soap to lather and forms a scale as it evaporates; usually has high concentrations of calcium and magnesium ions.

Infiltration practice—stormwater control measures (SCMs) that capture and temporarily store stormwater runoff before allowing it to infiltrate into the underlying soil.

Ion and ionic compound—an atom or compound that has lost or gained one or more electrons and therefore has a negative or positive charge.

Lysimeter—a device for measuring change due to moisture loss undergone by a body of soil.

Microbial chlorination—chlorination of organic matter as soil is fermented by microbes with the aid of enzymes and time.

Meromictic—applied to a lake which has layers of water that do not intermix.

Mounding (groundwater)—the temporary, localized rise in the groundwater surface below an infiltration practice, resulting from infiltration of stormwater runoff.

Neutralization reaction—a reaction between an acid and a base that results in a solution with neutral pH of 7.

Rational Method—a simple technique for estimating a design discharge from a small watershed, often used to predict peak flows.

Redox—an oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron.

Redox-stratification—the biogeochemical sorting of reductants and oxidants according to redox potential with the most reducing conditions at depth, where oxygen does not penetrate.

Reduction—gaining of electrons by one of the atoms involved in the reaction between two chemicals.

Sorption—absorption or adsorption occurring jointly or separately.

Stormwater Control Measure—structural and nonstructural practices designed to retain or detain stormwater runoff and improve the quality of stormwater runoff. Examples of nonstructural practices include pollution prevention and street sweeping. Examples of structural practices include sedimentation ponds, filtration practices, and infiltration practices.

Stormwater runoff—precipitation (rain or melted snow) that runs off the landscape via overland flow to a surface water (e.g. lake, river, wetland).

Turnover (of lakes)—the process of a lake's water turning over from top (epilimnion) to bottom (hypolimnion). During the summer, the epilimnion, or surface layer, is the warmest and lightest as it is heated by the sun. When it becomes cold in winter, it may become denser than water at depth. Wind also plays a role.

Vertical transport retention—retention of a chemical, such as chloride, during vertical infiltration of water in geologic material (e.g. soil, engineered media).

Water softening—the removal of calcium, magnesium, and certain other metal cations in hard water. The resulting soft water requires less soap for the same cleaning effort, as soap is not wasted bonding with calcium ions.

Water softening resin regeneration—flooding a reactive resin with brine water, thereby removing minerals to restore the resin to its proper ionic form for service.

Abbreviations and acronyms

AGQS—Dakota County's Ambient Groundwater Quality Study of private drinking water wells

CAFO—Concentrated Animal Feeding Operation

Ca—chemical symbol for calcium

Cl—chemical symbol for chloride

Cl:Br ratios—chloride to bromide ratios, a way of determining if salt is from a natural or anthropogenic source

DWSMA—Drinking Water Supply Management Area

ERA – Emergency Response Area

I_{filt}—Infiltration through stormwater filtration practices

I_{imperv}—Infiltration through impervious surfaces

I_{infil}—Infiltration through stormwater infiltration practices

I_{perv}—Infiltration through pervious surfaces

I_{ponds}—Infiltration through stormwater ponds

L—liter

L_{pi}—Leakage from water supply pipes

L_{sw}—Leakage from storm sewer pipes and conveyances

L_{ww}—Leakage from sanitary sewer pipes and conveyances

IDS—Minimal Impact Design Standards

MDA—Minnesota Department of Agriculture

MDH—Minnesota Department of Health

MDNR—Minnesota Department of Natural Resources

MPCA—Minnesota Pollution Control Agency

MS4—Municipal Separate Storm Sewer System

Na—chemical symbol for sodium

NAWQA—National Water Quality Assessment

NPDES—National Pollution Discharge Elimination System

pH—a measure of the hydrogen ion activity in a solution; a measure of how acidic or basic a solution is.

PICP—permeable interlocking concrete pavement

SCM—Stormwater Control Measure

SDS—State Disposal System

SDWA—Safe Drinking Water Act

SSTS—Subsurface Wastewater Treatment System

SSURGO—Soil Survey Geographic

SMCL—Secondary Maximum Contaminant Level

SWMP—Stormwater Management Plan

SWPPP—Stormwater Pollution Prevention Plan (construction stormwater) or Stormwater Pollution Prevention Program (municipal stormwater)

TCMA—Twin Cities Metropolitan Area

US EPA—United States Environmental Protection Agency

USGS, U.S. Geological Survey—United States Geological Survey

Units

1 centimeter (cm) = .3937 inches (in)

1 inch = 2.54 centimeters

Hectare—a square of 100m sides

1 hectare = 2.47 acres

1 acre = 0.4047 hectares

kg/lane-km, kg/ha—kilograms per road lane per kilometer; kilogram per hectare

1 meter (m) = 3.28 feet (ft)

1 ft = 0.3048 m

mg—milligram, a unit of mass equal to one thousandth of a gram (10^{-3}g)

mg/L—milligram per liter; a measure of the concentration by weight of a substance per unit volume in water

mg/d—milligram per day

t—tonne, a unit of weight equal to 1,000 kilograms

1 t = 2,205 lb

t/y—metric tons per year

Executive Summary

Chloride concentrations are increasing in Minnesota's surface waters and groundwater. Fifty lakes or rivers currently exceed the 230 mg/L chronic aquatic life standard and are thus classified as chloride-impaired. Shallow groundwater monitoring in the Twin Cities Metro Area shows that nearly 30 percent of sampled wells exceed the non-health-based Secondary Maximum Contaminant Level drinking water standard of 250 mg/L. Typical chloride concentrations in shallow urban groundwater are 60-80 mg/L, while "background" (forested area) concentrations are typically less than 5 mg/L.

While there are several natural and anthropogenic sources of chloride, use of chloride-based deicers accounts for 42 percent of the annual chloride contribution to Minnesota's environment. In urban areas, deicer use accounts for most of the chloride load to surface water and shallow groundwater.

Deicer application rates are the primary determinant of chloride concentrations in stormwater runoff. In winter, deiced area runoff frequently exceeds 1000 mg/L, and sometimes 10,000 mg/L chloride, while concentrations are typically below 50 mg/L in non-deiced areas. Infiltration of stormwater runoff is a favored management strategy. There are many water quality and hydrologic benefits from infiltration, but effective chloride treatment remains infeasible. The effects of increased stormwater infiltration are largely uncharacterized; there are no known studies of stormwater infiltration impacts on groundwater chloride at the regional scale.

We developed an estimation approach for groundwater chloride budgets. We then varied three inputs directly related to stormwater infiltration: stormwater runoff chloride concentration, impervious surface (%), and infiltration implementation (%). While increasing each variable effectively increases groundwater chloride loading, runoff concentration appears to be the most important factor.

Although there is still a need to better understand chloride's environmental sources and fate, we know that treatment and remediation remain highly impractical. Thus, we identify the following upstream management strategies to reduce stormwater-related chloride sources to the environment:

- Identify and map groundwater areas vulnerable to chloride contamination by stormwater infiltration
- Properly site and design infiltration practices to minimize impacts to groundwater and to surface waters that receive significant baseflow
- Avoid storing snow containing chloride deicers in infiltration practices
- Use permeable pavements, which require little or no deicer use, where appropriate

Ultimately, the only effective long-term strategy to manage stormwater-related chloride in receiving waters is to decrease the use of chloride-based deicers.

1.0 CHLORIDE IN THE ENVIRONMENT

This section provides an overview of chloride chemistry and its occurrence in the environment, including natural and anthropogenic sources.

1.1 Chloride Chemistry

Salts, formed by acid-base neutralization or solid compound precipitation, are composed of an anion, such as chloride (Cl-), and a cation, such as sodium (Na+). There are many kinds of salts with different uses based on attributes such as taste and solubility. Sodium chloride, often referred to as halite or "salt", is an abundant and widely used natural resource, with an estimated 42 million metric tons of 2016 U.S. domestic production (United States Geological Survey, 2019). It is used especially for cooking, water softening, and deicing roads and pavements. Other common chloride-based salts include potassium chloride (KCl) or "potash," a commonly used fertilizer, magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$). Each of these is often used for road deicing.

1.2 Natural Chloride Sources

Natural chloride sources, in descending order of importance, include the oceans, weathered bedrock, surficial sediments and soils, geologic deposits of salt rocks, and groundwater brines.

The most visible representation of large volumes of salt is in ocean basins. Typically, surface seawater chloride concentrations are near 19,000 mg/L (Feth, 1981), and chloride is the most concentrated ion in seawater. Salt-filled closed inland basins (e.g., The Great Salt Lake, Utah) generally have higher chloride concentrations due to evaporation. Salton Sea (southern California) chloride concentrations are generally 18,000 to 19,000 mg/L and have been increasing since its 1905 creation (Tetra Tech, 2004). Some of these basins (e.g., Lake Bonneville) are major sources for manufacturing and consumer-grade salt.

Evaporite rocks have been widely studied (Norris, 1978). Bedded evaporites can be important oil and natural gas reservoir cap-rocks, can readily dissolve and lead to localized karst, and frequently occur as secondary clasts in bedded sedimentary rocks (Norris, 1978; Johnson, 1997; Weary & Doctor, 2014). Bedded evaporites occur as either marine or lake deposits, with thicknesses of a few meters for inland lake deposits to thousands of meters for marine deposits (Weary & Doctor, 2014). Salt deposits, primarily as halite, exist in 25 of the 48 coterminous United States (Johnson, 1997) and have been described and mapped (Norris, 1978; Weary & Doctor, 2014). Dissolution of salt from evaporite beds leads to groundwater brines within and commonly above and below these layers (Norris, 1978). However, most halite deposits are deep and do not impact surface waters or shallow aquifers (Feth, 1981). No bedded evaporite deposits, including halite, have been mapped in Minnesota, although saline groundwater occurs in some areas of Minnesota.

Natural terrestrial chloride deposition usually occurs atmospherically through precipitation or wind-blown drift of particulates. Atmospherically deposited chloride in the U.S. constitutes between 28 and 62% of total chloride in areas with minimal human activity, with the greatest deposition rates occurring along the coasts (Mullaney, Lorenz, & Arntson, 2009). Chloride in Illinois precipitation (both rain and snow) ranged from 0.1 to 0.3 mg/L (Panno, Hackley, Hwang, Greenberg, Krapac, Landsberger, & O'Kelly, 2005). Statewide, Minnesota monthly average precipitation chloride concentrations range from 0.006 to 3.2 mg/L, with the highest values in winter; U.S. coastal regions typically have much wider ranges (National Atmospheric Deposition Program, 2019). Moving inland, precipitation and dry deposition rates and associated chloride concentrations typically decrease. Nonetheless, tropical storms may transport high chloride concentrations inland (Feth, 1981). Arid inland areas (e.g., the Great Salt Lake basin) may contribute unknown chloride amounts locally via aerosol or wind-blown particle deposition (Feth, 1981). Overall the effect of precipitation and windblown particulate deposition on current concentration trends in Minnesota is minimal, as anthropogenic contributions have increased through activities outlined below.

1.3 Anthropogenic Sources and Uses

Magnesium, calcium, and sodium chloride salts are widely used as deicers in regions that experience snowfall. In the U.S., widespread chloride deicer use began in the 1940s, reached an annual average of 17.7 metric tons (19.5 million tons) in 2011 (Kelly & Matos, 2013), and is currently about 20 million metric tons per year (Kelly, Findlay & Weathers, 2019). Deicers are an important chloride source in urban and suburban areas with high impervious surface cover. Estimated average Minnesota use from 2011 to 2018 was 664,900 t/y, with the Twin Cities Metropolitan Area (TCMA) accounting for 236,700 t/y (Overbo, Heger, Kyser, Asleson, & Gulliver, 2019).

Deicer application rates vary by surface type and salt product. Fortin and Dindorf (2012) estimated that per-event application to highways in Minnesota ranges from 14-106 kg/lane-km. Application rates for parking lots are typically 2 to 4 times higher than for highways (Granato, DeSimone, Barbaro, & Jesnach, 2015), as parking lots may be subject to private liability for injuries, heavy pedestrian traffic, and staff untrained in proper application. In Madison, Wisconsin, commercial application rates for parking lots, converted to mass per lane km, were estimated at approximately 115-246 kg/lane-km/yr (Madison, Wisconsin Salt Use Committee, 2006), while higher rates were reported for driveways and walkways, approximately 126-420 kg/lane-km/yr (Madison, Wisconsin Salt Use Committee, 2006; Omer, Mirotabi, Liaqat, & Fu, 2014). Thus, deicer application in parking areas can be a substantial chloride source in urban and suburban areas.

of transportation typically cover salt storage areas, but businesses and local governments often use unsheltered storage (Meegoda, Marhaba, & Ratnaweera, 2004 as cited in Granato, DeSimone, Barbaro, & Jeznach, 2015). Chloride concentrations in a monitoring well near a former outdoor salt storage in Massachusetts reached 11,300 mg/L (Ostendorf, Hinlein, Rotaru, & DeGroot, 2006). Water quality criteria include the chronic aquatic life criteria of 230 mg/L for surface water (US EPA, 1988) and Secondary Maximum Contaminant Level of 250 mg/L for drinking water (US EPA, 2019). Thus, although perhaps a relatively small chloride source at the watershed scale, salt storage can have major impacts on proximal surface water and groundwater resources.

Residential water softener salt is an important chloride source in areas with "hard" water (i.e., high source-water calcium and magnesium concentrations). Nationally, the Salt Institute estimated that water softening accounts for 3.2 million t/y of salt (Salt Institute, 2009 as cited in Kelly, Panno, Hackley, Hwang Martinsek, & Markus, 2010). Water softening salt is discharged to wastewater treatment plants or subsurface sewage treatment systems (SSTS). Chloride mass discharge by softeners is affected by factors such as water use, water hardness, and softener efficiency. The brine discharged during softener resin regeneration has over

21,000 mg/L estimated chloride (Thomas, 2000). As Minnesota groundwater is generally hard, the Minnesota Pollution Control Agency (MPCA) identified water softeners as an important chloride source. The MPCA estimates approximately 100 Minnesota wastewater treatment plants have potential to exceed chloride water quality criteria based on monitoring data, chloride inputs of softener brine to these facilities, and the inability of these facilities to effectively treat for chloride (Kyser & Doucette, 2018).

Commercial and industrial entities can discharge high chloride loads, depending on activity type and intensity. Chloride contributions occur through industrial water softening and production processes. Minnesota industries with high chloride discharges include food processing, mining, and industrial and ethanol manufacturing (Overbo, Heger, Kyser, Asleson, & Gulliver, 2019). Many industries soften water for cooling or other processes. Businesses such as laundromats, restaurants, hotels, and car washes often soften water to improve cleaning and reduce detergent use (HDR Engineering, 2009).

Other domestic chloride sources include dietary salt excretion and household products. Many household products contain chloride, particularly bleaches. However, these are relatively minor chloride sources (Mullaney et al., 2009; Tjandraatmadja, Pollard, Sheedy, & Gozukara, 2002).

When households discharge wastewater through SSTSs, chloride may reach groundwater or surface waters. Domestic SSTS effluent chloride concentrations range from 21-5,620 mg/L (Panno, Hackley, Hwang, Greenberg, Krapac, Landsberger, & O'Kelly, 2006). SSTS plume chloride concentrations were at least two times above background, with maximums of 57-652 mg/L across Minnesota sites (Minnesota Pollution Control Agency, 1999). Collectively, over 25% of Minnesotans use a reported 537,354 SSTSs statewide (University of Minnesota Onsite Sewage Treatment Program, 2017; Robinson, 2018). Residential SSTS are estimated to discharge 33,100 t of chloride annually, which is largely attributable to water softening (Overbo et al., 2019).

Agricultural uses are also important sources of chloride in the environment. Nationally, potash fertilizer use increased until 1975 and has since plateaued (Kelly & Matos, 2013). A typical potash-based chloride application rate estimate is 49.9 kg/ha (Thunqvist, 2004; Novotny, Sander, Mohseni, & Stefan, 2009). Respective chloride concentration ranges (mg/L) were 5.7-36.5 (potash-applied fields) versus 0.7-1.7 (non-potash applied fields) in tile drainage (Panno et al., 2005).

Livestock waste can be an important chloride source in agricultural areas. Chloride concentrations reported for hog and horse excreta are between 440-1,980 mg/L (Panno et al., 2005). Respectively, open lots, earth-lined animal waste lagoons, and unlined lagoons had chloride concentrations 54, 54, and 203 mg/L higher in downgradient vs. upgradient monitoring wells; upgradient well concentrations were below 20 mg/L (Minnesota Pollution Control Agency, 2001). Minnesota has numerous concentrated animal feeding operations (CAFOs); for example, there are approximately 4 million pigs in 1,252 CAFOs statewide (Montgomery, 2015). Most Minnesota CAFO animal waste is applied to land. CAFO-associated chloride may migrate to groundwater or surface water via this land application, improper disposal, open feedlot runoff, or leaching from waste lagoons.

Chloride is also contributed to the environment in road-applied dust suppressants that contain calcium chloride or magnesium chloride and are generally applied once or twice annually. Typical application rates are 2.9-18.7 kg Cl/ha (Gesford & Anderson, 2007; Kestler, 2009; Piechota, van Ee, Batista, Stave, & James, 2004). In several Colorado streams, chloride concentrations were significantly higher downstream versus upstream of dust suppressant-treated roads (Goodrich, Koski, & Jacobi, 2009).

The above discussion indicates there are many anthropogenic sources to a Minnesota chloride budget, with deicers contributing nearly half of the chloride entering the environment (Figure 1). Concomitant environmental impacts are discussed in the next section.

