Road Salt Deicers as Contaminants in the Environment:

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ROAD SALT DEICERS AS CONTAMINANTS IN THE ENVIRONMENT

Oriana Battifarano

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> Boston College Morrissey College of Arts and Sciences Graduate School

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Abstract

Over 10 million tons of deicers are applied on impervious surfaces during winter storms in the United States every year to create safer driving and walking conditions. Road salt, or sodium chloride, is the most common deicer due to its low price and wide availability. Increasing concentrations of sodium chloride (NaCl) over the past decades have been measured in surface waters and groundwater throughout North America and it is projected to continue increasing. As there are no cost effective alternatives available to road salt, its potential role as an environmental and drinking water contaminant needs to be investigated. Field measurements from previous studies reveal the homogenization of NaCl in the subsurface through consistent elevated levels year-round. Through the integration of field and laboratory methods, this thesis aims to investigate the role of subsurface processes in the transport and pathways of deicers from the point of deposition to eventual emergence in surface waters and its potential impact on drinking water supplies. To understand the contamination pathways of NaCl that result in the observed surface water concentrations, experimental simulations were designed that indicate that gravitational/convective processes are the most important initial processes influencing deicer transport, but that other processes such as diffusion, surface tension, and dispersion/advection also play important roles.

Executive Summary

Deicers are used in regions that receive snow and ice during the winter months as they lower the freezing temperature of water and help maintain traction on impervious surfaces. Their use first became widespread in the United States with the expansion of the highway system in the 1940s. For the past 30 years, more than 10 million tons of deicers have been deposited nationally every year. The most common deicer is road salt, or sodium chloride (NaCl), as it is inexpensive and widely available. While other types of deicers are used, they are far less common, tend to be much more expensive, and are not considered particularly better for the environment.

Increasing levels of NaCl have been measured in surface waters and groundwater throughout North America for decades. Although there are other sources of sodium and chloride, these increases have been tied to road salt application. Studies have found that a percentage of NaCl is trapped within watersheds every year, with estimates ranging up to 80% retention. This retention is contributing to a buildup in the subsurface over time and increasing NaCl concentrations in surface waters. Increasing levels of road salt contamination pose risks for freshwater species, soil quality, vegetation, and drinking water sources. There are already surface waters that have exceeded levels deemed safe by the Environmental Protection Agency.

This thesis utilizes a two-pronged approach of field and laboratory methods to attempt to understand the transport mechanisms and patterns of deicer contaminants. First, two sensors placed at different depths in Bogle Brook (Weston, Massachusetts) downstream of a highway provide NaCl concentration measurements of the main streamflow as well as the local discharge from December 2015 to October 2019. The

iv

sensors show elevated levels of NaCl throughout the year despite application only occurring before and during winter storms, revealing the subsurface homogenization of deicers. Second, experimental simulations help provide insight on the transport pathways and mechanisms that result in the homogenization observed in the field. The combination of these two approaches allows for a more complete understanding of the inputs and outputs of the system as well as the processes that influence deicer transport in the subsurface.

The field data show that the NaCl concentration of the local discharge is consistently higher than that of the main streamflow. Although the concentrations increase in the winter months, they remain elevated throughout the year, which indicates there is a homogeneous, diluted source of NaCl. The experimental simulations demonstrate that the most important initial subsurface processes for subsurface transport is gravity/convection. Once the dissolved deicer has infiltrated further, surface tension/osmotic pressure and diffusion likely play more of an important role. These processes, along with dispersion/advection, influence contaminant transport and therefore influence drinking water quality.

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The rage	1
Copyright Page	ii
Abstract	. iii
Executive Summary	. iv
Acknowledgements	. vi
Table of Contents	vii
List of Tables	. ix
List of Figures	. ix
 1.0 Introduction	1 3 9 .14 .14
 2.0 Background. 2.1 Field Site Monitoring. 2.2 Subsurface Transport 2.2.1 Role of Precipitation 2.2.2 Role of Soils 2.2.3 Role of Groundwater	17 17 20 21 23 27 29
 2.0 Background 2.1 Field Site Monitoring 2.2 Subsurface Transport 2.2.1 Role of Precipitation 2.2.2 Role of Soils 2.2.3 Role of Groundwater 2.2.4 Subsurface Deicer Transport Processes 3.0 Objective 	17 20 21 23 27 29 33
 2.0 Background	17 17 20 21 23 27 29 33 34 34 34 38

Table of Contents

5.2.1 Infiltration Experiments	57
5.2.2 Convection Experiments	63
6.0 Discussion	72
6.1 Field Monitoring	72
6.1.1 Overall Patterns	72
6.1.2 Main Stream vs. Local Baseflow Discharge	73
6.1.3 Seasonal Response	73
6.1.4 Precipitation Response	74
6.1.5 Groundwater Transport	75
6.2 Experimental Observations	75
6.2.1 Infiltration Experiments	75
6.2.2 Convection Experiments	77
6.2.3 Subsurface Groundwater Transport	78
7.0 Conclusions	79
7.1 Field Observations	79
7.2 Experimental Study	80
7.3 Deicer Contaminant Transport	82
-	
References	83

Table 1. Visual timeline of data acquisition44
Table 2. Ion chromatography concentration comparison of Bogle Brook 49
Figures
Figure 1. Freezing point depression comparison2
Figure 2. Annual average of dissolved NaCl in Stillwater River, Mass
Figure 3. Annual average of dissolved NaCl in Hobbs Brook, Mass
Figure 4. Yearly average sodium and chloride concentration5
Figure 5. Chloride concentration estimates at different percentile flow rates
Figure 6. Long-term increases in chloride baseline concentrations
Figure 7. A comparison of summer and winter chloride concentrations
Figure 8. Road salt build-up model results9
Figure 9. Profiles of soil extracted from cores11
Figure 10. Future progression of chloride concentration in baseflow discharge13
Figure 11. Charles River watershed map18
Figure 12. Photo of road salt storage facility on I-90
Figure 13. Chloride applied to roads and exported
Figure 14. Chloride concentration from summer to winter
Figure 15. Daily mean electric conductivity and discharge
Figure 16. Na ⁺ vs. Cl ⁻ concentration of Mohawk River
Figure 17. Na ⁺ vs. Cl ⁻ concentration of aquifer
Figure 18. Simulated chloride concentrations
Figure 19. Demonstration of plume patterns

Tables

Figure 20. Change in chloride concentration with depth	32
Figure 21. AquaTROLL 200 data logger sensors	35
Figure 22. Placement of sensors within Bogle Brook	35
Figure 23. Bogle Brook location	37
Figure 24. Specific conductance v. chloride calibration curves	37
Figure 25. Top experiment	40
Figure 26. Bottom experiment	40
Figure 27. Setup for benchtop experiments	42
Figure 28. Temperature difference between probes	45
Figure 29. Stream discharge	45
Figure 30. Water column difference between probes	46
Figure 31. Specific conductance difference between probes	47
Figure 32. NaCl concentration and water column comparison of main stream flow	47
Figure 33. NaCl concentration and water column comparison of local discharge	48
Figure 34. NaCl concentration and discharge comparison	48
Figure 35. Summer NaCl concentration difference	50
Figure 36. Summer stream discharge	51
Figure 37. Summer water column difference	51
Figure 38. Winter NaCl concentration difference	52
Figure 39. Winter stream discharge	53
Figure 40. Winter water column difference	54
Figure 41. October precipitation NaCl concentration comparison	55
Figure 42. January precipitation NaCl concentration comparison	56

Figure 43. 1% NaCl top experiment progression	
Figure 44. 1% NaCl top experiment image analysis	
Figure 45. 1% dextrose top experiment progression	
Figure 46. 1% dextrose top experiment image analysis	61
Figure 47. 1% CsCl top experiment progression	
Figure 48. 1% CsCl top experiment image analysis	
Figure 49. DI water bottom experiment progression	64
Figure 50. DI water bottom experiment image analysis	65
Figure 51. 1% NaCl bottom experiment progression	
Figure 52. 1% NaCl bottom experiment image analysis	
Figure 53. 1% dextrose bottom experiment progression	
Figure 54. 1% dextrose bottom experiment image analysis	
Figure 55. 1% CsCl bottom experiment progression	
Figure 56. 1% CsCl bottom experiment image analysis	

1.0 Introduction

Deicers are chemicals applied to impervious surfaces during subfreezing periods before or during winter storm events. They prevent the formation of ice layers on these surfaces and therefore create safer driving and walking conditions. Although they have been used widely in North America for over 60 years, their role as a contaminant in the environment and in drinking water sources are only just beginning to be understood (Ludwikowski and Peterson, 2018).

1.1 What Are Deicers?

The melting of ice into a liquid form through the introduction of a solute is known in physical chemistry as freezing point depression (Fig. 1). Figure 1 compares the freezing point depression of several deicing chemicals. The left liquidus lines show the temperature at which each solution has a particular concentration in equilibrium with ice (% by weight). These lines all originate at 32°F on the left axis, the freezing point of water, and then diverge. The eutectic points show the temperature and concentration at which each solution freezes/melts, or the lowest temperature at which the solution can exist with ice. For example, at 20°F a NaCl solution will have a concentration of about 10% by weight (Fig. 1).

Deicers suppress the formation of ice by replacing ice with liquid which maintains traction between tires and the road. A study of vehicle accidents in four northern states found that the use of deicing salts on road surfaces reduced the accident rate on highways

1

by 88% (Keummel, 1992). Among common deicers, NaCl is by far the most widely used, with calcium chloride (CaCl₂) as the second choice and followed by calcium magnesium acetate (CaMg₂(CH₃COO)₆) and potassium acetate (K(CH₃COO)). While acetate-based compounds are considerably less harmful to plants and aquatic life (Wagner and Yaggi, 2010), their cost is typically 10 to 20 times more expensive, ranging anywhere from \$700 to \$1200 a ton while granular road salt is only \$50 to \$60 a ton (Shi et al., 2009).



Figure 1. A comparison of the freezing point depression of several deicing chemicals.

The sale of rock salt for highway use was 149,000 Mg in 1940 while today it is more than a hundred times higher at ~18 million Mg (Jackson and Jobbagy, 2005). The average annual road salt use in Massachusetts is approximately 19.4 tons per lane 1.61 kilometers, which has remained constant since the 1970s, with any changes due to variability in the severity of winter storm conditions (Transportation Research Board, 1991; Huling and Hollocher, 1972). The quantity of road salt used on private property, such as parking lots and driveways, is very difficult to estimate with any degree of reliability as good records are generally not kept (Perera et al., 2013). Current best management practices are focused on reducing and optimizing the amount of road salt released into the environment during storage and handling as well as ensuring salt application at an optimal rate with properly calibrated salt spreaders (Perera et al., 2013). There is potential for developing practices that target road runoff and infiltration, minimizing discharge of chlorides into surface and groundwater (Perera et al, 2013).

1.2 Trends in Concentration Levels of Deicers in Surface Water

Once deicers are applied on impervious surfaces they quickly dissolve and enter the environment as contaminants. The continuous use of NaCl as a deicer in winter months leads to the pattern of increasing NaCl in surface waters with some annual variation. There are other sources of sodium and chloride such as weathering and natural salt deposits and well as septic and sewage effluent, water softeners, and agriculture (Kelly et al., 2008). However, a strong positive-linear relationship has been observed between the application rate of chloride based deicers and both the maximum chloride concentration and total mass accumulated within watersheds (Ludwikowski and Peterson, 2018). In regions that receive snow, increasing chloride levels in surface water have been tied to increases in impervious surfaces and urbanization (Rhodes et al., 2001). Impervious surfaces now cover more than 118,000 km² and are projected to increase (Elvidge et al., 2004). In some locations in the northern U.S., chloride concentrations have outpaced the rate of urbanization and the greatest increase in chloride concentrations were in watersheds with the greatest urban land cover percentage (Corsi et al., 2015).

The trend of increasing NaCl can be observed in watersheds throughout northern North America. Godwin et al. (2003) found that over 50 years of road-salt application in the Mohawk River in New York has increased the concentration of sodium by 130% and chloride by 243%. Surface water chloride has increased by as much as 760% in the Merrimack River watershed, New Hampshire, over the 20th century (Robinson et al., 2003). In Stillwater River, a tributary to the Quabbin reservoir in Massachusetts, the documented increase of NaCl was 1.7 parts per million per year for the past two decades (Fig. 2), and in Hobbs Brook, a part of the City of Cambridge, Massachusetts, water supply, there was an increase of 8.6 parts per million per year for the past decade (Fig. 3). In a rural stream in southeastern New York chloride increased 1.5 mg/L per year and sodium increased 0.9 mg/L per year with no increase in road salt use (Fig. 4) (Kelly et al., 2008). Rates of increase for several streams near Chicago, Illinois are in excess of 10 mg/L per year (Kelly et al., 2012).



Figure 2. Annual average dissolved NaCl in Stillwater River. Measures are derived from USGS SpC readings using conversion equation NaCl (ppm) = .447*SpC-26.47. Flux represented by year-to-year changes in NaCl content.



Figure 3. Annual average dissolved NaCl in Hobbs Brook. Measures are derived from USGS SpC readings using conversion equation NaCl (ppm) = .447*SpC-26.47. Flux represented by year-to-year changes in NaCl content.



Figure 4. Yearly average sodium and chloride concentration (mg/L) of Wappinger Creek in Millbrook, NY from Kelly et al. 2008.

NaCl concentrations have not only increased in the winter, but also in the summer months. Corsi et al. (2015) found that concentrations increased in most streams in all seasons throughout the northern U.S., with levels above 230 mg/L in the winters and above 100 mg/L in the summers (Fig. 5). Kaushal et al. (2005) observed chloride concentrations remaining up to a hundred times greater than unimpacted forested streams during summers in streams of Maryland, New York, and New Hampshire (Fig. 6). Demers and Sage (1990) also reported that high chloride concentrations were not restricted to months of salt application in the Adirondack Mountains, New York. The trend of increasing NaCl concentrations in the summer months has also been attributed to NaCl year-to-year retention in the subsurface (Fig. 7) (Kelly et al., 2008).



Figure 5. Chloride concentration estimates at 10, 50, and 90 percentile flow rates over time from Corsi et al. 2015. Graphs are presented in order of decreasing watershed size and increasing urban land cover from left to right. The dashed line is the USEPA chronic water quality criteria of 230 mg/L.



Figure 6. Examples of significant, long-term increase in baseline concentrations of chloride for streams and rivers of the northeastern United States from Kaushal et al. 2005.



Figure 7. A comparison of summer (May-September) and winter (October-April) chloride concentrations (mg/L) of Wappinger Creek in Millbrook, NY from Kelly et al. 2008.