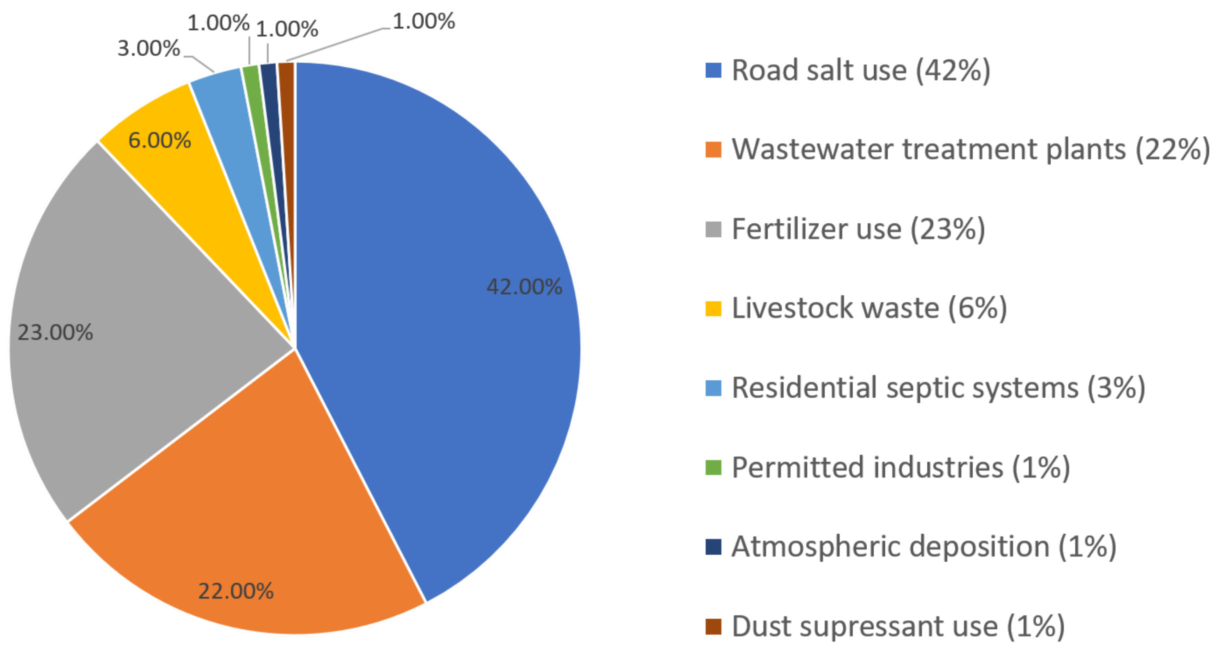

Figure 1. Chloride contributions to the environment. Chloride released to the environment is illustrated for major sources, expressed as a fraction of the total annual chloride budget for Minnesota. From Overbo et al. (2019).

1.4 Environmental Impacts of Chloride

Minnesota Rules, Chapter 7050, establish chronic and acute Class 2 water quality standards for chloride at 230 mg/L and 860 mg/L, respectively. Elevated surface water chloride concentrations have many negative effects on plants and aquatic life, including reduced amphibian survival (Dougherty & Smith, 2006; Karraker, Gibbs, & Vonesh, 2008), aquatic insect diversity (Demers, 1992), algal density (Dickman & Gochnauer, 1978), and bacterial density (Dickman & Gochnauer, 1978). Elevated chloride concentrations reduce species richness among amphibians (Collins & Russell, 2009), macroinvertebrates (Williams, Williams, & Cau, 1997), and bog and marsh vegetation (Miklovic & Galatowitsch 2005; Richburg, Patterson, & Lowenstein, 2001; Wilcox, 1986).

Chloride does not degrade and thus gradually accumulates in water resources when inputs exceed exports. Elevated lake chloride concentrations may inhibit mixing and turnover by increasing deep-water density. This contributes to redox stratification, methane accumulation (Dupuis, Sprague, Docherty, & Koretsky, 2019), and oxygen depletion in the hypolimnion (Novotny & Stefan, 2012; Sibert, Koretsky, & Wyman, 2015; Novotny, Murphy, & Stefan, 2008a; Wyman & Koretsky, 2018). For example, Brownie Lake (TCMA) is saline and meromictic, with a permanent saltwater layer that prevents turnover (Swain, 1984), which is attributed to accumulated deicers from I-394 and other major traffic arteries (Murphy & Stefan, 2006).

In soils, sodium can decrease soil permeability through clay dispersion, thus contributing to increased erosion and overland flow (Ramakrishna & Viraraghavan, 2005). Elevated chloride is also a suggested cause of nutrient release from sediment and soil. Elevated soil chloride may induce manganese and iron reduction and increase the dissolution of phosphorus and toxic trace metals (e.g., copper, zinc) (Kim & Koretsky, 2011). Salts, particularly sodium, also mobilize trace metals in roadside soils. Sodium chloride may decrease total organic carbon in shallow groundwater (Norrström & Jacks, 1998) and increase mobility of calcium and some toxic metals (particularly cadmium and zinc) in soils while retarding others with affinities for organic matter (e.g., lead, copper)(Bäckström, Karlsson, Bäckman, Folkeson, & Lind, 2004; Paus, Morgan, Gulliver, Leiknes, & Hozalski, 2014). Calcium and magnesium released through soil exchange with sodium increases surface water pH and dissolved salt concentrations. This may increase mussel shell thickness and impact CO2 uptake in coastal waters, which has global climatic implications (Kaushal, Groffman, Likens, Belt, Stack, & Kelly, 2018).

Elevated chloride imparts a salty taste to water, which may cause people to stop using their drinking water supply. To minimize taste problems with public drinking water, the EPA set a 250 mg/L chloride Secondary Maximum Contaminant Level (SMCL). SMCLs are not enforced, but provide guidelines for public drinking water suppliers to manage aesthetic issues. However, the chloride SMCL was adopted as a Minnesota Class 1 domestic consumption use standard and thus applies to all our groundwater. Although human health impacts are not associated directly with chloride, they are for some chloride-bound ions; for instance, elevated sodium is a hypertension risk factor. Additionally, elevated drinking water chloride increases corrosion and promotes lead release from pipes and fixtures (Edwards & Triantafyllidou, 2007; Stets, Lee, Lytle, & Schock, 2018; Pieper, Nystrom, Parks, Jennings, Faircloth, Morgan, Bruckner, & Edwards, 2018). For example, Edwards & Triantafyllido (2007) observed that chloride-to-sulfate concentration ratios above 0.5 resulted in lead leaching from solder connections in copper drinking water pipes, with lead found in all monitored systems, frequently above Safe Drinking Water Act action concentrations.

Chloride is also a concern in communities where wastewater treatment plants do not meet chloride water quality standards. Methods to remove chloride from water resources (e.g., reverse osmosis) are capital-intensive and can present additional environmental challenges (e.g., energy requirements, wastewater disposal).

Corrosion of vehicles and steel reinforcements used in bridges, roads, and other infrastructure by chloride runoff presents major design, maintenance, and fiscal challenges for concrete and metal structures and products (Tang, Boubitsas, Utgennant, & Abbas, 2018). For example, Sohanghpurwala (2008) estimated that one ton (0.907 metric ton) of chloride deicer causes $1,460 in damages to TCMA bridges.

2.0 Chloride in Stormwater, Surface Waters, and Groundwater

This chapter provides a brief discussion of chloride concentrations found in urban stormwater, surface waters, and groundwater.

2.1 Chloride in Stormwater Runoff

Chloride concentrations in urban stormwater runoff vary temporally and spatially, primarily in response to deicer applications. During winter months (typically December to March), median runoff concentrations (mg/L) typically range from hundreds to thousands, with maximum concentrations of thousands to tens of thousands, in areas receiving deicer applications. Several factors affect runoff concentration, including deicer application rate (positive correlation), time since runoff initiation (negative correlation), and runoff volume (negative correlation) (Herb, Janke, & Stefan, 2017; Machusick & Traver, 2009; Granato & Smith, 1999; Drake, 2013). At two Minnesota sites, winter highway runoff accounted for just 16% of annual runoff volume but 97% of annual chloride mass exported in runoff; runoff with ≥350 mg/L chloride accounted for only 4% of annual runoff volume but 90% of total chloride mass transport (Herb, Janke, & Stefan, 2017). In that study, chloride concentrations (mg/L) ranged from 683-9,278 in highway runoff and 254-1,346 in an adjacent ditch.

Non-winter runoff from impervious surfaces typically has much lower chloride concentrations that nevertheless vary with winter deicer applications. In spring following snowmelt, median concentrations (mg/L) are typically 50-100 versus less than 10 in areas with and without winter deicing, respectively (Winston, Davidson-Bennett, Buccier, & Hunt, 2016; Herb et al., 2017; Machusick & Traver, 2009; Granato & Smith, 1999; Drake, 2013). Concentrations decrease through summer and are generally less than 20 mg/L by autumn. This suggests gradual residual chloride release from soil following the deicing season.

Permeable pavements receive lower salt application rates than traditional pavements. In runoff from traditional asphalt pavements receiving deicers in Guelph, Ontario, mean chloride concentrations in winter were 5,177 mg/L versus 3.4 mg/L in spring and summer (Drake, 2013). The maximum winter concentration was greater than 40,000 mg/L, and several samples had greater than 10,000 mg/L chloride. In contrast, mean winter runoff concentrations from porous interlocking concrete pavers and porous concrete were 359-543 mg/L due to lower salt application rates (Drake, 2013).

Additional important chloride sources to runoff include salt storage facilities and snow storage piles. Runoff from salt storage facilities in Charlottesville, Virginia, contained chloride concentrations of 597-2,604 mg/L (median: 1,665 mg/L) (Fitch, Smith, & Bartelt-Hunt, 2004). At a municipal snow storage and disposal site in Ontario, chloride concentrations in snow pile samples reached 6,300 mg/L, and the average snow pile meltwater concentration was 4,200 mg/L (Exall, Rochfort, & Marsalek, 2011).

Several studies report occurrences of an initial, high-concentration chloride “flush” during runoff events in deicing seasons. For example, Granato and Smith (1999) observed an initial runoff pulse with approximately 4,200 mg/L chloride that lasted approximately four hours; concentrations decreased to 550 mg/L for the remainder of the event. Other researchers observed similar high initial concentration patterns in runoff (Dugan, Bartlett, Burke, Doubek, Krivak-Tetley, Skaff, Summers, Farrell, McCullough, Morales-Williams, Roberts, Ouyang, Hanson, & Weathers, 2017; Rivers, 2011). First flush patterns also occurred in summer, but with peak concentrations less than 100 mg/L.

2.2 Chloride in Surface Waters

In Minnesota, 50 lakes and rivers exceed the chronic chloride criterion of 230 mg/L and are classified as impaired. Forty-one of these waters have US EPA-approved chloride Total Maximum Daily Loads (TMDLs). An additional 120 surface waters are "high risk", meaning one sample in the last 10 years was within 10% of the chronic criteria. The MPCA's Chloride Project website contains information on chloride in Minnesota's surface waters, including an interactive map showing assessed, impaired, unimpaired, and high risk waters.

From roughly 1950 onward, many northern U.S. and Canadian streams in both urban (Mullaney, Lorenz, & Arntson, 2009) and rural watersheds (Kaushal et al., 2005) showed increasing chloride concentrations that tracked with increased in-catchment deicer use (Kostick, Milanovich, & Coleman, 2007; Kelly & Matos, 2013). Similarly for Minnesota lakes, fossil evidence-based chloride concentration reconstructions show significant increases over the last 50 years (Ramstack, Fritz, & Engstrom, 2004). In U.S. regions with heavy chloride deicer use, surface water chloride concentrations have doubled since 1990 (Corsi, De Cicco, Lutz, & Hirsch, 2015). Due to increased deicer use since 1984, chloride concentrations were 25 times greater in urban vs. non-urban Minnesota lakes (Novotny, Murphy, & Stefan, 2008a).

Several studies have correlated groundwater and in-stream chloride concentrations to impervious cover (Kaushal et al., 2005; Howard & Maier, 2007; Cunningham, O'Reilly, Menking, Gillikin, Smith, Foley, Belli, Pregnall, Schlessman, & Batur, 2009; Gardner & Royer, 2010) and road density (Rhodes, Newton, & Pufall, 2001; Heisig, 2000; Halstead, Kliman, Berheide, Chaucer, & Cock-Esteb, 2014). Among 371 midwestern and northeastern North American lakes, most urban and rural lakes with greater than 1% surrounding impervious cover exhibited long-term chloride concentration increases (Dugan et al., 2017). Likewise, among individual TCMA lakes, chloride concentrations correlated strongly with catchment urbanization (Ramstack, Fritz, & Engstrom, 2004).

Another factor potentially contributing to elevated chloride concentrations in surface water is infiltration of chloride into shallow groundwater and subsequent transport to surface water as baseflow. Surface waters with significant baseflow contribution typically have elevated chloride concentrations throughout the year but decreased peak concentrations in winter compared to surface waters with little or no baseflow contribution (Stirpe, Cunnignham, & Menking, 2017; Perera, Gharabaghi, & Howard, 2013).

2.3 Chloride in Groundwater

Anthropogenically-derived chloride is gradually accumulating and increasing in concentration in groundwater in northern climates. This is particularly true of urban areas, where increases primarily stem from deicing chemical use (Kelly, Panno, & Hackley, 2012; Cassanelli & Robbins, 2013; Medalie, 2013). Here, chloride sources, monitoring, and general occurrence patterns in Minnesota's groundwater are discussed.

2.3.1 Sources to Groundwater

Chloride is naturally present in groundwater. Many minerals comprising sand and gravel aquifers and bedrock contain chloride, and weathering can release some or all of it to groundwater. Sedimentary rocks, especially those containing halite (sodium chloride, often called "rock salt"), usually have more chloride than igneous rocks. In very old groundwater, natural chloride results from connate water in marine sedimentary deposits (Hem, 1985). This chloride type occurs in hydrogeologic settings with very slow aquifer recharge and thus limited flushing of natural chloride (Berg & Harold, 2018), or where water flows upward from deep, isolated aquifers to shallow aquifers (Berg, Johnson, & MacDonald, 2016). Some aquifers contain chloride naturally transported from saline aquifers.

Elevated chloride concentrations, particularly in shallow groundwater, are often related to human use near pollution-sensitive aquifers. Monitoring of chloride and bromide in the groundwater showed chloride-based deicers are the predominant chloride source in urban areas. In Minnesota urban areas, chloride-to-bromide (Cl:Br) ratios were greater than 1,000 in over half of sand and gravel aquifer wells sampled from 2007-2011, suggesting a halite source (Kroening & Ferrey, 2013). In almost 60% of bedrock aquifer wells, primarily in the Prairie du Chien-Jordan aquifer, Cl:Br ratios were >300, suggesting wastewater or mixed halite and native groundwater sources.

A study from the Toronto metropolitan area estimated 40% of deicer-applied chloride entered the underlying shallow aquifer (Perera, Bahram, & Howard, 2013). A significant amount of chloride appears to be retained in groundwater, likely due to long residence times. Novotny, Sander, Mohseni, & Stefan (2009) estimated 77% of applied chloride deicer was retained in the TCMA watershed, though the authors did not determine the amount of chloride retained in groundwater (e.g. compared to lakes, soil, etc.). The authors cited retention rates ranging from 28%-65% in other metropolitan areas. The authors reported temporally increasing concentration trends in several TCMA lakes and shallow groundwater, but did not calculate chloride retention in these sinks.

Using Chloride to Bromide Ratios to Determine Chloride Sources

In natural groundwater systems, both chlorine and bromine occur primarily as monovalent anions, chloride and bromide. Ratios of chloride to bromide (Cl:Br) differ for different sources. Atmospheric precipitation will generally have mass ratios between 50 and 150, shallow groundwater not affected by human-caused contamination between 100 and 200, domestic sewage between 300 and 600, water affected by dissolution of halite between 100 and 10,000, and summer runoff from urban streets between 10 and 100. Since movement of chloride and bromide ions in groundwater is generally conservative, Cl:Br ratios are useful in the reconstruction of the origin and movement of groundwater (Davis et al., 2005). Other specific Cl:Br ratios reported in the literature include 13,500 for deicers, 4289 for softener salt, 510 for potash (KCl), 292 for ocean water, and 90 for soil water (Panno et al., 2006).

The unsaturated zone stores some of this retained chloride. Lax and Peterson (2008) investigated the transport of chloride in the unsaturated zone near a roadway in Illinois that received deicing chemical applications. Modeling conducted as part of this study showed chloride concentrations in the unsaturated zone near the roadway remained high after the source was removed, even after one year. Long-term modeling projections showed that chloride inputs and outputs to the unsaturated zone reached an equilibrium after about a decade, and the accumulated chloride became a long-term source to the underlying groundwater.

2.3.2 Groundwater Monitoring in Minnesota

Chloride monitoring in Minnesota is mainly conducted by state, local, and federal agencies. State agencies collect data to meet statutory roles and responsibilities to protect the state's groundwater. The USGS monitored chloride for the National Water Quality Assessment (NAWQA) and conducts cooperative studies with state, local, and tribal governments. Approximately 19,000 Minnesota wells have been tested for chloride since 1932 (Appendix A), the majority of which were domestic wells. The MPCA, MDA, and USGS analyze chloride from monitoring wells near the water table, which represent <10% of the aforementioned data.

Minnesota Pollution Control Agency (MPCA)

The MPCA primarily collects chloride data in pollution-sensitive urban aquifers for its Ambient Groundwater Monitoring Network Program. "Ambient" refers to groundwater not affected by localized contamination, spills, or leaks. Many data were also collected in the 1990s for an assessment of Minnesota's principal aquifers (MPCA, 1998a) and land use studies (MPCA, 2000a; MPCA, 2000b; MPCA, 2001; Trojan, Maloney, Stockinger, Eid, & Lahtinen, 2003).

MPCA's ambient network design has been described in detail (Kroening & Ferrey, 2013; Kroening & Vaughan, 2019). Briefly, it consists of about 270 wells which are primarily in urban areas. All of these wells are sampled annually for chloride; this is one of the few networks in the state that has sufficient data to determine whether concentrations in the groundwater are changing. The network wells mostly are shallow but also include some deep monitoring wells. The shallow wells are an "early warning system" whereby MPCA can understand chemicals rapidly transported to groundwater, land use effects on groundwater quality, and shallow groundwater trends. The deep, primarily domestic, wells in the Prairie du Chien-Jordan aquifer provide information on Minnesotans' drinking water quality and the fate of contaminants previously transported to shallow groundwater.

Minnesota Department of Agriculture (MDA)

Chloride data are collected occasionally from MDA's ambient monitoring network, which is described in detail by the MDA (2011). In 2014, MDA cooperated with MPCA to sample this network for chloride.

Minnesota Department of Natural Resources (DNR)

The DNR collects chloride data for routine production of county groundwater atlases across Minnesota. For each atlas, wells in aquifers most important for domestic and community water supply are sampled. Berg (2019) describes the well network sampling design for atlases produced since 2013.

MDH

MDH collects chloride data for its drinking water protection programs. These programs focus on Minnesota's 7,000 public water suppliers, which by definition serve at least 25 people. The water samples are collected by MDH staff or a facility's water operators.

USGS

The USGS assessed groundwater chloride concentrations for National Water Quality Assessment (NAWQA) studies and periodically for cooperative studies with state, local, and tribal governments. Two NAWQA studies were conducted in Minnesota: one in the Red River of the North Basin, and the other in the Upper Mississippi River Basin.

Dakota County

Dakota County monitors groundwater chloride concentrations for ambient monitoring and special studies. Dakota County's Ambient Groundwater Quality Study (AGQS) focuses on sampling untreated groundwater from about 80 rural domestic wells in the sand and gravel, Prairie du Chien, and Jordan aquifers (Dakota County, 2006). The County collected chloride data from private wells in rural residential areas with SSTSs in Burnsville, Lakeville, Greenvale Township and Inver Grove Heights (Scher & Demuth, 2017). Eighty-five to 92 percent of these wells supplied households that that discharge water softener brine to the SSTS. In addition, two wells near highways in the Vermillion River Watershed were tested frequently for conductivity in March-April 2014.

Dakota County collects sufficient data to quantify changes in chloride concentrations in the groundwater. All wells in the AGQS are sampled annually for chloride. In 2014, Dakota County sampled two wells frequently for conductivity during spring snowmelt. Select samples from the two wells were analyzed for chloride; when chloride levels are above 25 mg/L, conductivity is a good surrogate for chloride (p-value = 0.001). One of them appeared to be impacted by deicer in runoff from US Highway 52 with a maximum chloride result of 282 mg/L (V. Demuth, personal communication).

Olmsted County

Olmsted County collects chloride data from its long-term groundwater monitoring network. Established in 1989 primarily to track agricultural-related contamination, monitoring occurs for the full anion suite (nitrate, nitrite, chloride, sulfate, and fluoride), coliform bacteria, cations, pesticides, and volatile organic compounds. Chloride data is used as an indicator of contamination from anthropogenic sources (e.g. fertilizer, septic, road salt etc.). The monitoring network assesses agricultural contamination that originates in the Galena aquifer, flows laterally along the Decorah shale aquitard to areas where this shale is fractured or absent, and then travels downward to the St. Peter, Prairie du Chien, and Jordan aquifers. The network includes wells from each of the aquifers mentioned. The most pronounced chloride contamination monitored by this network likely occurs in the vicinity of Rochester, where chloride moves directly downward from the land surface to the Prairie du Chien aquifer and subsequently is transported to the Jordan aquifer. The County also maintains a database of well chloride testing required for property transactions since 1970.

2.3.3 General Distribution in Groundwater

High chloride concentrations in Minnesota groundwater are usually related to human chloride use in naturally pollution-sensitive areas. These areas typically have near-surface aquifers covered by thin layers of permeable sandy sediment that readily allow water and chloride to flow through them. In addition, karst areas, which originate primarily by dissolution of soluble rocks like limestone, are very sensitive to pollution since karst features (e.g., sinkholes, conduits, and caves) allow rapid subsurface water and chloride transport.

In Minnesota, the largest anthropogenic chloride concentrations, indicated by red triangles in Figure 2, often occur in groundwater beneath urban areas, especially the Twin Cities Metropolitan Area (TCMA), St. Cloud, and some smaller cities including Cloquet and Moose Lake. The greatest concentrations generally occur in very shallow wells, which strongly suggests surficial chloride sources.
Aquifers beneath some cities (e.g., western Hennepin County cities and Mankato) have low pollution-sensitivity, and high chloride concentrations are not evident in their

groundwater. In these areas and western Minnesota, elevated anthropogenic chloride concentrations are far less common owing to the fine-grained surficial materials that cover the aquifers.

Some unpolluted Minnesota aquifers nonetheless contain groundwater with naturally high background chloride concentrations of 1500-2,000 mg/L (Maclay, Winter, & Bidwell, 1972; Woodward & Anderson, 1986). These include buried sand and gravel aquifers in western Minnesota, the Red River and Winnipeg aquifers of northwestern Minnesota, some crystalline bedrock aquifers along Lake Superior in northeastern Minnesota, and some Cretaceous aquifers in south-central and southwestern Minnesota (Winter, 1974).

Chloride concentrations are stratified in the series of aquifers underlying southeastern Minnesota. High concentrations (shown in red in Figure 2) often are observed near the water table, especially near urban areas, due to the human use of this chemical for pavement deicing, water softening, and other activities. Kroening and Vaughan (2019) reported that the median concentration was 17.7 mg/L in ambient groundwater near the water table in the sand and gravel aquifers. Concentrations as high as 815 mg/L were measured.

Concentrations in most of the underlying aquifers, except the Mount Simon-Hinckley, progressively decrease from a median concentration of 13.2 mg/L in the Galena aquifer to 1.4 mg/L in the Tunnel City aquifer (Kroening & Vaughan, 2019). Tipping (2012) attributed the presence of elevated concentrations in these aquifers to recently recharged water which contains anthropogenically derived chloride. High chloride concentrations naturally occur in the lowermost aquifer in this series, the Mount Simon-Hinckley aquifer, with concentrations as high as 130.9 mg/L (Berg & Pearson, 2012).

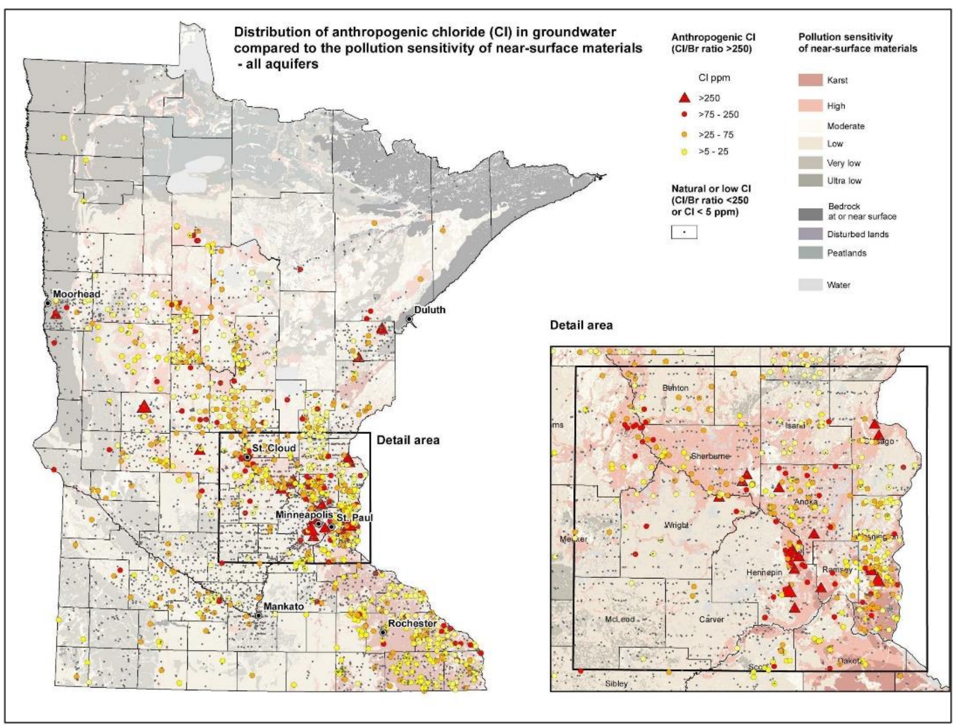

Figure 2. Chloride concentrations related to anthropogenic sources in Minnesota's groundwater. Triangles show locations where samples exceed the drinking standard of 250 mg/L. Groundwater sensitivity to pollution is illustrated by different shading patterns, with areas in pink having high pollution sensitivity [Groundwater sensitivity to pollution data from Adams (2016)].

2.3.4 Chloride in Urban Minnesota Groundwater

Understanding chloride's fate in Minnesota's urban areas is essential to predicting long-term impacts to receiving waters and developing management strategies to minimize these. Chloride accumulated in shallow groundwater can travel in baseflow to surface waters (Eyles & Meriano, 2010) and contribute to their long-term salinization (Paul & Meyer, 2001; Rosenberry, Bukaveckas, Buso, Likens, Shapiro, & Winter, 1999). This chapter summarizes chloride monitoring in urban Minnesota areas. This includes chloride distribution in urban Minnesota groundwater, land-use effects, seasonality, temporal trends, and groundwater discharge to surface waters (baseflow).

Distribution in Urban Areas

Chloride concentrations are highly variable in the shallow sand and gravel aquifers beneath Minnesota's urban areas (median: 17 mg/L; range: <1 mg/L- 8,900 mg/L (Kroening & Ferrey 2013; Kroening & Vaughan, 2019), but the TCMA typically shows the greatest concentrations (median: 86 mg/L). The majority of wells exceeding the chloride SMCL or Minnesota Class 1 standard are in the TCMA. Twenty-seven percent of sand and gravel aquifer wells in the TCMA had concentrations above 250 mg/L. Only about 1% of non-TCMA wells exceeded the chloride SMCL or Minnesota Class 1 standard. These were primarily in central Minnesota (Figure 2, Minnesota Department of Natural Resources, 2016a).

Most groundwater samples that exceeded the 250 mg/L chloride SMCL were from wells <10 m deep. Chloride also exceeded the SMCL in 14 of the 6,056 wells with depths of 16-154 m (concentration range: 260-1,640 mg/L).

Land-use Effect

MPCA and USGS have studied land-use effects on Minnesota's groundwater chloride concentrations at various scales since the 1990s. In an early land-use-related groundwater assessment, Anderson (1993) studied about 100 wells in a five-county area of the Anoka Sand Plain northwest of the TCMA. Trojan et al., (2003) studied 23 St. Cloud-area wells to assess agricultural, urban, and forested land use effects. For NAWQA, Fong (2000) monitored chloride in about 75 shallow groundwater wells under a northwest TCMA urban-residential area, an Anoka Sand Plain (central Minnesota) agricultural area, and a forested area near Bemidji. Kroening and Vaughan (2019) updated this analysis with chloride data from >300 Minnesota wells. Almost 200 of these are in MPCA's ambient monitoring network; the rest are in MDA's ambient network, which focuses on agricultural areas.

These studies all reported that groundwater chloride concentrations were lowest beneath forested lands (study medians: 1.1-3.5 mg/L), and highest in shallow wells beneath commercial/industrial areas (e.g., median of 43 such wells: 81.9 mg/L (Kroening & Vaughan, 2019). This value is greater than typically reported for other urban and agricultural areas (Table 1). Trojan et al. (2003) found relatively high shallow groundwater chloride concentrations in residential areas (median concentrations of 78.8 mg/L in areas served by municipal sewers and 82.7 mg/L in areas served by SSTS), but this represented a small sample size. The second-highest chloride concentrations were typically measured in groundwater beneath residential settings (median: 16.1-46 mg/L (Table 1)); recent data suggest that median concentrations are about three times greater beneath sewered than unsewered residential areas (Table 1). Groundwater concentrations beneath agricultural lands (median: 14.1-17 mg/L) were lower than in urban settings (Table 1), with greater concentrations beneath irrigated than non-irrigated agricultural areas possibly due to increased fertilizer and recharge inputs.

In many urban areas, constructed stormwater ponds are the primary treatment practice, and data collected by Dakota and Olmsted Counties suggest these ponds may locally affect groundwater chloride concentrations. Though designed as sedimentation practices with low seepage rates, stormwater ponds eventually generate groundwater chloride plumes. A study in Inver Grove Heights, Minnesota, reported 30% greater chloride concentrations in wells within 150 m of ponds versus wells farther away. A similar study in Rochester, Minnesota (Crawford, 2019), found no difference in chloride concentrations between wells within 1.6 km and those farther from ponds. These studies indicate that stormwater ponds significantly affect urban groundwater chloride concentrations locally, but may not regionally. Geologic conditions most likely determine how much an individual pond affects groundwater. For example, stormwater infiltration may impact the groundwater less in areas with low permeability materials, such as clay or shale.

Elevated chloride concentrations were also observed in bedrock aquifers beneath pollution-vulnerable TCMA areas. A median concentration of 66 mg/L (maximum chloride detected was 451 mg/L) was recorded for 66 Burnsville domestic wells that were mainly installed in the St. Peter or Prairie du Chien aquifers (V. Demuth, personal communication). In 2015-2017 samples from Inver Grove Heights domestic wells in the Prairie du Chien and Jordan aquifers, respectively, the median concentrations were 14.7 and 18.7 mg/L (maximum chloride detected was 288 mg/L) (V. Demuth, personal communication), compared to a 3.0 mg/L median reported for non-TCMA wells in the same aquifers (Kroening & Vaughan, 2019). In 2019, sampling of 89 private wells in rural Greenvale Township, found a median of 3 mg/L (maximum chloride detected was 110 mg/L) and a median of 4.0 mg/L in 100 private wells in Lakeville (maximum chloride detected was 225 mg/L). Deicers were not the only chloride source to the private wells in Dakota County; most households using these wells have water softeners and SSTSs.

Study	Land Use					
	Commercial/ Industrial	Residential Sewered	Residential SSTS	Agriculture Irrigated	Agriculture Non-irrigated	Forest
Anderson (1993)	NA	NA	26 mg/L (29)	19 (35)	5.3 (25)	3.5 (11)
Fong (2000)	NA	46 (30)	NA	17 (29)		1.2 (15)
Trojan et al. (2003)	59.0 (3)	78.8 (3)	82.7 (3)	40.9 (3)	15.5 (3)	1.8 (3)
Kroening and Vaughan (2019)	81.9 (43)	44.6 (50)	16.1 (51)	14.1 (113)		1.1 (50)

Table 1: Median chloride concentrations (mg/L) in shallow groundwater beneath various land uses, by study. The number of wells sampled for each study is shown in parenthesis [NA: not available].

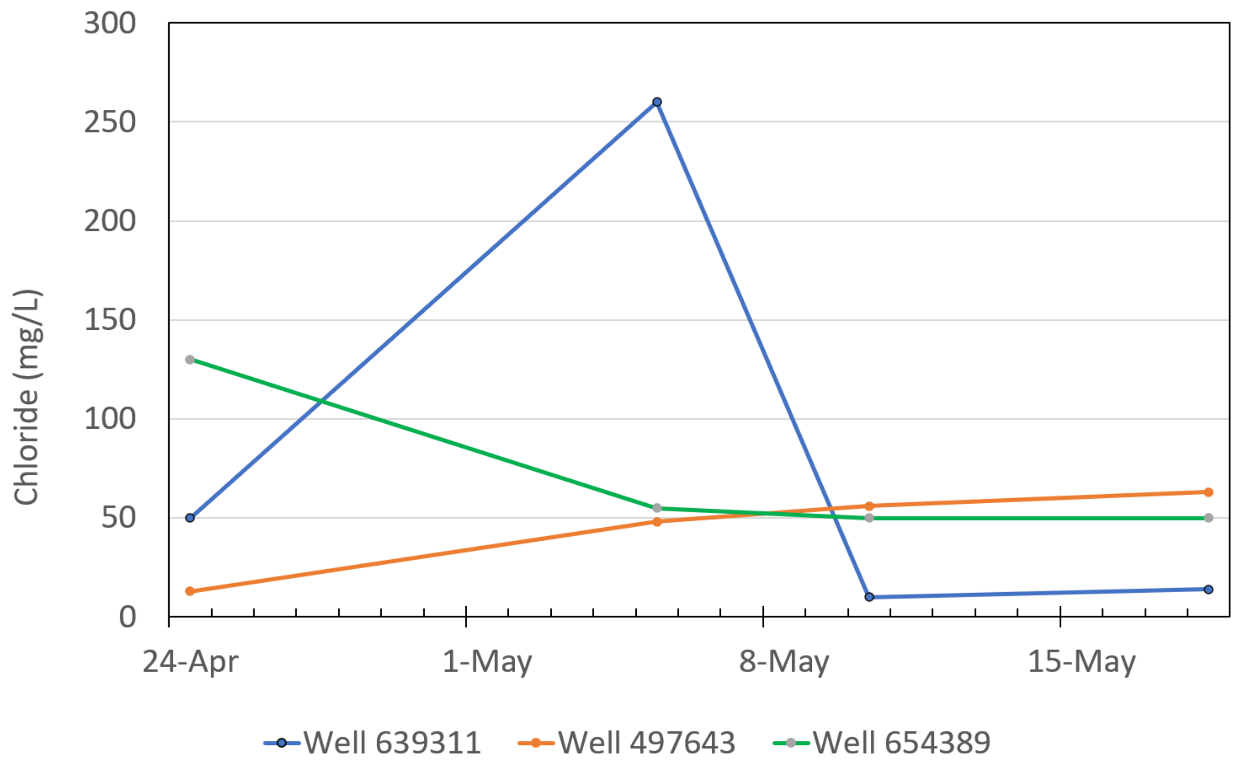

Figure 3. Seasonal concentration patterns from three shallow Hennepin County wells. Plots illustrate short-term fluctuations in chloride concentrations in wells 639311, 497643, and 664389, April-May 2006.