Based on projections of the rise of impervious surfaces in the United States, some authors have argued that many surface waters in the northeast will soon be unsafe to use as sources of drinking water due to increased salinization (Kaushal et al., 2005). In urban aquifers, Cl⁻ concentrations often exceed the safe levels of the Environmental Protection Agency's chronic chloride threshold of 250 mg/L, with increasing trends also found in rural watersheds (Mullaney et al., 2009; Corsi et al., 2015). Ludwikowski and Peterson (2018) ran build-up scenarios to simulate road salt application for 60 winter seasons, with each scenario having a different application rate. As the application rates increase, the maximum chloride concentration also increases in a linear relationship and for each application rate the maximum chloride level increases every year (Fig. 8a-b). The amassing of chloride within the system occurs regardless of the rate of application and after 60 years, only the lower rates of application show signs of nearing a steady-state (Fig. 8d). (Ludwikowski and Peterson, 2018).



Figure 8. Build-up model results for the groundwater of Little Kickapoo Creek drainage basin (central Illinois), wherein road salt was applied for 60 winter seasons from Ludwikowski and Peterson 2018. a) Relationship between the application rate and maximum chloride concentration at the end of 60 winter seasons. b) Maximum chloride concentration at the end of each five-year period. c) Relationship between the application rate and the mass of chloride within the system. d) Net mass of chloride at the end of each five-year period. The dashed line represents the EPA secondary drinking water standard (250 mg/L).

1.3 Trends in Concentration Levels of Deicers in Groundwater

Increasing concentrations of NaCl have also been observed in groundwater across North America. As early as 1970, chloride concentrations in town wells in Massachusetts

were already reaching values exceeding 100 mg/L, with one well showing peak

concentrations greater than 200 mg/L (Huling and Hollocher, 1972). Pilon and Howard (1987) measured chloride concentrations of up to 14,000 mg/L in shallow groundwater close to downtown Toronto. Labadia and Buttle (1996) measured sodium and chloride concentrations exceeding 500 mg/L and 1000 mg/L respectively during late summer at depths >2m (Fig. 9). Rosenberry et al. (1999) found that deicing salts had penetrated at least 123 m into the bedrock. Novotny et al. (2009) measured concentrations as high as 2000 mg/L in shallow groundwater wells in Minnesota. Sarwar et al. (2012) found average chloride concentrations of 2700 mg/L in shallow groundwater below primary and secondary roadways.



Figure 9. Profiles of (a) soil water content, (b) δ^{18} O levels in soil water, (c) Na⁺ and (d) Cl⁻ concentration in soil water extracted from cores obtained in spring and autumn from the Oak Ridges Moraine in southern Ontario, Canada from Labadia and Buttle 1996.

Paine (1979) was one of the first researchers to suggest that deicers might be accumulating in the subsurface and could one day reappear to cause serious damage. Increasing NaCl in streams indicates a lag effect of long-term road salt use and subsurface buildup. Soil retention and accumulation in groundwater might act as reservoirs of NaCl, behaving first as a sink and then eventually a source of NaCl (Kincaid and Findlay, 2009). A gradual accumulation of chloride in groundwater can lead to elevated concentrations during periods dominated by baseflow discharge in the summer months and can contribute to long-term increases in the baseline salinity of surface waters (Rosenberry et al., 1999; Paul and Meyer, 2001). The gradual accumulation of salt in aquifers and its subsequent release in baseflow discharge to streams can cause chronic impacts that extend long beyond the period of salt application. Chloride discharge by baseflow has a year-round, long-term impact on aquatic flora and fauna as opposed to chloride in surface runoff that normally occurs during short events in winter and early spring (Perera et al., 2013).

Estimates of the portion of deicers that remains in the watershed reservoir each year vary widely depending on its location and properties. Kelly et al. (2012) found that only about 14% of the deicer salt is retained in the subsurface near Chicago, Illinois. Huling and Hollocher (1972) estimated that close to 35% of the salt applied in winter in Massachusetts would infiltrate into the groundwater. By contrast, a study in Minnesota in 2016 found that 70-78% remains in the watershed each year (Minnesota Pollution Control Agency, 2016). Howard and Haynes (1993) reported that only 45% of deicers applied in an urban Toronto catchment was released annually and that concentrations in the subsurface increased even though application rates did not.

Other studies have postulated that continual application of deicers and the incremental removal on an annual basis will eventually lead to steady-state situation in which the application rate would become balanced by removal. However, estimates of when the steady-state will be reached and what the maximum concentration would be vary widely (Howard and Haynes, 1993). Huling and Hollocher (1972) assumed that if application rates remained similar in Massachusetts, the steady-state would be reached at about 160 mg/L. On the other hand, Perera et al. (2013) found that late summer baseflow concentrations would increase to around 505 mg/L, double present levels (Fig. 10). Boutt

12

et al. (2001) found that watersheds will reach steady-state conditions in 50 years while Howards and Haynes (1993) estimated a steady-state of $426 \pm 50 \text{ mg/L}$ in 60 years. Bester et al. (2006) predicted that under conditions of continuous salt input, equilibrium concentrations attainment may be on the order of hundreds of years. Meriano et al. (2009) estimated that present day groundwater chloride concentrations are about 80% of longterm concentrations when the system reaches steady-state. The time it takes for a system to reach a steady-state depends on the rate of application as well as land-use over the period of time (Ludwikowski and Peterson, 2018).



Figure 10. Future progression of chloride concentration in baseflow based on historical observations in Highland Creek, Toronto, Canada from Perera et al. 2013. The projections take into account a potential $\pm 20\%$ variability in private road salt contribution and predict steady-state levels at around 505 mg/L.

1.4 Deicer Transport in Aqueous Systems

Effective deicers are highly soluble and travel to streams either through surface runoff or first as dissolved components in groundwater before reaching surface waters. During precipitation events, some portion of dissolved deicers are transported as overland flow directly into surface streams. Dissolved deicers can also reach surface waters quickly through drainage ditches and storm sewers alongside impervious surfaces (Huling and Hollocher, 1972). Chloride loads in rivers and streams are detected within hours of road salt deposition unlike yearlong increased levels observed in section 1.3 in groundwater (Kelly et al., 2012). Deicers that are transported by groundwater travel at a much slower pace. Following precipitation, water infiltrates and moves through the ground based on porosity and fractures in the underground rock. As void space increases, possible volume of transport pathways increases as well. Water generally moves down the slope of the water table with decreasing pressure and elevation (hydraulic head) (Kirchner et al., 2000).

1.5 Environmental Implications

Long-term impacts of increasing concentrations of NaCl in surface water and groundwater is a major concern. Individuals with hypertension, over 25% of the adult population in the United States, are particularly vulnerable to increasing sodium in water (Siegel, 2007). There is also an ecological impact seen on a variety of species that are sensitive to small changes in salinity. Streams will become toxic to aquatic life if chloride

14

concentrations chronically exceed 250 mg/L and a few freshwater species are vulnerable at even much lower levels (Kaushal et al., 2005; EPA). There are changes in the mortality and reproduction of aquatic plants and animals with increased NaCl (James et al., 2003). There may be permanent alteration of the species present in fresh surface water ecosystems and sustained high concentration of NaCl during the more biologically active summer months may increase ecological effects (Kincaid and Findlay, 2009). Very large seasonal fluctuations in chloride concentrations could also be detrimental to freshwater life that is not able to adapt to rapid changes in salinity (Kaushal et. al, 2005).

Vegetation is also impacted as NaCl influences soil chemistry and cation exchange capacity, which mimics drought-like environments (MassDOT, 2012). Toxic metals can be mobilized through ion exchange or impurities in road salt (Lewis, 1999). Additionally, sodium cations tend to displace nutrients from soil and reduce soil permeability, soil stability, soil pH, and overall fertility (Berkheimer and Hanson, 2006). Increased concentrations of chloride can also lead to the acidification of streams (Lofgren, 2001). It also interferes with the natural mixing of lakes (Paul and Meyer, 2001). Additionally, salt has been shown to alter the structure of microbial communities and inhibit denitrification (Elshahed et al., 2004; Groffman et al., 1995). These effects may influence broader ecosystem processes in aquatic systems relating to primary productivity, decomposition, nutrient cycling, and the trophic complexity of food webs (Kaushal et al., 2005).

Many of the projections involving road salt have not taken into account a changing climate. Salt removal and transport is influenced by storm frequency and intensity, both of which are projected to change as a result of anthropogenic climate

15

change. If winter precipitation shifts towards a higher portion of rainfall, or summer experience a greater frequency of tropical storms, then long-term residence time of road salt in watersheds may be shorter than previously anticipated. Conversely, if the climate becomes drier, with increased evapotranspiration, reduced infiltration and baseflow discharge may prolong salt storage, which could exacerbate biotic stresses from high chloride concentrations in streams. Although there may be fewer snowfall events, the application of road salt is not likely to decrease significantly in the near future (Stirpe et al., 2017). As NaCl will continue to be used as a deicer for the foreseeable future, its role as a contaminant in the environment should be of concern.

2.0 Background

The transport mechanisms of deicer contaminants need to be better understood: where the deicers are applied, where they enter the subsurface, and how they travel through the subsurface toward the points of discharge into surface waters. Monitoring of surface streams reveals the pattern and concentration of NaCl release depending on the season, precipitation, and other factors. However, it does not provide insight into the transport pathways and mechanisms in the subsurface that cause changes in concentration. Therefore, this project has two parallel tracks: field observations and laboratory investigations.

2.1 Field Site Monitoring

In this section, the focus is on the collection of high frequency (every 15 minutes) field data that could provide information about the pattern of deicer discharge and how it varies by season and precipitation events. The field site chosen is on Bogle Brook at Winter Street in Weston, Massachusetts, a subcatchment of the Charles River Watershed. The drainage area is small, only 7.69 km², which is an advantage as sources of contaminants are more easily constrained in smaller areas. The specific location is at the Rivers School (42.322932 °N, 71.324010 °W) (Fig. 11) and is downstream from Nonesuch Pond (42.324847 °N, -71.328740 °W). It is situated next to a local road and where the bankfull width of the stream is about 3.66 m. This section of Bogle Brook is an ideal site to observe the patterns of discharge of deicers into surface waters as this

location is not only downstream of Interstate-90, but also downstream of a salt storage site operated by MassDOT (Fig. 12). Some of the deicers applied on I-90 will predictably infiltrate into the ground and a portion will be flushed directly into Bogle Brook as well as several other branches of the stream that feed into it. The salt storage facility is adjacent to the highway and while it is covered, some portions remain uncovered during the months leading up to winter storms when salt is stockpiled. Thus, the uncovered portions of the salt piles are exposed to rain events, which causes salt to be flushed into the nearby stream, into Bogle Brook.



Figure 11. Map showing the delineation for the Bogle Brook watershed. The blue marker on the right is the location of the sensors in Bogle Brook. The subcatchment of Bogle Brook has a drainage area 7.69 km² and 107.83 total lane kilometers. The map was obtained from StreamStats version 4.0 from USGS https://streamstatsags.cr.usgs.gov/streamstats/.



Figure 12. Photo of road salt storage facility located just north of Bogle Brook on the south side of Interstate I-90. On the left is a dual storage shed that is filled prior to the winter months and on the right is a deicer application truck. Photos taken on 3/9/17 by James Besancon.

USGS monitoring site 01103425 was active at Bogle Brook between 1968 and 1970, showing that the established stream and the surface water system have not undergone major recent changes. Land use of the subcatchment is characterized as follows: 51% residential, 31% forest, 6% commercial, 6% open space, 3% wetland and 3% other (Birnbaum and Zink, 2008) with a total of 107.83 lane kilometers, which was calculated using StreamStats. Based on the road salt application rate of 19.4 tons per lane 1.61 kilometers per year in Massachusetts, a theoretical input of 1,306 tons of NaCl are introduced to the watershed annually. The chosen site has clearly identifiable sources of deicers and will allow for determinations of the NaCl concentrations reaching surface waters and understanding of the processes of how the deicer concentrations reach surface waters and how they fluctuate throughout the year.

2.2 Subsurface Transport

With the exception of overland flow during precipitation events, the large portion of deicers are transported through the subsurface (Fig. 13) (Stirpe et al., 2017). Therefore, processes in the subsurface determine the speed at which deicers are transported towards surface waters as well as interactions with freshwater groundwater that may influence deicer concentration patterns. The factors controlling these processes include precipitation, soil composition, and groundwater flow.



Figure 13. Amount of chloride applied to roads and exported from the upper Casperkill watershed, New York, by water year from Stirpe et al. 2017. Numbers show percentage of export via baseflow vs. runoff.

2.2.1 Role of Precipitation

The main influences of precipitation on the presence of deicers in freshwater systems is dilution, spikes in NaCl concentration during winter storms, and increased NaCl concentration during periods of no precipitation that are dominated by baseflow. Stirpe et al. (2017) found that deicer (chloride) export in a wet year was almost twice the amount observed in a dry year. Summer storms play a significant role in the export of salt from watersheds and extreme precipitation events can produce disproportionately rapid salt export. For small rain events, most precipitation infiltrates into soils, raising the water table and increase baseflow discharge, which contains high chloride concentrations, to the stream channel. As rainfall increases, however, soils become fully saturated, and excess rainfall runs off the surface without picking up chloride from soils. This finding indicates that there is a threshold in the amount of chloride that can be removed from a watershed by a single storm. The magnitude of baseflow discharge varies dramatically and depends on precipitation patterns.

Stirpe et al. (2017) found that the chloride levels during baseflow conditions in a tributary to the Hudson River were 200-230 mg/L year-round with the lowest concentrations in summer after rain events, as dilution by precipitation sharply reduced chloride values. Winter precipitation caused spikes in chloride concentrations, which were associated with salt and/or snowmelt events and reached a maximum of 655 mg/L (Fig. 14). The most important factor in yearly chloride export was precipitation during non-salting season which determined overall moisture conditions and baseflow discharge volumes. Frequent storms maintained an elevated baseflow, kept soils moist, and

21

presumably increased the movement of shallow groundwater that enabled mobilization of accumulated salts (Stirpe et al., 2017). A strong negative correlation between electric conductivity, which serves as a proxy for NaCl concentration, and stream discharge was observed during a 2-year period on Pine Creek near Lake Ontario (Fig. 15). This trend is explained by the dilution effect of adding water to the stream during precipitation events (Meriano et al., 2009). The pattern of precipitation in a particular region will alter the transport of NaCl deicers through the subsurface stage of deicer transport.



Figure 14. Chloride concentration and stream discharge in the transition from summer to winter conditions from the upper Casperkill watershed, New York, from Stirpe et al. 2017. Winter is shaded gray.



Figure 15. Daily mean electric conductivity and discharge, Pine Creek, Ontario, Canada, January 22, 2004 to November 1, 2005 from Meriano et al. 2009.