Seasonal Effects

Few Minnesota data have been collected for assessing seasonal or short-term fluctuations in chloride concentrations in Minnesota's shallow urban groundwater, and these limited data have not suggested consistent seasonal or short-term chloride concentrations patterns.

Trojan et al. (2003) sampled nine wells in various urban settings four times annually for chloride from 1997-2000. No significant difference was found among chloride concentrations by season. The MPCA collected chloride samples weekly from four shallow Hennepin County wells (4.6-8.5 m deep) from late April through May 2006. The short-term chloride variability in each well was vastly different, likely due to chloride source proximity, precipitation timing, soil infiltration characteristics, and local hydrogeology (Figure 3). The USGS reported similar results in shallow agricultural groundwater in west-central

Temporal Trend

MPCA analyzed their Ambient Groundwater Monitoring Network data available to 2011 (Kroening & Ferrey, 2013), and reported increasing chloride concentration trends in over 30% of sampled wells. The majority of sampled wells were in sewered residential areas having chloride data since the mid-1990s; some wells near Bemidji had data since 1987.

Kroening and Vaughan (2019) updated this analysis with data from a common period of record (2005-2017) when MPCA's ambient network had been in place for greater than 10 years and represented Minnesota's urban areas more broadly than in the previous trend analysis. Well trend analysis was feasible near Austin, Rochester, and Wabasha, along with (previously analyzed) Brooklyn Center, Bemidji, and St. Cloud. This analysis also included more wells in the Prairie du Chien and Jordan aquifers; some were 100 m deep. Of the 14 wells with identified increasing chloride trends, 7 were in the Prairie du Chien and Jordan aquifers and three in the Galena and St. Peter aquifers (southern MN), at depths of 27-103 m (Appendix B). The average increase was 1.4 mg/L/y), with the greatest increases occurring in water table wells. Significant upward chloride trends were also found in four of 20 shallow sand and gravel monitoring wells in heavily urbanized TCMA and St. Cloud areas (median increase: 3.7 mg/L/y).Dakota County reported similar temporal trends using 1999-2018 data. Thirty of 67 monitored wells (45%) had increasing chloride trends (median increase: 0.55 mg/L/y), and only one had a decreasing trend. The wells with increasing trends were split among the sand and gravel (33%), Prairie du Chien (46%), and Jordan (20%) aquifers, with no clear pattern of geographic location among them (Figure 4). The 23 wells (34%) with chloride concentrations >3 mg/L and no significant trend were assumed in steady state with chloride sources.

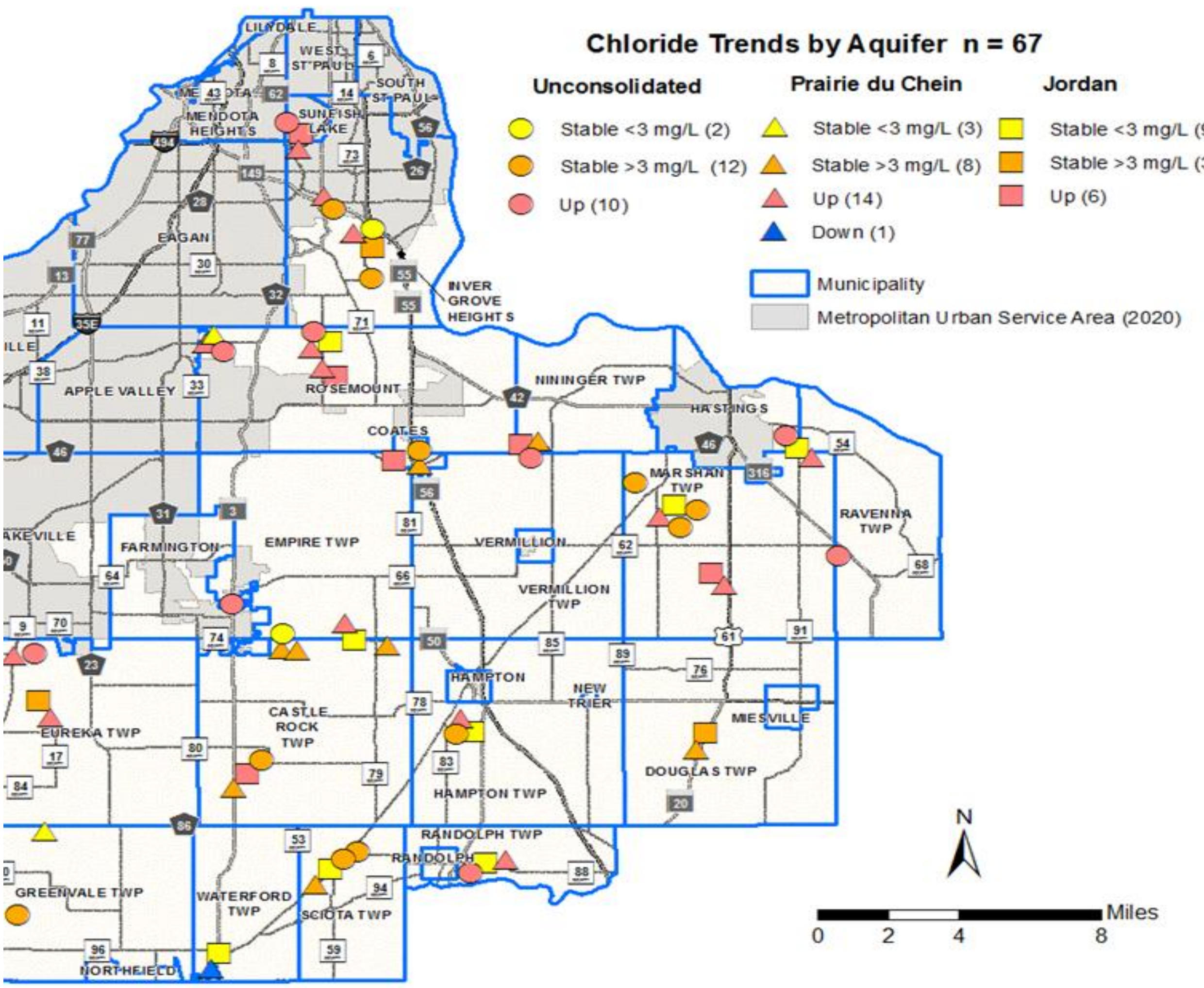

Figure 4. Ambient chloride trends in Dakota County private water wells, 1999-2018. Darker red colored symbols illustrate wells with increasing concentration trends in surficial (unconsolidated) aquifers and in the Prairie du Chien and Jordan aquifers. Prepared by Stephen Scott of Dakota County Environmental Resources Department.

2.4 Groundwater Discharge to Surface Water

In many Minnesota areas, groundwater discharges locally to lakes and streams. In urban areas with elevated groundwater chloride concentrations, this baseflow is an important component. In areas with deicing activities, baseflow should diminish peak surface water concentrations in winter but increase concentrations in other seasons. Shallow groundwater with concentrations over Minnesota's 230 mg/L chloride Aquatic Life Standard will contribute to surface water impairments, while groundwater with lower concentrations may mitigate them. For example, Bassett Creek has an important baseflow component that reduces winter peak concentrations but increases concentrations the remainder of the year. Conversely, Miller Creek has limited baseflow, and its concentrations thus mirror stormwater runoff concentrations (i.e., very high winter and low summer chloride concentrations). Figure 5 illustrates these concepts.

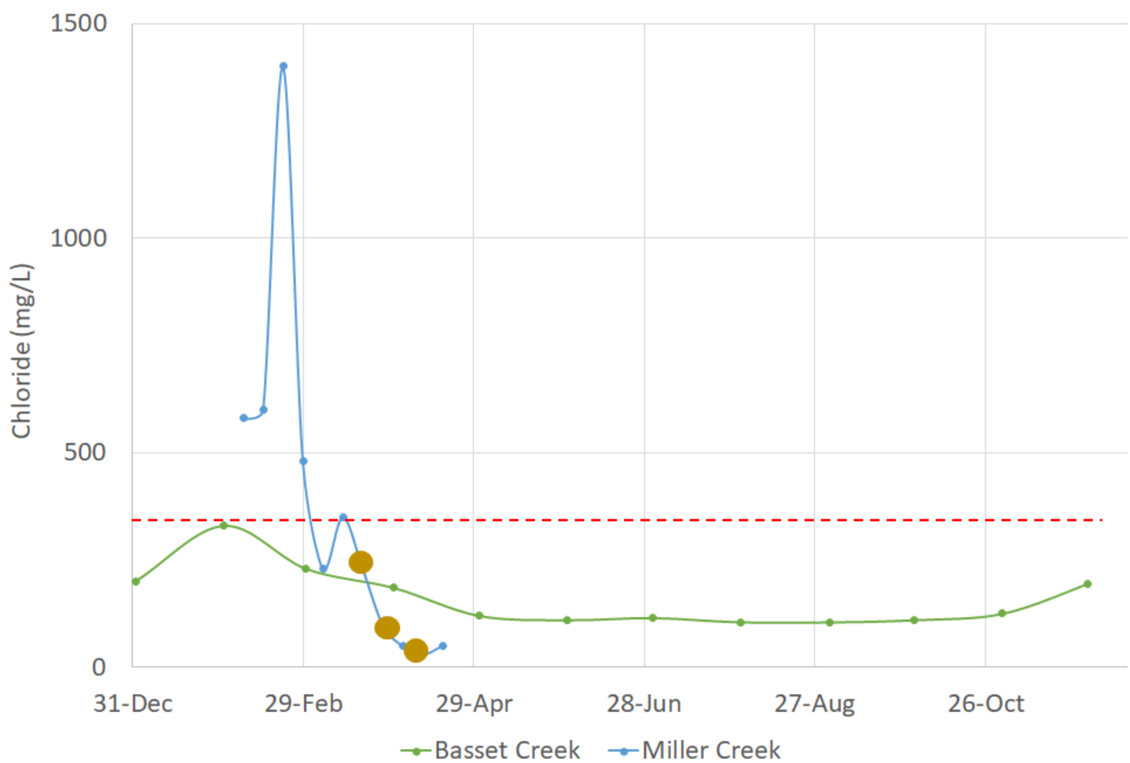

Figure 5: Chloride concentrations in two creeks with different baseflow components. Bassett Creek (Minneapolis) has a large baseflow component and Miller Creek (Duluth) has a negligible baseflow component. The three brown circles represent measured chloride concentrations in stormwater runoff samples in Duluth. The water quality standard of 230 mg/L is shown as a red dashed line.

3.0 STORMWATER INFILTRATION

This chapter discusses stormwater infiltration practices and chloride fate within them. This includes estimated relative chloride loadings from stormwater infiltration practices versus other sources to groundwater.

3.1 Infiltration Stormwater Control Measures

Infiltration stormwater control measures (SCMs, also known as best management practices or BMPs) capture and temporarily accept large runoff volumes and focus infiltration in a relatively small area. For example, a 93 m^2 (1,000 ft^2) infiltration basin designed to instantaneously capture 2.54 cm of runoff from 0.4 ha (1 ac) of impervious surface (drainage area ratio of 43.5:1) constructed in a sand (native sand, not engineered media) location that receives 76 cm precipitation annually will infiltrate about 28 m water store stormwater runoff. SCMs are typically designed to infiltrate runoff into the underlying soil within 48 hours (Figure 6). Infiltration SCMs annually; a similar basin constructed in loamy soil will infiltrate about 15 m water.

Infiltration SCMs include bioinfiltration, infiltration trenches and basins, infiltration swales, and permeable pavement (Figure 7). Although these SCMs utilize similar design principles, there are important differences discussed below.

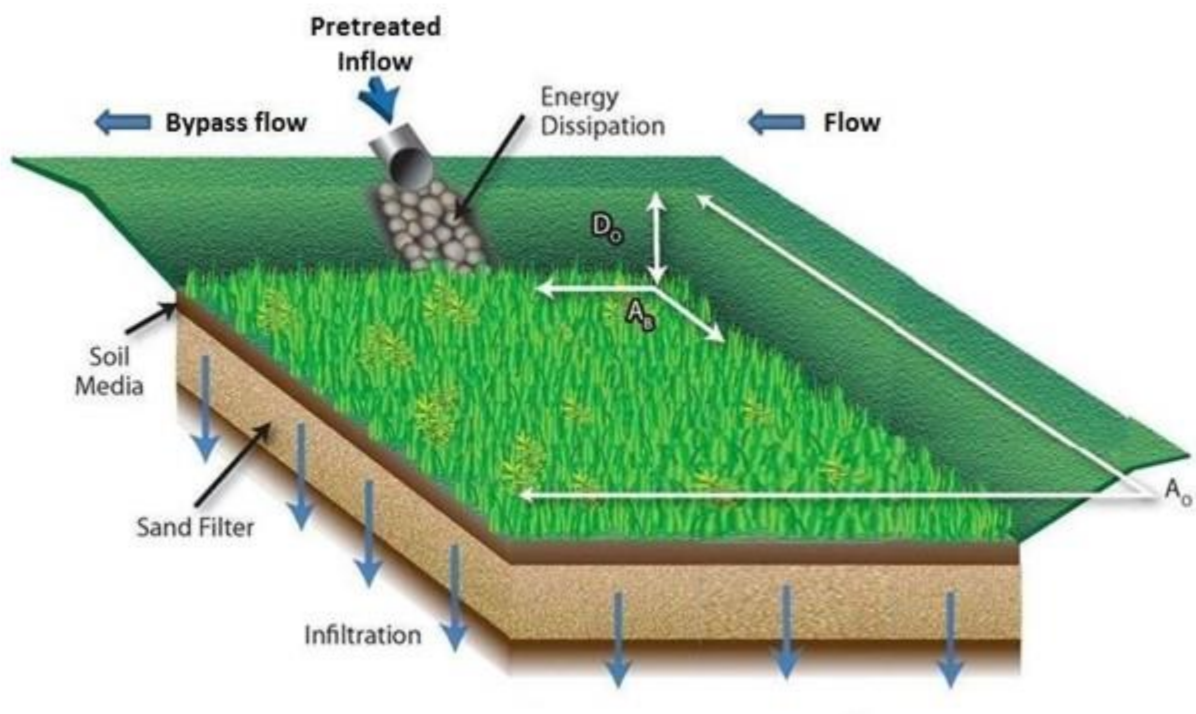

Figure 6: Schematic of a typical infiltration stormwater control measure (SCM). Stormwater runoff ("flow") enters the SCM and is temporarily stored. If the storage area fills, additional runoff bypasses the SCM. The stored water infiltrates into the underlying soil within 48 hours.

Figure 7: Examples of infiltration SCMs. From top to bottom: bioinfiltration, infiltration basin, swale with check dams, and permeable pavement (concrete pavers).

3.1.1 Bioinfiltration

Bioinfiltration SCMs utilize engineered media and vegetation and include rain gardens, tree trenches, and tree boxes. Bioinfiltration media have a rapid infiltration rate and typically contain 10-20% organic matter to support vegetation and attenuate pollutants. These are versatile practices that can be incorporated into many landscape designs. Rain gardens are relatively small surface SCMs, while tree trench systems are potentially extensive, underground SCMs.

3.1.2 Infiltration Swales

Infiltration swales, or bioswales, are similar to bioinfiltration SCMs, but do not always have engineered media (i.e., they may utilize native soils) because the typical drainage ratio is 3:1. Swales designed for infiltration include check dams to temporarily store water and allow it to infiltrate, or exist on permeable soils that allow for rapid infiltration as water flows along the swale.

3.1.3 Infiltration Trenches and Basins

Infiltration trenches and basins utilize native soils rather than engineered media. Unlike bioinfiltration, they are not restricted to depths of 0.46 meters (1.5 feet) or less and are thus a preferred practice on sandy soils. Due to these factors, they generally capture and infiltrate greater volumes of water versus bioinfiltration and infiltration swales, but are less effective at retaining various pollutants. These SCMs utilize space efficiently; they may be constructed above ground or, when space is limited, below ground.

3.1.4 Permeable Pavements

Permeable pavements allow stormwater runoff to filter through surface voids to an underlying stone reservoir for storage and infiltration. The most common permeable pavement surfaces are pervious concrete, porous asphalt, and permeable interlocking concrete pavers (PICP). They perform best in light-traffic commercial and residential locations (e.g., low-speed roads, alleys, parking lots, driveways, sidewalks, plazas, and patios). Their impermeable:permeable area ratio is typically less than 2:1.

3.2 Implementation of Infiltration SCMs

Until the 1990s, the primary stormwater management practice was the regional retention pond. Retention ponds effectively remove medium- and coarse-textured sediments and associated pollutants, but are less effective for smaller particles and ineffective for dissolved pollutants. Partly due to federal regulations and the realization that these retention practices would not meet water quality goals, the concept of “conservation design”, originally developed in the 1970s, took hold in the late 1990s. Conservation design allows development while retaining a site’s natural hydrology to the extent possible. Although conservation design encompasses several stormwater management strategies, the most important is stormwater runoff capture and infiltration. Infiltration is the primary component of green stormwater infrastructure.

Stormwater infiltration is now a preferred stormwater runoff management practice. It is difficult to determine the current extent of infiltration implementation, but of 233 entities covered under the 2013 Municipal Stormwater General Permit, 210 had implemented some regulatory volume control mechanism, typically

Hydrologic Soil Groups

Soils are classified by the Natural Resource Conservation Service into four Hydrologic Soil Groups (HSG) based on a soil’s runoff potential (U.S. Department of Agriculture, 1986).

Group A includes sand, loamy sand, sandy loam, and gravelly soils. These soils are well-drained with low runoff potential and high infiltration rates.