2.2.2 Role of Soils

Soils may act as a reservoir for NaCl as it starts to infiltrate into the subsurface (Kincaid and Findlay, 2009). Kindcaid and Findlay (2009) found that although the likely source of NaCl is shallower groundwater, a variety of common soils could retain chloride over a several week period. They also found that Cl retention could persist even after precipitation events. In general, Cl is considered to behave as a conservative tracer in soils, moving through a system with little or no effect on its concentration. However recent studies have found that significant amounts of Cl are retained in catchment areas (Lovett et al., 2005). Bastviken et al. (2006) showed that longer soil water residence time and higher chloride load resulted in higher initial retention and subsequent release rates than shorter residence times and lower chloride load did. At some point, when the

retention capacity of soils is reached and if no more NaCl is applied the soils will gradually release Na and Cl for at least 2.5-5 months after. Much longer retention periods are probable depending on variable moisture conditions, periodically higher road salt applications rates, and more complicated water flow paths (Heather et. al., 2015).

An important quality of a soil is its cation exchange capacity, which is its total capacity to hold exchangeable cations. Chloride tends to be more conservative while sodium is more attracted to cation exchange. If there is significant transport through soils where Cl anions are more mobile than Na cations, then the ratio of Na to Cl could decrease as Na displaces Ca, Mg, K, and protons in the soil (Jackson and Jobbagy, 2005). Rhodes et al., (2001) found that in salt-impacted streams, chloride exceeded sodium by 10-15%. However, in other studies, a near 1:1 ratio of sodium to chloride is observed with only a slight deficit in sodium (Fig. 16) (Godwin et al., 2003). Rhodes and Guswa (2016) found that the sodium/chloride ratio imbalance increases with depth, with sodium decreasing at faster rates. Locat and Gélinas (1989) found that up to 25% of the Na⁺ ions are adsorbed on the minerals as is shown by the departure from the Na = Cl line (Fig. 17). Higher levels of sodium may also be attributed to the fact that NaCl deicers are sometimes applied alongside CaCl deicers, which provides additional chloride but not additional Na ions, thus altering the overall Na/Cl ratio.


Figure 16. Na⁺ vs. Cl⁻ concentration from 1990-1998 in the Mohawk River from Godwin et al. 2003. The trend shows 8.47% excess of Cl⁻ over Na⁺. The 1:1 line is dashed.



Figure 17. Relationship between the concentration of Cl⁻ and the concentration of Na⁺ in the saturated zone of the aquifer underlying Trois-Rivières-Ouest, Quebec, Canada, from Locat and Gélinas 1989.

The processes that result in chloride retention and release within the watershed are still up for debate (Bastviken et al., 2006). Larsson and Jarvis (1999) suggest that

heterogeneous vertical transport patterns with varying flow through pores of different size reduce leaching and can cause retention of soil water solutes. Robinson et al. (2017) found that soils retained 62% of the applied Cl and 66% of the applied Na on average, which was largely stored in porewater. The correlation between Cl and water content indicates a link between Cl retention and porewater retention. Water content is higher in soils with larger pore spaces so it is possible that while sandier soils facilitate faster infiltration, they also include more variability in flowpaths, with water draining rapidly through preferential pathways between sand grains (Robinson et al., 2017).

Porewater can move both vertically through a soil profile of variable depth and horizontally along lateral flow paths (Robinson et al., 2017). Even if the volume of the pore water is replaced multiple times, there is still salt retention, which may be due to some water following preferential flow paths while other pore water clings to soil particles and is retained (Robinson et al., 2017). Porewater alone cannot explain retention, other factors (chlorination of soil organic matter, uptake by microbes or plants, or non-specific adsorption) also play a role (Robinson et al., 2017). The type of soil or material in the subsurface will have a complex impact on the transport of NaCl deicers.

2.2.3 Role of Groundwater

The rate of sodium transport in groundwater depends on, among other factors, the recharge rate of the aquifer system and the hydraulic conductivity of the material. Areas dominated by glacial till have higher chloride concentrations and continue to store it for longer periods of time (Ludwikowski and Peterson, 2018). Once in groundwater, chloride

27

transport is a function of groundwater flow and therefore the residence time can be decades to thousands of years (Daley et al., 2009). Rhodes and Gusway (2016) found that road salt contamination is greatest within the upper 2 m of a peat profile and that groundwater contamination is largely a near-surface phenomenon. The stored chloride may not be evenly distributed within the subsurface and water quality stratification will occur depending on the local groundwater flow regime (Howard and Haynes, 1993).

Bester et al. (2006) performed simulations of how chloride could be distributed and transported through the subsurface from several different points of infiltration to better understand chloride behavior in the subsurface. Their results suggest that the aquifer system contains a large and heterogeneously distributed mass of chloride and that concentrations in the aquifer can be substantially higher than the concentrations in the well water. Salt plumes originating at arterial roads are seen to first migrate vertically downward through the unsaturated zone and once they reach the aquifer, they follow the hydraulic gradient toward the wells. Chloride concentration gradients generally decrease with depth as the plumes become dispersed and as plumes from different roads merge (Fig. 18). Aquifer heterogeneity can lead to very heterogeneous chloride distribution in the aquifer system, even at depth.



Figure 18. Simulated chloride concentrations across cross-sections from Bester et al., 2006.

2.2.4 Subsurface Deicer Transport Processes

To be released into streams as baseflow, deicer brines are subjected to interactions with groundwater. These processes may include, but are not limited to, gravitational forces (the density contrast), diffusion (as a static counterpart to dispersion), flow mixing/dispersion, and osmotic/surface tension. The role of these processes will depend greatly upon other factors of the subsurface such as those discussed above (precipitation, soil, and groundwater) and could vary significantly between different regions or even adjacent watersheds. Due to these complex factors, simplified simulations can allow for more direct observation of the processes at play. When fluids infiltrate the ground they enter the soil zone followed by the intermediate zone, where they are referred to as suspended or vadose water. In these zones, the primary influence of movement is gravitational, and denser liquids will move downward at a more rapid rate. Below is the capillary fringe in which material with air pockets transitions to fully saturated material. The tendency of water molecules to adhere to surfaces of solids combined with surface tension of water causes capillary forces. Surface tension is due to molecular attraction forces in the surface of a liquid when exposed to a fluid with which it does not mix (i.e. water and air). Air pockets slow the movement of fluids as they migrate down towards the saturated zone. Simulations by Lax and Peterson (2009) show that within the unsaturated zone, chloride transport is predominantly vertical, driven by molecular diffusion. An initial plume of elevated chloride forms close to the road and migrates primarily downward, the concentration decreasing with depth.

Once in the saturated zone, deicer brines encounter a large supply of freshwater and the processes of dispersion and flow mixing/dispersion may start to have an increased influence. While the movement of the deicer brines is likely to be primarily downward initially, lateral movement could increase once they begin to mix with the freshwater. Gravitational influences continue due to density-driven free convection, which may occur alone or simultaneously with hydraulically driven forced convection. It forms lobe-shaped instabilities or fingers and accelerates the spreading of solutes when the density of the invading solute is significantly greater than that of the ambient groundwater (Xie et al., 2012). Xie (2012) concludes that infiltration and percolation speeds depend on the continuous effect of vertical penetration due to differences in

30

density. Demonstrations of flow in this study point to characteristic plume patterns as a result of density difference (Fig. 19).



Figure 19. Demonstration of plume patterns over time when a dense fluid is introduced to a less dense matrix (Xie, 2012).

Diffusion is the process in which thermal motion of individual molecules causes a flux of dissolved solutes from areas of higher concentration to areas of lower concentration and is largely a function of temperature. Diffusion of the deicer brine into the freshwater results in lower concentrations of NaCl as it is highly soluble. Flow mixing/dispersion is a mechanical process that largely depends on the hydraulic conductivity and other characteristics of the subsurface material. Dispersion of deicer brines results in the distribution of the solute at the leading edge of the flow. Jaques and Gélinas (1989) found that salt solutions proceed into the saturated zone along flow lines, 20).



Figure 20. Change in chloride concentration with depth in the sediments of the unsaturated zone from Jaques and Gélinas 1989.

3.0 Objective

The purpose of this project is to study the contamination transport mechanisms and pathways of deicer brines from the infiltration sites through the subsurface to discharge points in local streams and ponds. Deicers are deposited on impervious surfaces and then removed as deicer solutions in episodic events at the points of infiltration. While transported as solutions in the environment, deicers enter water supplies as contaminants. Sensors at NWIS sites located next to major highways show very sharp NaCl loading pulses of 10,000 ppm (1%) or even higher directly following storm events. The concentration levels during these events closely match those of the deicer saturated solutions at mean freezing temperatures (Fig. 1). However, field data collected over multi-season time periods at sites some distance from the highways show consistently elevated levels of NaCl concentration in the range of 400 ppm. These measurements are in contrast to the levels recorded near the highway runoff points.

Processes during the subsurface transport must lead to homogenization and spreading of heterogeneous deicer solutions between infiltration and baseflow discharge points. These processes may include, but are not limited to, gravitational forces (the density contrast), diffusion (as a static counterpart to dispersion), flow mixing/dispersion, and osmotic/surface tension. The observed patterns in the field must therefore be due some combination and/or interaction of these processes. These processes result in the near constant concentration of NaCl at the baseflow discharge point. Explaining the difference in NaCl concentration at or near the infiltration sites as opposed to local discharge points is the principal objective of this project.

4.0 Methods

This project uses two interrelated approaches to decipher the transport mechanisms of deicers between the points of application and ultimately flushing from the system through streams. One approach is detailed field monitoring and the other is laboratory experimental simulations to help explain field observations. The methodology section is accordingly divided into two respective parts.

4.1 Field Research

The field study part of this project is designed to collect a detailed set of data on stream water quality and long term trends at a field station in the Bogle Brook subcatchment of the Charles River watershed (Fig. 11), located downstream of a salt storage facility. Field data are collected using a pair of In-Situ, Inc. Aqua TROLL 200 Data Logger probes (Fig. 21). A dual-probe setup is selected to test fluctuations in the flowing stream. One probe, or sensor, is installed a few centimeters above stream bed and measures the water quality of the local baseflow discharge. The second sensor is installed at mid-depth, 9.1 cm above the first sensor, and measures the water quality of the main stream flow (Fig. 22). Both sensors record data at 15 minute intervals of three parameters: 1) specific conductance (μ S/cm), 2) temperature (°C), and 3) the water column measured as pressure (kPa). Water level (ft) is obtained from pressure and the specific gravity of water.



Figure 21. An image of the AquaTROLL 200 data logger sensors used in the field component of the study that measure temperature, pressure, and specific conductance every 15 minutes.



Figure 22. A diagram of the placement of the sensors within Bogle Brook at the Rivers School with one sensor placed at the stream bed (the lower conductivity sensor) and is only open to the discharge while the other was placed at mid-depth (the upper conductivity sensor) and is open to the main stream flow.

Specific conductance (SpC) is a measure of electrical conductivity referenced to 25° C, which is proportional to the total concentration of dissolved ions and provides information on the amount of dissolved deicers. Conductivity is measured by determining the resistance between two electrodes at a fixed distance and SpC is derived by correcting for temperature differences between 25°C and the actual temperatures. The correction is automatically applied within the sensor. The water column, or the pressure, is also impacted by changes in temperature due to thermal expansion.

SpC data are used as a reliable and swift method for the determination of the ionic content of a solution. At 25° C, the conductivity of distilled water is $0.055 \ \mu$ S/cm, drinking water is typically in the range of 50-500 μ S/cm, and seawater is 50,000 μ S/cm. SpC is a composite measure and does not distinguish between the individual types of ions present in solution. SpC values are related to the total dissolved solids and they depend on the chemical composition of the solution as well as the dissolved NaCl. The SpC values need to be calibrated in order to obtain the deicer (NaCl) concentrations.

The calibration of SpC is done by plotting known Cl⁻ concentrations against known SpC values using data from the USGS NAWQA water quality database for the Charles and Neponset Rivers (Fig. 23). The Charles River was chosen as a reference watershed as it is located close to the study site, likely receiving similar deicer inputs. The Neponset River was chosen due to its similar size. A calibration equation for SpC was derived from the average of the two linear fitting lines of the reference watersheds to obtain chloride values (Fig. 24). Chloride levels are then multiplied by the stoichiometric multiplier 1.648 to give apparent NaCl estimations.

36

(Atomic weight of sodium + Atomic weight of chloride)/Atomic Weight of Chloride = (22.99g/mol + 35.45 g/mol)/(35.45 g/mol) = 1.648



Figure 23. New England Coastal Basins NAWQA surface water sampling reference sites, Neponset River site at number 6 and Charles River at 7. The red star depicts Bogle Brook location.



Figure 24. Combined specific conductance v. chloride calibration curves average used to estimate chloride content of Bogle Brook

SpC and Cl concentrations are linearly related in the Charles and Neponset Rivers (Figure 24), indicating that the chloride content is controlled by one chemical or chemicals in a constant ratio. There appears to be a base SpC level (~70 μ S/cm), likely representing the natural chemical weathering of rocks (Fig. 24). As the geology and processes that govern the rate of weathering are similar through the northeast, this base SpC level in surface waters in this region are likely also similar. Any SpC values measuring higher than the base value are impacted by other sources, such as road salt.

In order to estimate the total stream discharge, which varies seasonally as well as with precipitation, the water level must be calibrated using a rating curve. Stream discharge (Q) is calculated by coordinating the average flows of the stream with the measurements of the permanent stream gage. The flow of the stream is converted into discharge (ft³/s) using the equation stream area (ft²)*stream flow (ft/s)=discharge (ft³/s). A rating curve is calculated in the format $q = K(z - z_0)^b$; q is discharge (ft³/s), z is stage (ft), and K, z_0 , and b are constants. The rating curve used in this study is from Rice (2017):

q=7.948633*(z-.588051).9704

4.2 Laboratory Experiments

Laboratory simulation experiments were designed to replicate the subsurface transport of deicers by monitoring the fluid flow through a porous substance over time in order to understand the influence of subsurface processes. The experiments used transparent 21x12x12 cm plastic tanks. A 1% NaCl solution was compared to deionized water as well as solutions of equivalent densities of dextrose, a non-polar solution, and cesium chloride (CsCl), a strong electrolyte. The role of surface tension is investigated through the comparison of the three solutions. Two different sets of experiments were run: infiltration and convection experiments. The first set of experiments tested infiltration and therefore they were initiated at the top of the tanks. The tank was filled with fine white quartz sand fully saturated with distilled water. An inclined scarp along the front wall of the tank was created and filled with 20 mL of the desired solution (Fig. 25). The solution was made visible by adding a few drops of blue tracing dye (CAS# 3844-45-9). A piece of clear plastic was placed on top of the tank to reduce evaporation. Each experiment ran for a few days until the majority of the solution reached the bottom of the tank and the sand at the front of the tank appeared fully blue. The second set of experiments tested convection and therefore they were initiated from the bottom of the tank. The tank was also filled with a fine white quartz sand fully saturated with distilled water. 5 mL of the desired solution was injected directly at the bottom of the tank with 1-2 drops of blue dye and the tank is covered in plastic (Fig. 26). Each of these experiments ran for three weeks to allow the solutions to travel and spread in the tank.