Group B includes silt loam and loam soils. These soils are moderately well-drained with low runoff potential and moderate infiltration rates.

Group C are sandy clay loam soils. These soils are poorly-drained with low infiltration rates and moderate runoff potential.

Group D include clay loam, silty clay loam, sandy clay, silty clay, and clay soils. These soils are very poorly-drained with high runoff potential and very low infiltration rates.

infiltration. As of 2017, municipal permittees subject to Total Maximum Daily Loads reported implementation of 1,198 stormwater ponds and 828 infiltration SCMs. Over 50% of the ponds were older than 10 years, while 75% of infiltration SCMs were under 10 years old. This reflects the trend of increased use of infiltration SCMs to manage stormwater runoff.

Even with aggressive requirements, infiltration SCMs are only feasible on permeable soils where other constraints (e.g., shallow bedrock or contaminated soils) do not prevent or limit infiltration. Hydrologic Soil Group (HSG) A and B soils are favorable for infiltration when no other constraints exist. Infiltration is difficult on HSG C soils and generally infeasible on HSG D soils. Based on an analysis of Natural Resources Conservation Service soil survey geographic drainage class maps and Minnesota Department of Health Wellhead Protection Area vulnerability maps, about 30% of Minnesota's urban areas have HSG A and B soils. This number may be lower in certain areas with infiltration constraints, or higher if runoff can be routed to more permeable soils.

3.2.1 Benefits of Infiltration SCMs

Where feasible, infiltration is a preferred stormwater runoff management method, and provides several benefits.

- Infiltration removes some pollutants that would otherwise flow directly to surface waters. Exceptions are some mobile pollutants, such as chloride, that may still enter surface waters indirectly in baseflow.
- Infiltration can eliminate flooding from small- and medium-sized rain events and reduce it from large events (Moore, Gulliver, Stack, & Simpson, 2016; Qin, Li, & Fu, 2013; Ferguson, 1990; US EPA, 2019).
- Some infiltration SCMs can be built underground or incorporated into landscapes (e.g., permeable pavement), thus utilizing space efficiently.
- Infiltration SCMs, particularly vegetated SCMs, often provide additional benefits (e.g., habitat, aesthetics, and improved air quality).
- Several studies show stormwater infiltration SCMs are more cost-effective than traditional SCMs over a full life cycle; yet others disagree (Wang, Eckelman, & Zimmerman, 2013; Nordman, Isely, Isely, & Denning, 2018; Auckland Regional Council, 2009; U.S. EPA, 2007; Conservation Research Institute, 2005; Weiss, Gulliver, & Erickson, 2005).

3.2.2 Limitations and Constraints of Infiltration SCMs

There are many situations where infiltration of stormwater runoff is not recommended or feasible unless specific conditions are met.

- Infiltration SCMs should be avoided or properly sited in areas with contaminated soils or groundwater.
- In locations with active or near-surface karst, small-scale infiltration SCMs (e.g., permeable pavements, rain gardens) may be appropriate but large-scale infiltration SCMs are not.
- Due to insufficient media or soil thickness for pollutant removal and to avoid flooding in adjacent structures, the minimum recommended separation distance between the bottom of an infiltration SCM and the seasonal high

water table is typically 0.6-1.2 m, depending on local or state rules (0.9 m in Minnesota).
- Coarse soils (gravel, coarse sand) should be amended to reduce infiltration rates and thereby improve pollutant attenuation.
- Adequate separation from drinking water receptors and baseflow-influenced surface waters must be ensured.

Minnesota's 2018 Construction Stormwater General Permit prohibits infiltration in several situations, including those identified above. Under specific conditions, infiltration SCMs may be allowed if properly sited or employed with specific engineering practices.

3.3 Fate of Chloride in Stormwater Infiltration SCMs

Although chloride does not readily form complexes or sorb to soil components, multiple factors affect its transport in soil. Chloride movement is retarded by reduced soil permeability from clay dispersal by sodium, soil freezing, presence of immobile regions in soil, and soil-pore clogging by fine-textured material. Other possible soil chloride attenuation mechanisms include plant uptake, geochemical sorption (including ion exchange), and microbial chlorination of soil organic matter (Bastviken et al., 2006; Svensson, Lovett, & Likens, 2011; Oberg & Sanden, 2005). These latter chloride attenuation mechanisms are not believed to be substantial.

Wogslund (1984) examined the effects of injecting stormwater runoff into Class V injection wells in Montana. Chloride concentrations in winter runoff (mg/L) reached 1589 and 953 at commercial and residential sites, respectively. In 4m-deep lysimeters in commercial areas, respective winter and summer concentrations (mg/L) were 298 and 58.9, while in residential areas they were 155 and 1.8. Sharp winter concentration peaks did not track with changing water table elevations, indicating that most chloride mass was infiltrated during relatively minor winter recharge events.

Van Seters (2008) monitored water and soil chloride beneath permeable interlocking concrete pavement (PICP) and biofiltration SCMs in Ontario. Runoff concentrations (mg/L) in winter exceeded 1,000, with maximums near 30,000, and for the rest of the year were below 100. In infiltrated water, winter concentrations were smaller but still exceeded several hundred mg/L, with maximums near 3,000 mg/L, then gradually decreased and exceeded runoff concentrations in non-winter months. Chloride accumulated in engineered media and soils beneath the PICP and biofiltration SCMs. Concentrations in the engineered media and soil beneath the PICP generally exceeded reference soil concentrations by a factor of 2-10 at the point of greatest accumulation. Biofiltration SCM media concentrations exceeded reference soil concentrations at some but not all sites, and typically within a factor of 2.

Machusick and Traver (2009) studied chloride fate in a Pennsylvania bioinfiltration basin. The monitoring network included runoff, lysimeters at depths of 0 (Lys-0), 1.2 (Lys-4), and 2.4 (Lys-8) m below the bioinfiltration basin's bottom, and shallow monitoring wells roughly 9 m below the basin's bottom (MW2 and MW3). Median chloride concentrations in runoff for two winter events were 2,799 mg/L and 8,521 mg/L (Figure

8). For the first event (0.46 cm runoff over 13 hours on 12/9/2007), concentrations in lysimeters were ≤10 mg/L, but were 400 mg/L for the second event (1.78 cm runoff over 11.5 hours on 1/17/2008). A similar delayed response occurred in shallow groundwater adjacent to the bioinfiltration SCM (3 mg/L for the first event, but >50 mg/L for the second event). Runoff samples collected for three subsequent March and April events showed no deicer influence, with concentrations from 6-36 mg/L. In the same months, however, 1.2 and 2.4 m deep lysimeters (Lys-4 and Lys-8, respectively) exceeded 300 mg/L chloride. By late May, lysimeter chloride concentrations decreased but were still elevated compared to the previous autumn. In well 2 (MW2), directly down-gradient of the bioinfiltration basin, concentrations increased through winter and early spring, peaking at 294 mg/L in early April, then began to decline. In well 3 (MW3), approximately 19 meters down-gradient of well 2, concentrations were relatively stable throughout the study, ranging from 61.5 mg/L (April) to 120 mg/L (November).

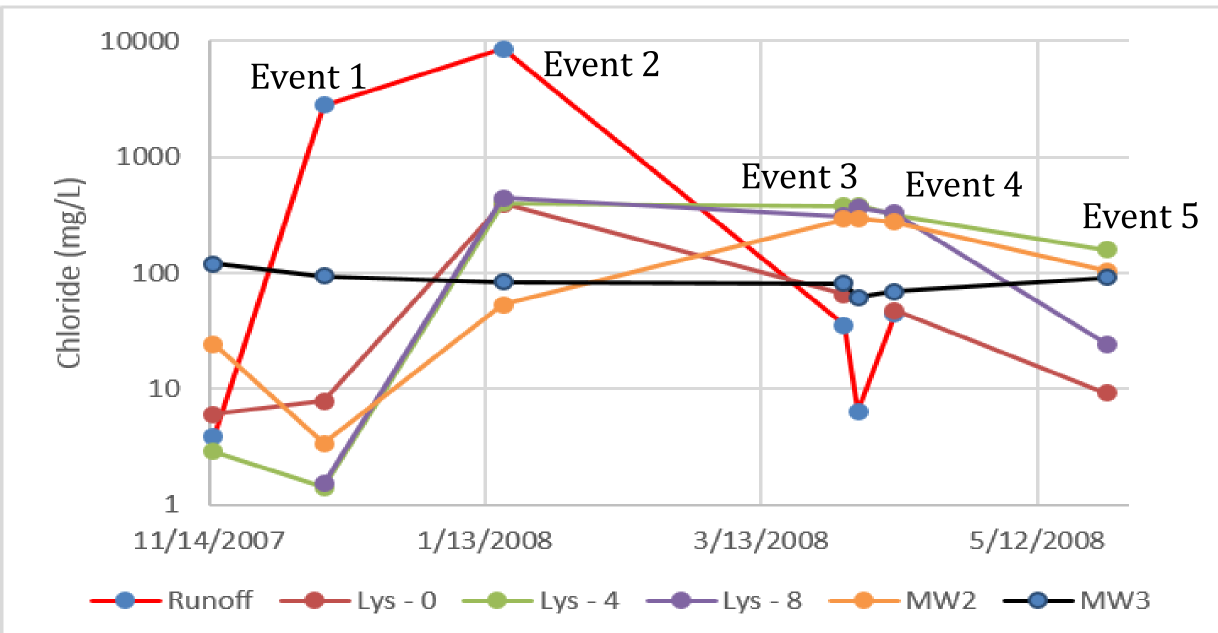

Figure 8: Chloride concentrations in runoff, lysimeters, and groundwater at a bioinfiltration SCM in Pennsylvania. Samples were taken over a 6 month period that included stormwater runoff prior to, during, and after deicing application (Machusick & Traver, 2009).

Gardner and Royer (2010) monitored chloride in five Indiana streams in different land use settings, with developed area percentages of: 5.1, 14.6, 16.1, 17.3, and 78.5 (sites 1-5, respectively). Sites 2-5 had elevated chloride concentrations in winter deicing months. During non-winter months, sites returned to background levels. Site 5 (78.5% developed) concentrations were elevated throughout the year, which the researchers speculated was due to salinization of shallow groundwater that supplied chloride to the stream as baseflow during non-winter months.

Nieber, Arika, Lahti, Gulliver, and Weiss (2014) observed chloride concentrations in lysimeters below three infiltration SCMs in Minnesota from <10 to about 1,000 mg/L. Although the concentrations were not statistically compared, the medians were roughly 100 mg/L at all three sites. There were no differences in chloride concentration among lysimeters installed at different depths (approximately 0, 1.5, 4.4, 7.8, 8.4, 10.1 m) at each site. Concentrations were greatest in late fall, and generally decreased after that. To explain this, the researchers stated that “It appears that movement of chloride in the unsaturated zone can be slow, possibly because of water caught between the small pores of the media, such that high concentrations at a given depth can be observed at any time of the year.”

Rife (2016) studied chloride patterns in soil, runoff, groundwater, and surface water in areas where deicers were applied. She observed winter spikes in soil and stream salinity, indicating a rapid response to sodium chloride inputs. These spikes were not evident in shallow groundwater beneath a bioinfiltration SCM. Instead, groundwater salinity increased in spring and early summer, peaking 4 to 5 months after the winter spikes in soil and surface water. Average salinity concentrations in soil gradually decreased from late winter until July, remaining steady until the following winter. Aside from the winter spikes, surface water salinity was steady throughout the year, suggesting baseflow inputs from shallow groundwater. She estimated that chloride travel time from the infiltration SCM to groundwater (approximately 10 m below) was 60 days, and that with current de-icing practices the groundwater chloride concentrations would continue to increase and exceed the water quality standard in 75 years.

McNaboe (2017) observed chloride concentrations in deicer-impacted soils of <10 near the soil surface (upper 1 m), up to 200 mg/kg at depths of 1-2 m, with a median concentration of 30 mg/kg throughout the 4.5 m profile. In that study, deicer-unimpacted soil chloride concentrations were always below 12 mg/kg and usually below 5 mg/kg.

These studies show that chloride attenuation and retardation occur in and beneath infiltration SCMs. This results in reduced peak chloride concentrations compared to stormwater runoff. However, mass transport occurs throughout the year, resulting in elevated concentrations in summer and fall compared to stormwater runoff.

4.0 Estimating Chloride Loading to Groundwater

This section discusses the most important chloride sources and estimates their loading to groundwater. This is necessary to understand stormwater infiltration impacts in an appropriate environmental context.

4.1 Chloride Sources to Groundwater

Chloride sources to groundwater in urban areas include: infiltration through pervious surfaces, impervious surfaces, filtration SCMs, infiltration SCMs, and constructed stormwater ponds and wetlands; leakage from piped inflows (e.g., public water supplies), wastewater infrastructure, and stormwater infrastructure; and contributions from or losses to surface waters (Figure 9).

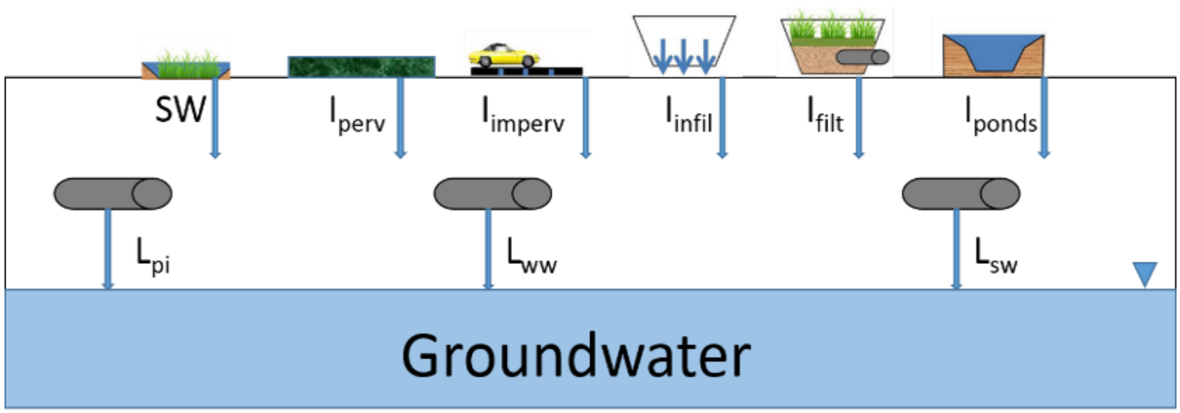

Figure 9: Schematic illustrating sources of chloride loading to groundwater. Sources include leakage from piped inflow (L_{pi}), wastewater infrastructure (L_{ww}), and stormwater infrastructure (L_{sw}); infiltration from pervious surfaces (I_{perv}), impervious surfaces (I_{imperv}), infiltration SCMs (I_{infilt}), filtration SCMs (I_{filt}); and seepage from surface waters (SW), and constructed ponds and wetlands (I_{ponds}).

Infiltration through pervious surfaces (Iperv)

Pervious surface infiltration (I_{perv}) includes infiltration of direct precipitation (e.g., rainfall), rerouted indirect precipitation-runoff (e.g., roof downspouts), and lawn irrigation. I_{perv} does not include infiltration of runoff delivered to SCMs or permeable stormwater conveyances such as open channels and swales.

Several studies have estimated annual recharge (pervious surface infiltration volume) as a fraction of total annual precipitation in urban areas at the city scale. For example, a Minnesota-based study estimated annual recharge in developed areas as 17-21% of annual precipitation based on infiltration rates of different hydrologic soil groups (Smith & Westenbroek, 2015). For St. Cloud, Trojan and others (2003) estimated a value of 28% based on continuous shallow groundwater level data, while 21% was estimated for Austin, Texas (Wiles & Sharp, 2008). Finally, O'Driscoll, Clinton, Jefferson, Manda, and McMillan (2010) estimated annual recharge as 10-40% of precipitation for several sites in the U.S. Based on these studies and depending on soils, climate, geology, and other local factors, a reasonable first estimate of pervious surface infiltration in urban Minnesota areas is 15-25% of annual precipitation.

Chloride concentrations in shallow groundwater that has not mixed with deeper groundwater represent infiltrating water concentrations. Minnesota data indicates 40-80 mg/L are typical shallow groundwater concentrations in urban areas (Minnesota Pollution Control Agency, 1998b; Kroening & Vaughan, 2019) served by municipal sewers, with lower concentrations in areas served by SSTS.

The aforementioned recharge estimates do not include irrigation or water redirected from impervious to pervious surfaces. Currently, data are lacking to estimate these components, but they are considered minor.

Infiltration through impervious surfaces (Iimperv)

Infiltration occurs through fractures in impervious surfaces. Impervious recharge estimates from several studies range from 6-40% of precipitation that falls on impervious surfaces (Watkins, 1962; Falk & Niemczynowicz, 1978; Davies & Hollis, 1981; Colyer, 1983; Hollis & Ovenden, 1988a, 1988b; Stephenson, 1994; Lee & Heaney, 2003; Ragab, Rosier, Dixon, Bromley, & Coop, 2003; Wiles & Sharp, 2007). None of these studies represented areas with seasonal freeze-thaw cycles or frozen soils. Water infiltrating through impervious surfaces is by definition not delivered to either a stormwater conveyance or SCM, which results in double counting when losses are accounted for from stormwater conveyance systems or SCMs if it is assumed that impervious surfaces have zero infiltration.

Using statewide average annual precipitation (72 cm), multiple scenarios were run with various impervious surface coverage (20-60%) and impervious surfaces infiltration rates (5-20% of annual direct precipitation to the impervious surface) (Figure 10). Estimated infiltration rates varied widely depending on these parameters, with most values ranging from 1.3-5.0 cm/y.