Figure 25. The experimental tank filled with sand with an artificial ditch at the top in which the dyed solution is placed.



Figure 26. The experimental tank with the dyed solution placed at the bottom.

In order to test if the weight of the blue dye has any influence on the progression of the experiments, the density of a 1% NaCl solution without the dye was compared to the density of the same solution, but with the blue dye present. A 10 cc pycnometer calibrated using distilled water was used and the solution without dye resulted in a density of 1.00669 g/mL and the solution with the blue dye resulted in a density of 1.0059 g/mL. The difference is statistically negligible indicating that the weight of the dye does not have an appreciable impact on the rate of percolation.

The deicer progress of each experiment was captured by high-resolution timelapse photography using the Canon Rebel T2i 18-megapixel camera (Fig. 27). An exposure time interval of 2 minutes was used for the first set of experiments as the solutions progressed quickly. An interval of 10 minutes was used for the second set of experiments as the solutions moved more slowly over a longer period of time. The sequential photos are then converted into time-lapse videos. Between each experiment, the sand is washed with bleach to remove all traces of the blue dye, then dried in an oven, and reused.



Figure 27. The setup for the benchtop experiments with the time-lapse photography.

The time-lapse photos taken during the course of the experiments were evaluated by raster image subtraction algebra using the image (raster) manipulation available inside the ArcGIS software package. The progression of the experiments can be algebraically evaluated by subtracting an earlier photo of an experiment from a later photo of the same experiment and observing the difference. The red band of the photos illustrates the progression of the solution over the course of the experiment and the darker parts of the image represent increased presence of the solution while the lighter portions indicate decreased presence of the solution.

5.0 Results/Data

The results section is divided into two respective, but interrelated parts: field monitoring and laboratory simulations of field processes. Collected field data consist of temperature, pressure, and specific conductance at two points within the stream, which provides information on variations of water quality. The laboratory simulations mimic the application of road deicing chemicals and compares them to solutions of equivalent density to understand transportation dynamics that result in the conditions observed in the field.

5.1 Field Data

The sensor positioned at the near-bottom of the Bogle Brook site collected data with several interruptions from December 2015 through October 2019. The mid-stream sensor collected data continuously from February 2016 through October 2019. There are continuous concurrent data for both sensors for four separate time periods: February 1, 2016-November 1, 2016, March 28, 2017-September 17, 2017, January 1, 2018-June 26, 2018, and October 1, 2018-October 16, 2019 (Table 1). Missing data for the near bottom sensor were caused by equipment malfunctions.

	2015	2016		.7	2018			2019		
Near- Bottom Sensor	Dec '15-Nov '16		Nov Mar '16-Mar '17- '17 Sep '17 '17-		Sep '17- Jan '18	Jan '18-Jun '18	Jun '18- Oct '18	Oct	'18-Oct '19	
Mid- Stream Sensor	Dec '1 Feb 16	5- Feb '16-Oct	' 19							

 Table 1. Visual timeline of data acquisition. Green indicates periods of uninterrupted data collection while red indicates periods of no data collection.

5.1.1 Overall Patterns

Temperatures in the stream during the monitored period varied between 0 and 33°C throughout the course of the year. There is only a slight difference between the measured temperatures in the upper and lower sensors, except during the summer months when there is a difference of up to 8°C with the lower sensor being warmer (Fig. 28). The water levels fluctuate between early spring and late summer by as much as 80 cm. The discharge of Bogle Brook can reach up to 16 ft³/sec during the early spring (Fig. 29). The pressure of the water column at the level of the upper senor ranged from 0 kPa in the summer when the stream level was below the level of the sensor to 6 kPa in the spring while the pressure of the water column at the level of the lower sensor was higher on average ranging from 1 to 8 kPa over the course of the year. The difference in pressure peaked at 3 kPa with the lower sensor always measuring a higher pressure (Fig. 30).



Figure 28: The difference in temperature between the lower and upper probe over time in Bogle Brook. The gaps represent no data periods.



Figure 29. The stream discharge over time. The gaps represent no data periods.



Figure 30. The difference in the pressure of the water column over time. The gaps represent no data periods.

The SpC of the main streamflow (upper sensor) typically ranges from 250 to 1250 μ S and drops to zero when the level of the stream falls below that of the mid-stream sensor during dry summer months. A particularly large spike observed during July 2018, was likely due to a nearby leach field (Fig. 31). The SpC levels of the local discharge (lower sensor) typically range from 500 to 1250 μ S. The local baseflow discharge tends to have a higher SpC, averaging about 150 μ S higher while spiking up to 1200 μ S higher during the summer months (Fig. 31). When compared to the water column (or pressure) the NaCl concentration decreases when the pressure increases and increases when the pressure decreases (Figs. 32, 33). This pattern is especially clear for the local discharge (Fig. 33). There is a similar pattern when comparing the discharge to the NaCl concentration, with the concentration increasing as the discharge decreases and the concentration decreasing when the discharge increases (Fig. 34).



Figure 31. The difference in the SpC value over time. The gaps represent no data periods.



Figure 32. A comparison of the water column (or pressure) in kilopascals and the NaCl concentration of the main streamflow.



Figure 33. A comparison of the water column (or pressure) in kilopascals and the NaCl concentration of the local discharge.



Figure 34. A comparison of the discharge in cubic feet per second and the NaCl concentrations of the main streamflow and local discharge.

5.1.2 Main Stream vs. Local Baseflow Discharge

The pattern of local baseflow discharge is similar to the main streamflow, but there is a difference in deicer concentration. There is a specific conductance (SpC) ratio of 0.9 of the upper sensor to the lower sensor. However, there are several days where the upper sensor recorded higher levels of SpC than the lower sensor resulting in a SpC ratio of >1. This pattern has only been observed in the summer months. A dual-channel ion chromatography comparison of the concentration of elements between the flow at the bottom of the stream and the flow at mid-depth demonstrates that the local discharge is more concentrated in almost every element (Table 2).

	Na	K	Mg	Ca	F	Cl	SO ₄	Br	NO ₃	PO ₄
	(mg/L)	(mg/L)	(mg/L)	(mg/L)						
Mid- Depth	77.6	3.13	4.03	17.72	0.00	133.2	12.23	0.03	3.69	0.02
Bottom	172.2	5.94	8.33	37.96	0.02	296.7	26.63	0.07	8.00	ND

Table 2. A dual-channel ion chromatography comparison of the concentration (mg/L) of elements betweenthe bottom of the stream and at mid-depth level of Bogle Brook.

5.1.3 Seasonal Response

During the early spring as the snow and ice melt, the NaCl concentration in Bogle Brook decreases before leveling out and maintaining a constant level of 300 mg/L, far lower than the concentrations deposited on roads. The local discharge concentration remains slightly elevated above the main streamflow by as much as 20 mg/L (Fig. 35). Occasionally during the summer months when there is less precipitation and greater evaporation, the level of the stream falls below that of the mid-stream sensor resulting in sudden drops in concentration. Several instances of a higher NaCl concentrations in the main streamflow can be observed in June and July (Fig. 35).