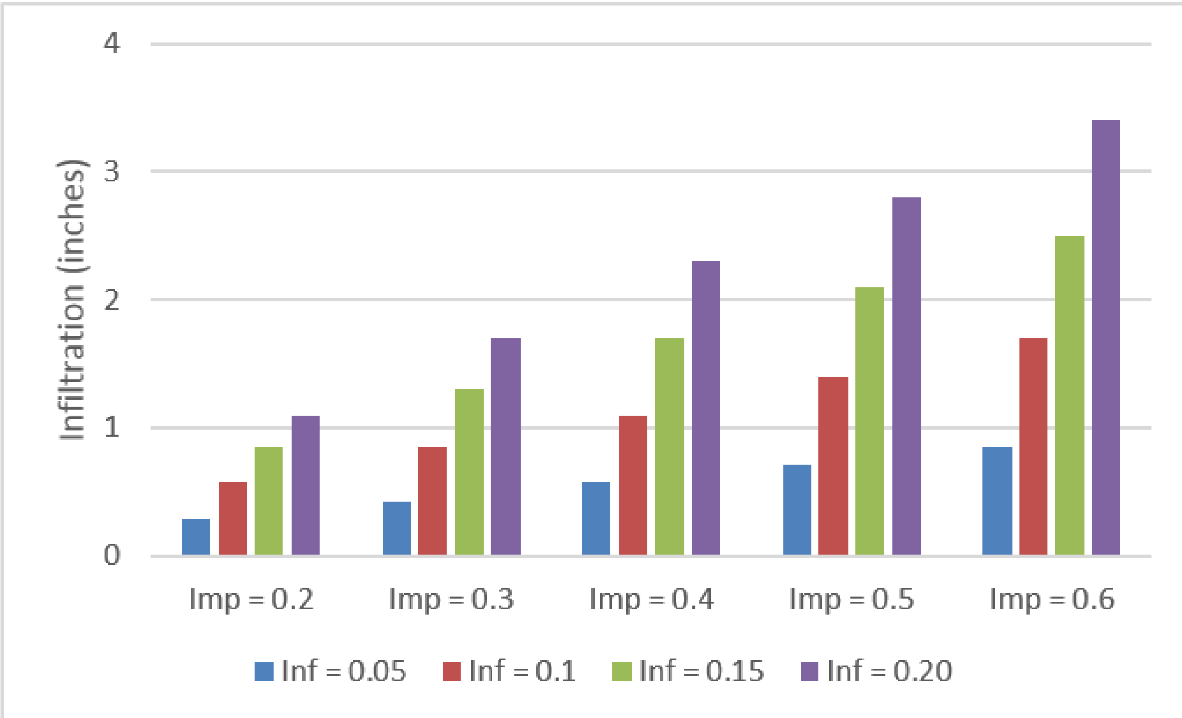

Figure 10: Relationship between infiltration, percent impervious surface, and extent of infiltration. Bars illustrate estimated annual infiltration (inches) through areas considered impervious (e.g. roads) as a function of the fraction impervious area (Imp) and impervious surface infiltration rates as a fraction of annual direct precipitation to the impervious surface (Inf).

Chloride concentrations in infiltrating water vary widely with season and land use. An estimate of the average chloride concentration over a year (C_{Cl}) can be derived in areas with high deicer application by the following equation:

$$C_{Cl} = C_{winter} * fRO_{winter} + C_{non\text{-}winter} * fRO_{non\text{-}winter}$$

where C_{winter} is the average winter concentration, $C_{non\text{-}winter}$ is the average non-winter concentration, fRO_{winter} is the fraction of runoff occurring in winter, and $fRO_{non\text{-}winter}$ is the fraction of runoff occurring outside winter. Using data from Herb and others (2017), estimated winter concentrations were 130-475 mg/L, with a median of 315 mg/L. Concentrations for the rest of the year were 15-30 mg/L. The fraction of runoff in winter (fRO_{winter}) was approximately 0.17 (17%).

Applying these values to the above equation, estimated average annual chloride concentrations are 35-105 mg/L in areas where deicing occurs.

Leakage from piped inflow (Lpi)

Drinking water supply systems are pressurized and thus always have some leakage. Where drinking water is supplied by surface water, this leakage represents an input to groundwater. Lerner (2002) estimated that infrastructure-based water imports (i.e., infrastructure) to urban areas in non-arid climates represent 30-90% of annual precipitation, and that 10-50% of this is lost to leakage (e.g. from leaking pipes). Vasquez-Sune, Carrera, Tubau, Sanchez-Vila, & Soler (2010) estimated leakage from water supply systems accounted for 22% of annual aquifer recharge in Barcelona, Spain. Yang, Lerner, Barrett, and Tellam (1999) estimated water supply systems accounted for 65% of groundwater recharge in Nottingham, UK. Garcia-Fresca and Sharp (2005) estimated 8% of water main flow was lost as recharge in Austin, Texas. Howard and Gerber (2018) compiled data for 22 U.S. cities across studies and found leakage rates of 5-30% (median: 16%).

Chloride concentrations in leakage from water supply systems are easily determined by sampling the supply source (i.e. surface water or groundwater), assuming chloride is conservative in the water distribution system and there are no additional inputs of chloride within the distribution system.

Leakage from wastewater infrastructure (Lww)

Note: if wastewater and stormwater systems are combined, they should be treated as a single input; if not, they should be treated separately.

Leakage from wastewater consists of leakage from sanitary sewer systems and discharges through septic drainfields. These sources are exclusive of each other in a particular area.

Vasquez-Sune, Carrera, Tubau, Sanchez-Villa, and Soler (2010) estimated leaking sewer systems accounted for 30% of annual aquifer recharge in Barcelona, Spain. Yang, Lerner, Barrett, & Tellam (1999) estimated leaking sewer systems accounted for 5% of groundwater recharge in Nottingham, UK. Several researchers reported leakage rates from 1% up to 56% of dry weather flow (Rutsch, 2006; Prigiobbe & Giulianelli, 2011). TCMA leakage rates are likely ≤5% because of system upgrades, improved leak detection, and because groundwater inflow occurs in much of the system (personal communication, Metropolitan Council). In older urban areas with deeper groundwater systems, higher leakage rates are likely.

In areas with SSTS drainfields, wastewater discharge varies with population and SSTS densities. Calculations are relatively simple as nearly all water routed to an SSTS will discharge through its drainfield. For one four-person household using an average 265 L water/d/person, annual drainfield discharge is just over 375,000 L/y (US EPA, 2005). Assuming a 0.8 hectare lot, this equals about 4.8 cm potential recharge/y.

Our review of chloride concentrations in WWTPs showed a range from 113 to 700 mg/L, with a median of 280 mg/L. (Kelly et al., 2010; Novotny, Murphy, & Stefan, 2008b; University of Minnesota Morris, 2013). Higher concentrations may reflect inputs from water softeners.

Leakage from stormwater infrastructure (Lsw)

Most studies of leakage from sewage infrastructure represent combined sanitary and storm sewers. It is therefore difficult to estimate storm sewer leakage. In the TCMA, where sanitary and storm sewers are separated, leakage rates are likely ≤5% because of system upgrades, improved leak detection, and because groundwater inflow occurs in much of the system (personal communication, Metropolitan Council). In older urban areas with deeper groundwater systems, higher leakage rates are likely. Influent storm sewer chloride concentrations should be similar to those of infiltration into impervious surfaces (I_{imperv}).

Inputs from surface water (SW)

We assume no chloride input from surface water to groundwater except in locations where:

- Surface water flows to groundwater are significant (i.e., losing streams and lakes); and
- Surface water chloride concentrations are much higher or lower than in surrounding groundwater.

In these cases, chloride concentrations can be determined through sampling. Monitoring data are readily available for many streams, lakes, and rivers, particularly in the TCMA. Surface water seepage rates and mixing ratios must be estimated or determined for individual water bodies, which presents more difficulty.

Infiltration from constructed stormwater ponds and constructed wetlands (Iponds)

Seepage occurs through constructed ponds and constructed wetlands. Ponds are generally considered to be self-sealing over time due to inputs of sediment and seepage rates decline as a pond fills with sediment. A pond or wetland with a 10^{-6} cm/s infiltration rate will infiltrate 31.5 cm water/y. The Minnesota Stormwater Manual (Minnesota Pollution Control Agency, 2019) recommends pond sizes of 1-3% of the pond's catchment area. At 2% sizing, a 0.4 ha (1 ac) pond that infiltrates 31.5 cm/y accounts for 0.64 cm/y infiltration over its catchment (20 ha). Note that a 10^{-6} cm/s infiltration rate is likely conservative for most constructed ponds and infiltration rates will typically be less than this. Higher infiltration rates reflect ponds that are not properly functioning and that could significantly impact groundwater locally.

Stormwater ponds and wetlands capture, retain, and slowly release runoff. This allows accumulation of chloride-enriched (denser) water deep in the pond or wetland. Several studies reported chloride plumes beneath ponds and wetlands, with the greatest concentrations in winter and gradual decreases over the rest of the year. For example, Snodgrass, Moore, Lev, Casey, Ownby, Flora, & Izzo (2017) observed mean concentrations (mg/L) of 7422, 4639, and 798 in February, June, and November, respectively, under two dry ponds. Forgione (2016) reported concentrations (mg/L) beneath a constructed stormwater wetland of 588 in the deicing season versus 213 in the non-deicing season. Other studies showed similar results, with concentrations ranging from several hundred mg/L (non-deicing season) to several thousand mgL (deicing season) (Van Meter, Swan, & Snodgrass, 2011; Tagachi, Olsen, Natarajan, Janke, Finlay, Stefan, Gulliver, & Bleser, 2018; Casey, Lev, & Snodgrass, 2013).

Infiltration through stormwater filtration SCMs (Ifilt)

Filtration SCMs include any SCM with an underdrain, swales not designed for infiltration, and filter strips. Some infiltration typically occurs through filtration SCMs, which are a preferred treatment method when infiltration SCMs are infeasible. The Minimal Impact Design Standards (MIDS) calculator was used to run several simulations for each of these filtration SCMs. For filtration practices having an underdrain and designed to capture and treat 1 inch of runoff, 15-25% of annual runoff infiltrates beneath the underdrain. Depending on design dimensions, infiltration accounts for 7-15% of annual runoff for swales and 5-25% for filter strips. For these SCMs, influent chloride concentrations are similar to those discussed for infiltration into impervious surfaces (I_{imperv}).

Infiltration through stormwater infiltration SCMs (Iinfil)

Infiltration SCMs infiltrate large runoff volumes and focus it to a relatively small area. The MIDS calculator was used to estimate groundwater inflows from an infiltration SCM across several scenarios that varied by fractions of (a) impervious area in the catchment (0.1, 0.3, 0.5, and 0.7) and (b) impervious area captured by the SCM (0.1, 0.4, 0.7, and 1.0). We designed the SCM to capture and infiltrate 90% of the annual runoff discharged to it, and converted this volume to an average annual infiltration rate. Figure 11 illustrates the results of this analysis. Establishing these relationships between fraction or percent impervious and fraction impervious area drained to a SCM allows us to estimate average annual infiltration over an area. For example, using Figure 11, for a 0.4 ha site (1 acre), if the area was 50 percent impervious and had 40 percent of the impervious area draining to an infiltration SCM, the average annual infiltration rate for that area draining to the SCM would be 5.03 cm. If the entire 0.4 ha of impervious surface drained to the infiltration SCM, the average annual infiltration across the area would be 12.6 cm. For estimating chloride loads to groundwater from infiltration SCMs, influent chloride concentrations similar to those discussed for infiltration into impervious surfaces (I_{imperv}).

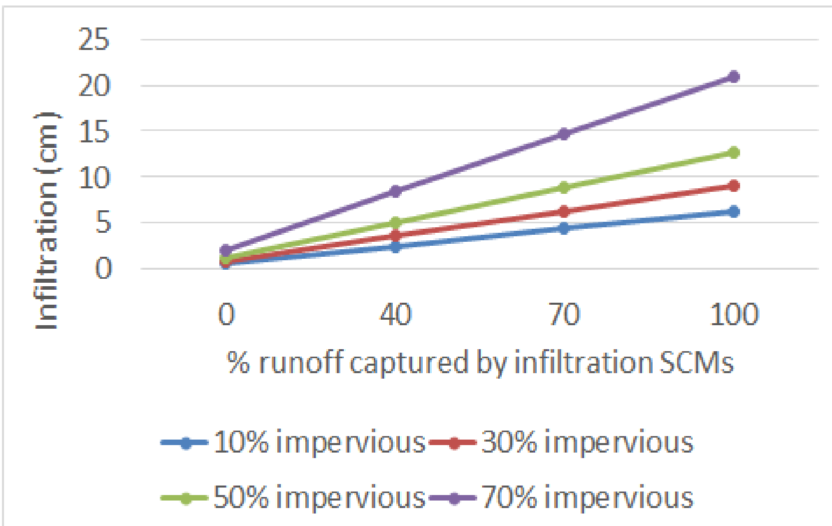

Figure 11: Infiltration as a function of impervious surface and extent of infiltration. Infiltration is expressed as an average annual value, in inches. The extent of infiltration reflects the percent of annual runoff captured by infiltration SCMs. Percent impervious reflects the extent of impervious surface in the watershed draining to an infiltration practice.

4.2 Example Estimates of Chloride Loading to Groundwater

We developed a spreadsheet to estimate chloride loading to groundwater based on information provided in the previous section and user-defined inputs for each source that contributes to infiltration. The spreadsheet normalizes annual loads to a per hectare or acre basis.

To evaluate the contribution of infiltration SCMs (I_{infil}) to annual chloride loading of groundwater, we varied (a) runoff chloride concentration, (b) extent of infiltration SCM implementation, and (c) percent imperviousness while holding other inputs constant. The three variables are described below and results summarized in Figures 12, 13, and 14.

1. Varying chloride concentration: chloride concentrations were 20, 50, or 100 mg/L. We calculated total load to groundwater and percentage of total load from infiltration SCMs. Assumptions for this scenario were imperviousness equaled 30% of catchment area and infiltration SCMs treated 50% of impervious surface runoff.
2. Varying the extent of infiltration SCM implementation: infiltration practices captured 0, 40, 70, or 100% of annual stormwater runoff from impervious surfaces. We calculated total chloride load to groundwater and percentage of total load from infiltration SCMs. Assumptions for this scenario included were imperviousness equaled 30% of catchment area; 70 mg/L chloride in runoff.
3. Varying the percentage of impervious surface: the percent impervious surface was 30, 50, or 70%. We calculated total chloride load to groundwater and percentage of total load from infiltration SCMs. Assumptions for this scenario included infiltration SCMs treated 50% of runoff from impervious surfaces and chloride concentration in runoff was 70 mg/L.

Default annual infiltration and chloride concentrations, based on information in the previous section, included the following:

- Pervious surfaces (I_{perv}): infiltrate 20% of annual direct precipitation; 50 mg/L chloride.
- Impervious surfaces (I_{imperv}): infiltrate 10% of annual direct precipitation; scenario-dependent chloride concentrations.
- Piped inflow leakage (L_{pi}): equals 50% of annual precipitation x 15% (leakage rate); 25 mg/L chloride.
- Sanitary sewer leakage (L_{ww}): applied Twin Cities Metro plant discharge data x 5% (leakage rate); 280 mg/L chloride.
- Storm sewer leakage (L_{sw}): 5% leakage rate; annual impervious runoff (%) that enters storm sewers varies inversely with I_{infil}; scenario-dependent chloride concentrations.
- Surface water contributions (SW): Assumed to be 0.
- Constructed ponds and wetlands (I_{ponds}): Half the impervious area not drained to infiltration SCMs drains to a pond; pond area is 2% of catchment; 10^{-6} cm/s seepage rate through pond bottom; 500 mg/L chloride.
- Filtration SCMs (I_{filt}): Half the impervious area not drained to an infiltration SCM drains to a filtration SCM; based on MIDS calculator runs, filtration SCMs infiltrate 20% of the water that infiltration SCMs do; scenario-dependent chloride concentrations.

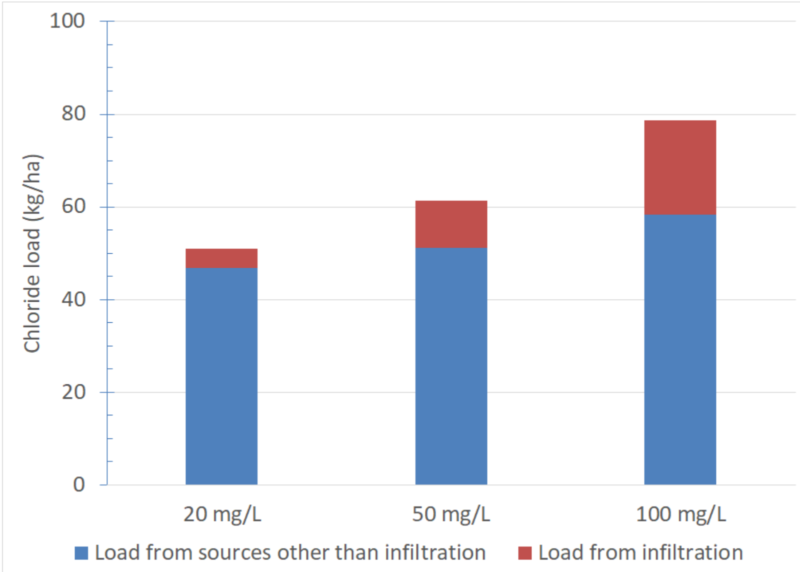

Figure 12: Effect of chloride concentration in stormwater runoff on chloride loading to groundwater from stormwater infiltration SCMs and non-infiltration sources.

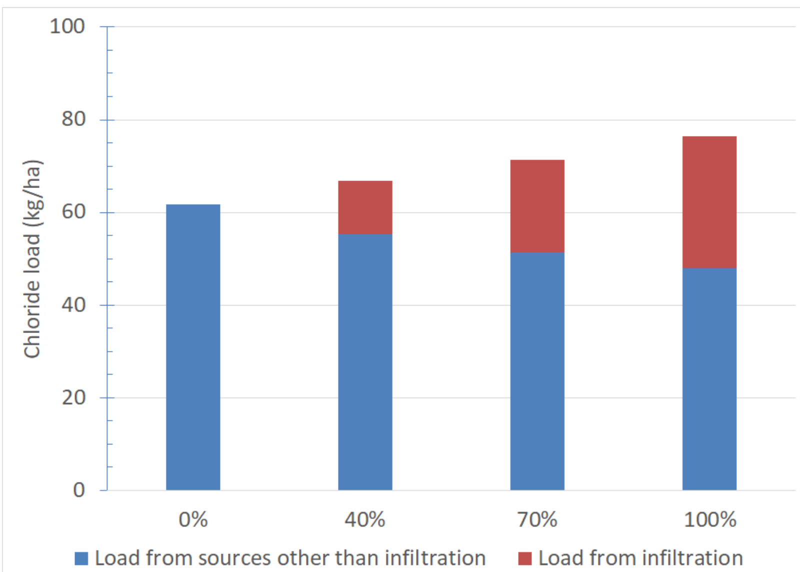

Figure 13: Effect of the percent of stormwater runoff treated by infiltration SCMs on chloride loading to groundwater from stormwater infiltration SCMs and non-infiltration sources.

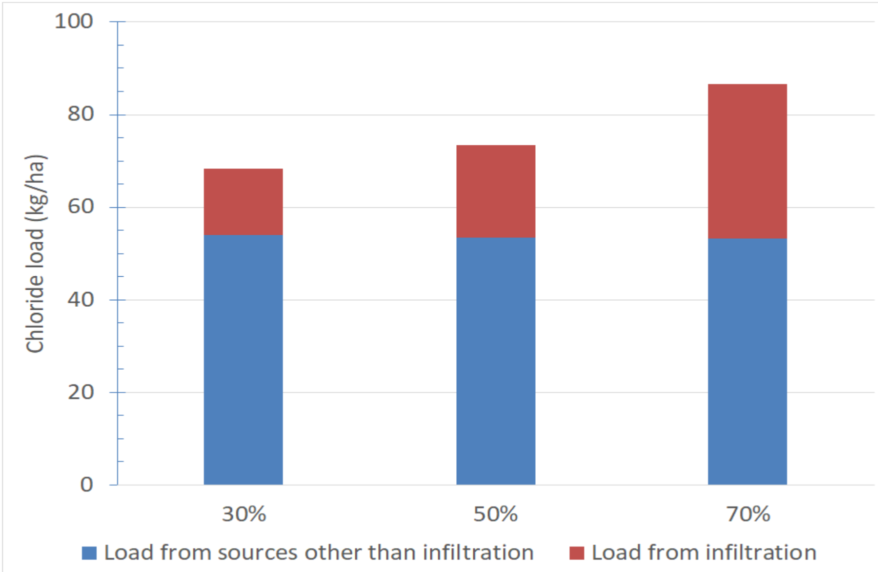

Figure 14: Effect of the percent impervious on chloride loading to groundwater from stormwater infiltration SCMs and non-infiltration sources.

Figures 12, 13, and 14 illustrate the effect of chloride concentration, changes in the amount of runoff routed to infiltration practices, and the percent impervious surface on chloride contributions from stormwater infiltration practices. As expected, increases in each of these three factors results in increasing groundwater contributions from stormwater infiltration, but the effects vary with each factor. For the scenarios discussed above, we calculated the change in chloride loading per unit change in each of the three factors (chloride concentration in runoff, percent of runoff captured by infiltration SCMs, and percent impervious). The increase in chloride loading was 0.356 kg/ha for each 1 mg/L increase in chloride concentration (Figure 12), 0.457 kg/ha for each 1% increase in impervious surface Figure 14), and 0.148 kg/ha per each 1% increase in the area routed to an infiltration practice (Figure 13). We also ran a scenario with a stormwater runoff concentration of 20 mg/L and varied the impervious surface from 30 to 70%, assuming 50% of stormwater runoff is infiltrated. Under this scenario, loading decreased at a rate of 0.11 kg/ha per 1% increase in impervious surface, illustrating water quality improvement in areas that do not receive deicer.

Appendix C contains pie charts illustrating the chloride loading from different sources for the scenarios discussed above.

5.0 Discussion and Recommendations

Shallow groundwater in urban areas statewide contains elevated chloride concentrations compared to undeveloped areas. The primary source of this chloride is deicers. Shallow groundwater concentrations in urban areas are increasing and sometimes exceed groundwater criteria. Chloride in shallow groundwater has the potential to migrate into deeper drinking water aquifers, or impact streams that have a significant baseflow component. Currently, drinking water aquifers do not contain concentrations of concern. Urban streams with significant baseflow typically have lower winter peaks but elevated non-winter chloride concentrations versus streams without a significant baseflow component. In the Twin Cities Metro Area, concentrations in most urban streams are trending upward, and several streams exceed water quality criteria (Metropolitan Council, 2018).

Chloride concentrations range from <50 mg/L in non-deicer impacted stormwater runoff to >1,000 mg/L in deicer-impacted winter runoff, when >80% of annual chloride loading typically occurs.

Stormwater runoff management increasingly relies on infiltration in stormwater control measures (SCMs) such as bioinfiltration (rain gardens), infiltration basins, permeable pavement, infiltration swales, and tree trench systems. Infiltration effectively treats many runoff pollutants, but not chloride. Chloride movement is retarded in infiltration SCMs and underlying soils. Consequently, peak concentrations in shallow groundwater beneath infiltration SCMs are lower than, and may lag several months behind those in deicing-impacted influent runoff. Groundwater concentrations are less variable seasonally and are generally elevated compared to runoff concentrations during the non-deicing season.

Several sources, including stormwater runoff infiltration, contribute to urban groundwater recharge. Although many studies have quantified urban recharge, they did not quantify chloride loading to groundwater. Information from published studies was used to estimate chloride loading to urban groundwater from various sources. Scenarios were modeled with variable input parameters including: stormwater runoff chloride concentrations; extent of infiltration SCM implementation; and percent imperviousness. For runoff unaffected by deicer application, increasing stormwater SCM implementation will always increase chloride loads to groundwater but decrease recharge concentrations through dilution. In areas with deicer application and implementation of infiltration SCMs, the most important influence on chloride loading and concentrations in recharge appears to be stormwater runoff concentration. Widespread implementation of stormwater infiltration SCMs in areas with extensive deicing will likely result in recharge water exceeding the SMCL of 250 mg/L.

Several aspects of chloride's fate in groundwater are poorly understood, such as eventual steady-state concentrations at current deicing rates, transport to urban streams in baseflow, or transport to deeper drinking water aquifers. Nevertheless, some general conclusions are evident:

1. Where deicer use is not extensive, infiltration SCMs are protective of

receiving surface waters. Infiltration may increase groundwater chloride concentrations, but not to concerning levels. In some cases, infiltration may offset other chloride sources (e.g. leaking infrastructure) and lead to water quality improvements.

2. Where deicing is extensive, infiltration SCMs will likely lead to criteria exceedances in shallow groundwater. This chloride-enriched groundwater may migrate to local streams or drinking water aquifers.

3. In baseflow-fed urban streams impaired by high winter chloride concentrations, infiltration SCMs may decrease in-stream winter concentrations through dilution. In-stream summer concentrations will be a function of concentrations in groundwater. If groundwater exceeds the aquatic life standard of 230 mg/L, baseflow-fed summer stream concentrations may exceed the standard.

The following recommendations are provided. Note these recommendations apply to urban areas.

1. Develop a method to assess shallow groundwater vulnerability to chloride contamination. Identify necessary variables such as geologically-based aquifer vulnerability factors and deicing information, for which road density or percent imperviousness can be suitable surrogates. Establishing relationships between groundwater chloride concentration and these surrogates may require enhancements of existing groundwater monitoring networks.

2. Use the aforementioned method to identify and map shallow groundwater vulnerable to chloride contamination.

3. Establish dedicated monitoring networks to better understand chloride fate and transport in shallow groundwater. These networks should focus on intensive monitoring in vulnerable areas (see Recommendation 2) and near vulnerable surface waters (e.g., baseflow-impacted streams). Monitoring should incorporate chloride input information (e.g., deicing data, stormwater runoff data). Because chloride concentrations are highly variable, especially in runoff, monitoring must include continuous measurement of specific conductance and corresponding conductance-chloride regressions.

4. Expand existing monitoring networks to allow trend analysis for drinking water aquifers identified as vulnerable (see recommendation 2) and where infiltration SCMs are widely implemented. Where possible, develop or use existing models to predict chloride fate, including steady-state concentrations under various loading scenarios.

5. Encourage proper stormwater infiltration where appropriate.

    a. Infiltrate in areas not vulnerable to chloride contamination (see recommendation 2).

b. In areas vulnerable to chloride contamination, distribute infiltration rather than focusing on a single location.

c. Properly site infiltration SCMs with respect to receptors (e.g., lakes, streams, and shallow drinking water wells). For example, locate an infiltration SCM within 4-8 months travel time from a baseflow-influenced receiving stream to offset peak winter in-stream concentrations.

d. Because permeable pavements require little or no deicing, encourage them for infiltration in suitable locations (e.g., walkways, driveways), particularly where deicing is common.

6. Do not store snow in infiltration SCMs or in SCMs that will receive runoff from melting snow piles, unless the SCMs are offline (i.e. runoff does not enter the SCM and instead bypasses it during snowmelt).

7. Use existing monitoring networks, especially groundwater networks, to expand chloride sampling.

8. Complete research to understand chloride fate in infiltration SCM soils and engineered media. This includes identifying and quantifying processes that retain chloride (e.g., organic matter chlorination) and retard its movement (e.g., entrapment in pore water).

9. Expand on University of Minnesota research to understand chloride sinks and residence times. Quantify chloride retention in groundwater, lakes, and soil. This will improve knowledge of long-term impacts to lakes and groundwater.

Ultimately, the solution to prevent or minimize chloride impacts to receiving waters is reduced deicer usage. Additional chloride management strategies include:

- implementing infiltration SCMs where appropriate,
- practicing proper deicer applications,
- establishing deicer-free zones near sensitive waters,
- reducing winter driving speeds, and
- developing and implementing new technologies (e.g., alternative, eco-friendly deicers)

For more information on chloride management, see the Twin Cities Metropolitan Area Chloride Management Plan (MPCA, 2016). Note this document is undergoing revision and an updated document will be released in the near future.

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7.0 APPENDICES

Appendix A

Summary of groundwater chloride monitoring by state agencies and federal, tribal, and local governments in Minnesota [MPCA, Minnesota Pollution Control Agency; MDA, Minnesota Department of Agriculture; MDNR, Minnesota Department of Natural Resources; MDH, Minnesota Department of Health; USGS, U.S. Geological Survey; NAWQA, National Water Quality Assessment].

Entity	Area	Project	Sampling Years	Well Types	Sampled Wells (#)	Sampling Frequency	Samples (#)
MPCA	Statewide	Ambient Groundwater Monitoring Network	2004-present	Monitoring	274	Once to Annually	2,564
				Water Supply	313		
		Baseline Study of Groundwater Quality and Special Studies	1992-2018	Monitoring	320	Once to Quarterly	3,632
				Water Supply	1,777		
MDA	Statewide	Ambient Groundwater Monitoring Network	2014	Monitoring/ Spring	113	1-2 times	155
MDNR	41 selected counties and regions	Groundwater Atlas	1982-present	Water Supply	3,200	Once	3,200
MDH	Statewide	Drinking Water Protection	1957-2018	Water Supply	2,500	Variable	7,000
USGS	Statewide	NAWQA	1991-2018	Monitoring	171	Variable	602
				Water Supply	194		
		Cooperative Studies	1932-2018	Monitoring/ Water Supply	3,052	Variable	5,131
Dakota County	Countywide	Ambient Groundwater Quality Study (AGQS)	1999-present	Water Supply	80	Annually	~1,700
	Inver Grove Heights	Wells and Increased Infant Sensitivity and Exposure	2015-2016	Water Supply	274	Once	274
	Burnsville	Burnsville Private Well Sampling	2018	Water Supply	66	Once	66
	Lakeville	Lakeville Private Well	2019	Water	100	Once	100

		Sampling		Supply			
	Greenvale Township	Greenvale Private Well Sampling	2019	Water Supply	89	Once	89
	Vermillion River Watershed	Chloride and Conductivity of two Ambient Groundwater Quality Study wells and the Vermillion River	March-April 2014	Water Supply	2	Frequent	19
Olmsted County	Rochester	Decorah Edge Recharge Monitoring	1989-present	Water Supply	62	Every 10 years	606
	Countywide	Property Transaction Testing	1970-present	Water Supply	6,408	Periodically	16,300
	Adjacent Counties				21,000	Periodically	34,500
Lower Sioux Community	Lower Sioux Reservation	Organization monitoring	2010-2015	Unknown	4		33
Upper Sioux Community	Upper Sioux Reservation	Organization monitoring	2007-2017	Unknown	4		193

Appendix B

Plots of groundwater chloride changes in wells with statistically significant upward trends from 2005-2017. All data are from the Minnesota Pollution Control Agency.

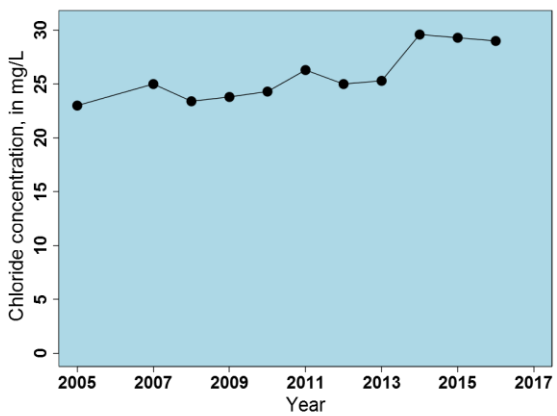


Figure B.1. Chloride concentrations in Minnesota Unique Well Number 105325, 2005-2017. [Well is located in Washington County, 187 feet deep, and installed in the Prairie du Chien aquifer.]

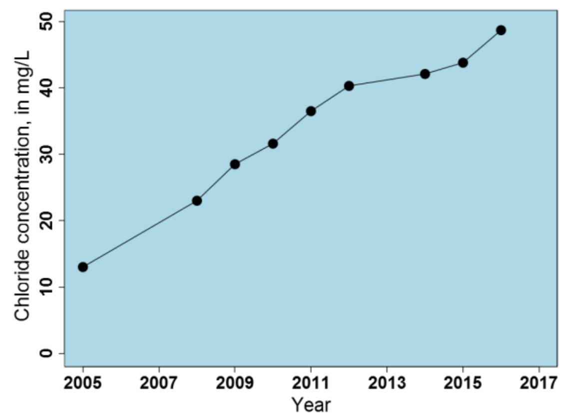


Figure B.3. Chloride concentrations in Minnesota Unique Well Number 217029, 2005-2017 [Well is located in Faribault County, 169 feet deep, and installed in the Galena aquifer].

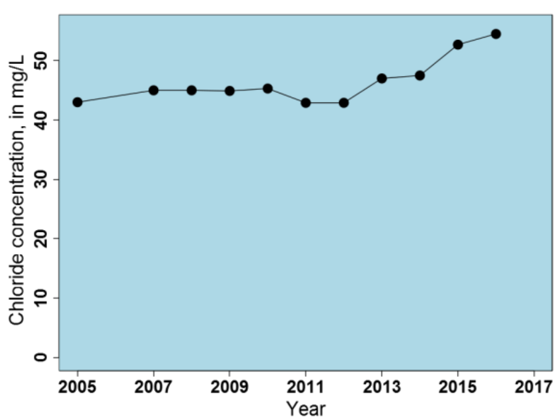


Figure B.2. Chloride concentrations in Minnesota Unique Well Number 194919, 2005-2017 [Well is located in Hennepin County, 183 feet deep, and installed in the Prairie du Chien aquifer].

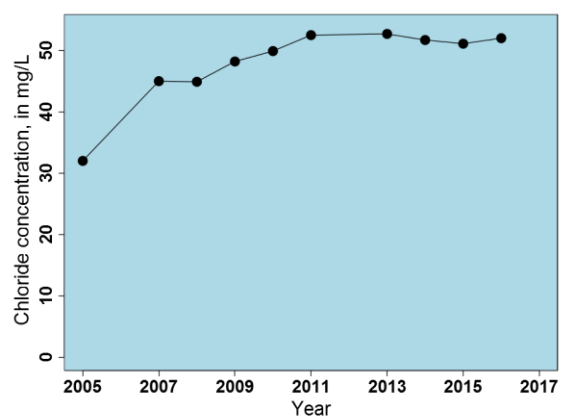


Figure B.4. Chloride concentrations in Minnesota Unique Well Number 406163, 2005-2017 [Well is located in Washington County, 184 feet deep, and installed in the Prairie du Chien aquifer].

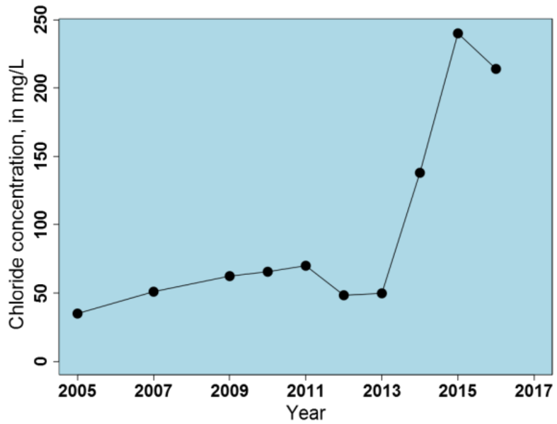


Figure B.5. Chloride concentrations in Minnesota Unique Well Number 417569, 2005-2017 [Well is located in Hennepin County, 240 feet deep, and installed in the Prairie du Chien aquifer].

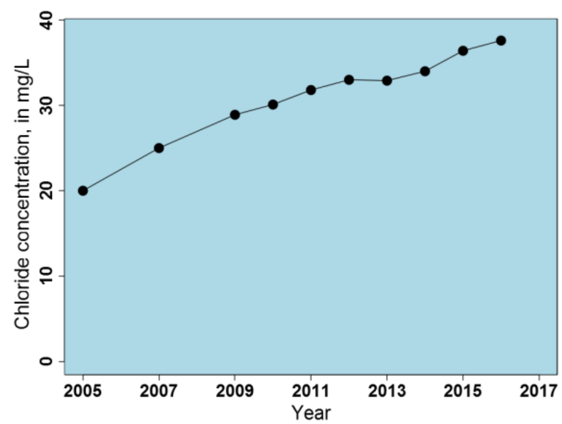


Figure B.7. Chloride concentrations in Minnesota Unique Well Number 512008, 2005-2017 [Well is located in Washington County, 160 feet deep, and installed in the Jordan aquifer].

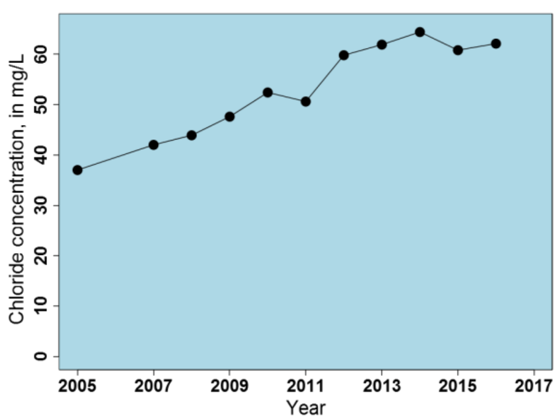


Figure B.6. Chloride concentrations in Minnesota Unique Well Number 435070, 2005-2017 [Well is located in Washington County, 161 feet deep, and installed in the Prairie du Chien aquifer].

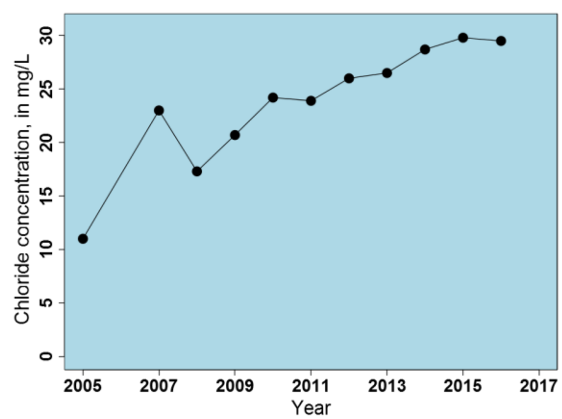


Figure B.8. Chloride concentrations in Minnesota Unique Well Number 532367, 2005-2017 [Well is located in Washington County, 121 feet deep, and installed in the Jordan aquifer].

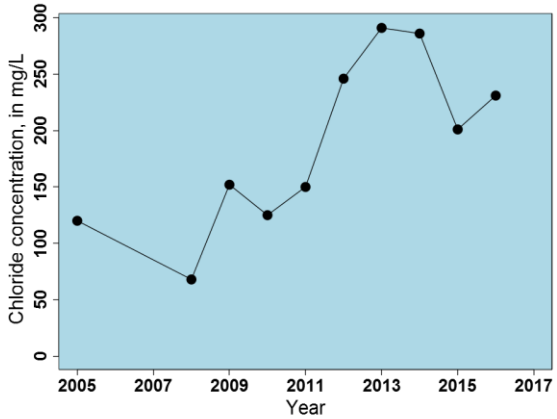


Figure B.9. Chloride concentrations in Minnesota Unique Well Number 560415, 2005-2017 [Well is located in Hennepin County, 18 feet deep, and installed in the sand and gravel aquifer].

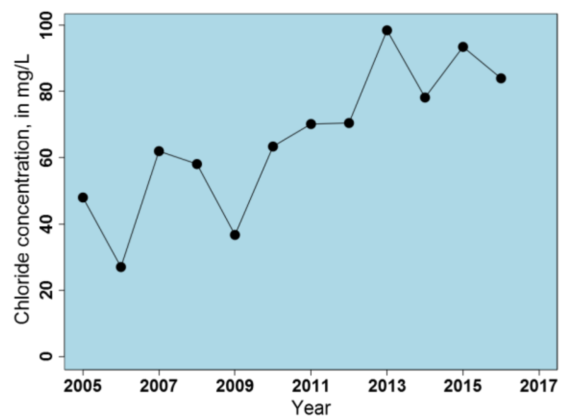


Figure B.11. Chloride concentrations in Minnesota Unique Well Number 561099, 2005-2017 [Well is located in Stearns County, 25 feet deep, and installed in the sand and gravel aquifer].

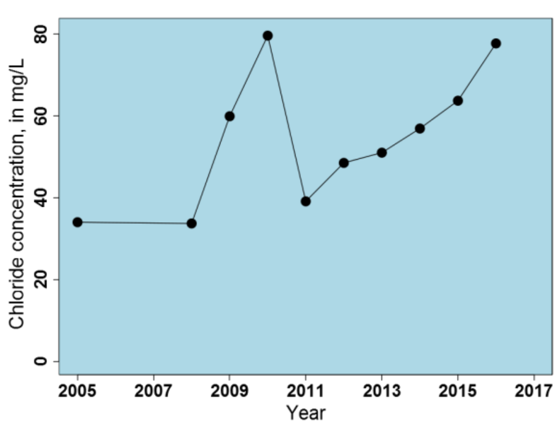


Figure B.10. Chloride concentrations in Minnesota Unique Well Number 560422, 2005-2017 [Well is located in Hennepin County, 18 feet deep, and installed in the sand and gravel aquifer].

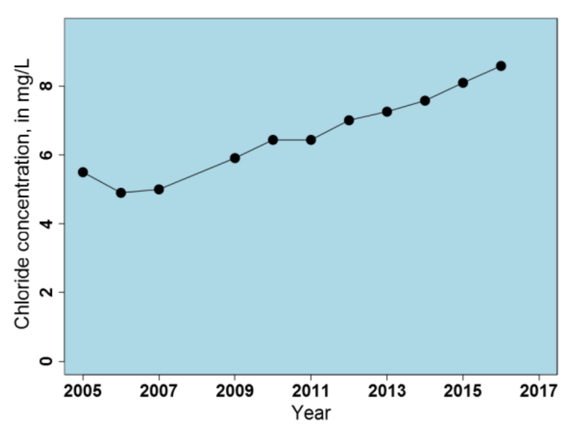


Figure B.12. Chloride concentrations in Minnesota Unique Well Number 562727, 2005-2017 [Well is located in Mower County, 340 feet deep, and installed in the Galena aquifer].

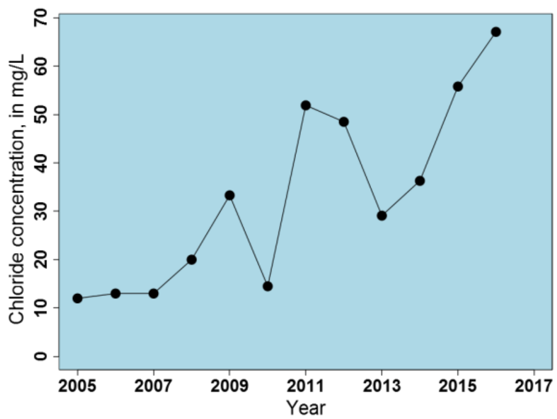


Figure B.13. Chloride concentrations in Minnesota Unique Well Number 639311, 2005-2017 [Well is located in Hennepin County, 19 feet deep, and installed in the sand and gravel aquifer].

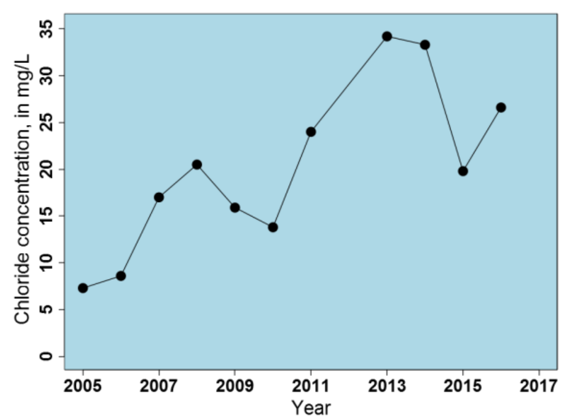


Figure B.14. Chloride concentrations in Minnesota Unique Well Number 695881, 2005-2017 [Well is located in Olmsted County, 90 feet deep, and installed in the St. Peter aquifer].

Appendix C

We developed a calculator to estimate chloride loading to groundwater from several potential sources. We varied input values for three factors that affect chloride loading:

- Chloride concentration in stormwater runoff
- Fraction or percent of an area that is impervious
- Fraction of stormwater runoff directed to stormwater infiltration practices.

All simulations were run for a 0.405 hectare (1 acre) area. Annual precipitation was 77.7 cm.

The potential sources and inputs for the simulations are described below.

- Pervious surfaces (I_{perv}): cover 70% of the area; infiltrate 20% of annual direct precipitation; 50 mg/L chloride.
- Impervious surfaces (I_{imperv}): infiltrate 10% of annual direct precipitation; scenario-dependent chloride concentrations.
- Piped inflow leakage (L_{pi}): equals 50% of annual precipitation x 15% (leakage rate); 25 mg/L chloride.
- Sanitary sewer leakage (L_{ww}): applied Twin Cities Metro plant discharge data x 5% (leakage rate); 280 mg/L chloride.
- Storm sewer leakage (L_{sw}): 5% leakage rate; annual impervious runoff (%) that enters storm sewers varies inversely with I_{infil}; scenario-dependent chloride concentrations.
- Surface water contributions (SW): Assumed to be 0.
- Constructed ponds and wetlands (I_{ponds}): Half the impervious area not drained to infiltration SCMs drains to a pond; pond area is 2% of catchment; 10^{-6} cm/s seepage rate through pond bottom; 500 mg/L chloride.
- Filtration SCMs (I_{filt}): Half the impervious area not drained to an infiltration SCM drains to a filtration SCM; based on MIDS calculator runs, filtration SCMs infiltrate 20% of the water that infiltration SCMs do; scenario-dependent chloride concentrations.
- Infiltration SCMs ((I_{infilt}): Half the impervious surface drains to infiltration SCMs; scenario-dependent chloride concentrations.

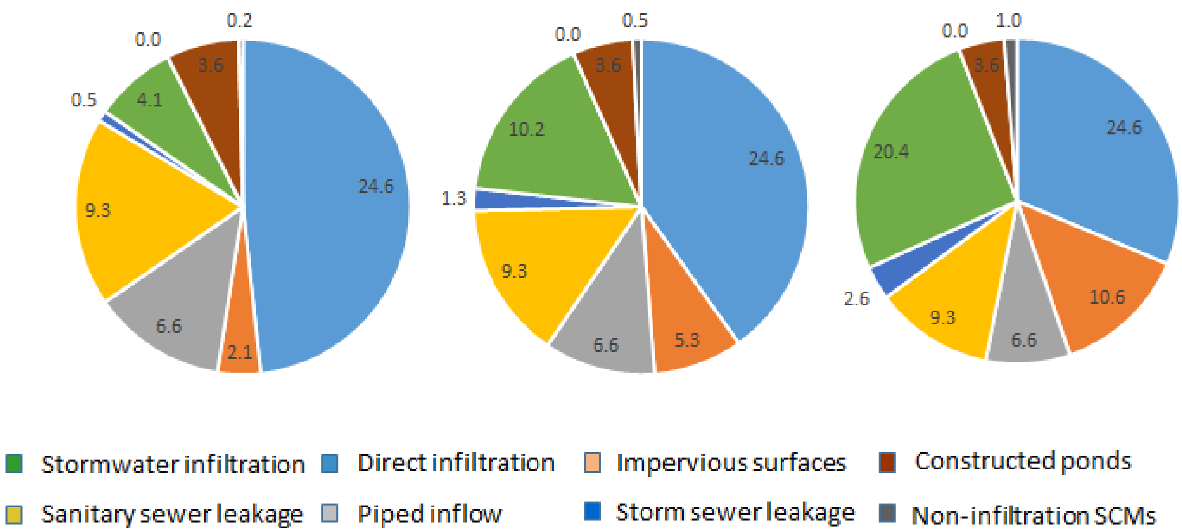
Results are shown below. Results are given in kilograms per hectare.

The following key applies to the pie charts. Values of “0” in the pie charts correspond with surface water discharges, which were assumed to be 0 in the simulations.

Stormwater infiltration	Direct infiltration	Impervious surfaces	Constructed ponds
Sanitary sewer leakage	Piped inflow	Storm sewer leakage	Non-infiltration SCMs

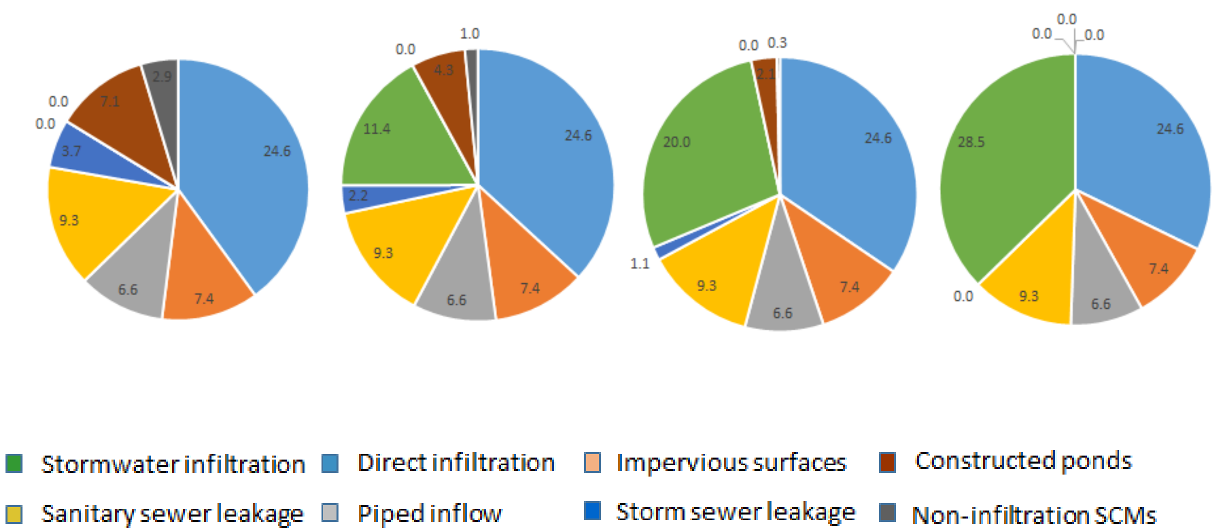
Scenario 1: Varying chloride concentration

For the base scenario described above, chloride concentration in runoff was varied. Inputs were 20 mg/L, 50 mg/L, and 100 mg/L.



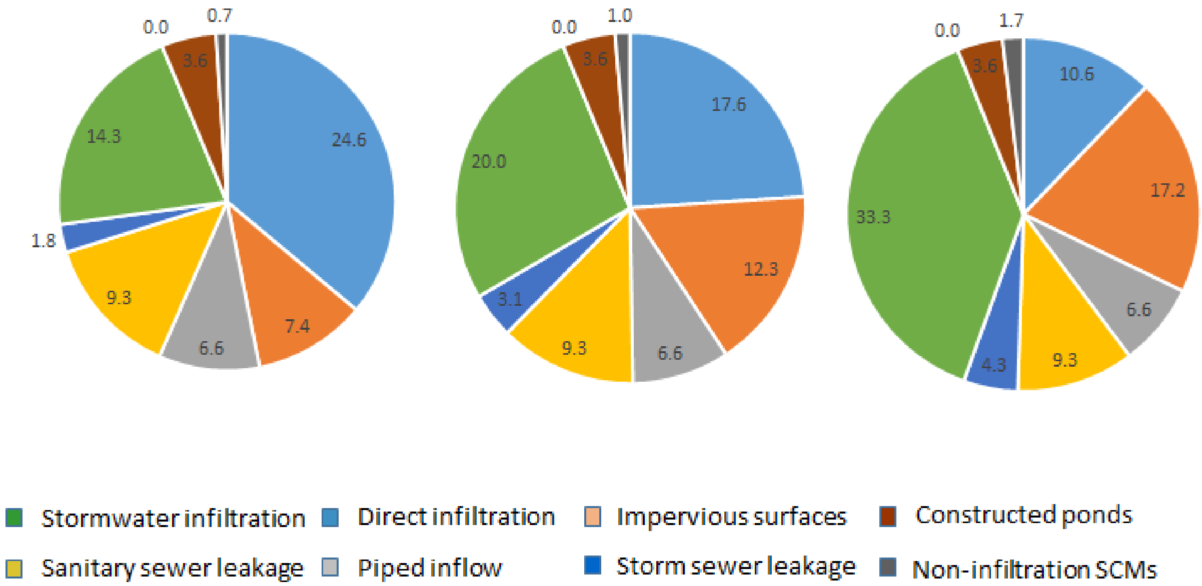
Scenario 2: Varying the area treated by infiltration practices

For the base scenario described above, the fraction (or percent) of runoff captured by an infiltration practice was varied. Inputs were 0, 40, 70, or 100% of runoff captured. Chloride concentration for all simulations was 70 mg/L.



Scenario 3: Varying the amount of impervious surface

For the base scenario described above, the fraction (or percent) of impervious surface was varied. Inputs were 30, 50, or 70% of the area being impervious. Chloride concentration for all simulations was 70 mg/L.



MINNESOTA GROUND WATER ASSOCIATION
NOVEMBER 2020