Figure 35. The difference in NaCl concentration of the local discharge and the main streamflow during the summer months of 2019.

The depth, discharge, and water column follow the same pattern with a peak in the early spring followed by a steady drop over the summer interrupted by spikes following precipitation events (Figs. 36, 37). The depth peaks at 65 cm before dropping 20 cm in August with spikes of up to 15 cm. The discharge peaks at 12 ft³/s, dropping to 1 ft³/s with spikes of up to 4 ft³/s (Fig. 36). The pressure at the lower sensor peaks at 7 kPa, falling to 2 kPa with spikes of up to 2 kPa. The pressure at the mid-stream sensor peaks at 4 kPa, dropping to nearly 0 kPa with spikes up to 1.5 kPa. The difference in pressure typically varies between 2.16 and 2.22 kPa (Fig. 37).



Figure 36. The stream discharge during the summer months of 2019.



Figure 37. The difference in pressure between the upper and lower sensor during the summer months of 2019.

During the early fall when there is increased precipitation, the NaCl concentration decreases slightly to around 200 mg/L with the local discharge concentration remaining slightly elevated in comparison to the main streamflow by about 40 mg/L (Fig. 38). During the late fall and into the winter, the concentration steadily increases with some sudden spikes following winter storm events until reaching a peak of 400-450 mg/L and the difference between measured between the sensors also peaks at over 80 mg/L. In the early spring, the NaCl concentration again starts to decrease and the difference measured between the sensors also decreases (Fig. 38). Throughout the fall and winter, the concentration of the main streamflow never surpasses that of the local discharge.



Figure 38. The difference between the NaCl concentration of the local discharge and the main streamflow during the winter months of 2018-2019.

The depth, discharge, and water column follow the same pattern during the winter months with an overall increase interrupted by spikes following precipitation events (Figs. 39, 40). The depth increases and varies between 65 and 40 cm with spikes of up to 25 cm. The discharge increases and varies between 12 and 6 ft³/s with spikes of up to 7 ft³/s (Fig. 39). The pressure at the lower sensor varies between 4 and 6.5 kPa with spikes of up to 2.5 kPa. The pressure at the mid-stream sensor varies between 2 and 4 kPa followed by a decline with spikes of up to 2 kPa. The difference in pressure typically varies between 2.15 and 2.3 kPa (Fig. 40).



Figure 39. The stream discharge during the winter months of 2018-2019.



Figure 40. The difference in pressure between the upper and lower sensor during the winter months of 2018-2019.

5.1.4 Precipitation Response

Precipitation events are seen as spikes of sudden increase of the stream level, or water column. These spikes can then be correlated to changes in the NaCl concentration of the stream and a comparison can be made of local discharge dominated stream water during periods of no precipitation to runoff dominated stream water during and after precipitation events. During precipitation events the sensors measure noticeably lower deicer concentrations as the stream flow gets progressively more diluted by overland flow. For example, a precipitation event in late October 2018 shows an increase in the deicer concentration in the main streamflow by 20 mg/L, which is followed by a decrease in concentration by 35 mg/L, which is then followed by a slow return to the baseline level of 250 mg/L over the course of a day (Fig. 41). The pattern of the concentration of the local baseflow discharge is similar, however there is a slight initial drop of 5 mg/L followed by the spike by the same amount. Then there is a slightly steeper drop of 25 mg/L followed by a more rapid return to the baseline of 300 mg/L (Fig. 41).



Figure 41. A comparison of the NaCl concentration of the local discharge and the main streamflow during a precipitation event in October 2018.

A larger precipitation event in late January 2019 shows a slightly different reaction. The concentration of the main streamflow initially drops 40 mg/L before spiking 100 mg/L, which is followed by a gradual return to the baseline of 220 mg/L (Fig. 42). The concentration of the local discharge follows an almost identical pattern. The concentration is depressed 40 mg/L to match the NaCl levels of the main streamflow, which is a rare occurrence and demonstrates that the difference between the concentrations of the sensors is not artificial. The deicer concentration increases rapidly by 130 mg/L before gradually returning to the pre-event level of 270 mg/L (Fig. 42).



Figure 42. A comparison of the NaCl concentration of the local discharge and the main streamflow during a precipitation event in January 2019.

During the rainy period of the fall, the pressure of the stream increases while the water becomes more diluted and therefore has a lower NaCl concentration (Figs. 38, 40). During periods of less precipitation, the pressure decreases and the NaCl concentration increases (Figs. 35, 37). The large precipitation event at the end of January shows the sudden large increase in both precipitation and pressure and although the pressure drops off, the NaCl continues to rise (Figs. 38, 40). The discharge follows a similar pattern to that of the pressure. Periods of high precipitation result in discharges of 10 to 12 cubic feet per second (Fig. 39).

Field data suggests that deicer concentration of groundwater is rather uniform in sharp contrast to deicer patterns during the infiltration stage. The next section (5.2) presents the results of experimental benchtop laboratory steps to get a better understanding of the processes of groundwater deicer transport.

5.2 Experimental Data and Observations

Two sets of experiments were conducted to simulate subsurface transport patterns and mechanisms that could explain data observed in the field including gravitational forces (the density contrast), diffusion (as a static counterpart to dispersion), flow mixing/dispersion, and osmotic/surface tension. Infiltration experiments initiate from the top of the tank while convection experiments initiate at the bottom. A 1% NaCl solution, equivalent to deicer concentrations deposited on roads, is compared to density-equivalent solutions of CsCl, a strong electrolyte, and dextrose, a non-polar solution.

5.2.1 Infiltration Experiments

A 1% NaCl solution, experiment shows how the brine solution quickly deviates from planarity to form finger-like convective cells as it encounters the freshwater. As the advancing front progresses through the sand, a strong gradient forms as evidenced by the color gradation with a stronger blue color towards the bottom of the tank. The concentration of the brines rapidly decreases with percolation progress. The active mixing at the brine-freshwater interface at the ends on the finger structures is indicated by the darker blue color and by the presence of a mixed zone that forms at the top as indicated by the lighter blue color (Fig. 43). Image analysis of this experiment demonstrates the formation of the fingers within the first 2 hours (Fig. 44). The fingers continue to travel downward at different rates over the next 18 hours until they reach the bottom of the tank (Fig. 44).



Figure 43. The progression of a 1% NaCl solution experiment from the top of the tank over 10 hours with photos taken every two minutes. The paler blue color indicates mixing zones.



Figure 44. The 1% NaCl experiment starting at the top of the tank from 0 to 2 hours, 2 to 5 hours, 5 to 10 hours, and 10 to 20 hours. Figure created through pixel by pixel subtraction. The dark color is the difference between the two images.

A density equivalent experiment of dextrose, a non-polar solution, was conducted to look at the impacts of surface tension. The experiment demonstrates a similar pattern of the formation of finger-like convective cells and the development of a gradient and mixing zones. However, the dextrose solution progressed through the sand at a slower rate, taking almost twice as long, 20 hours, to reach the bottom of the tank (Fig. 45). Image analysis of this experiment shows that the fingers that form in the first two hours are not as distinct as those in the 1% NaCl experiment (Fig. 46). The fingers become more distinct and travel downward at different rates over the next 18 hours until they reach the bottom of the tank (Fig. 46).



Figure 45. The progression of a 1% density equivalent dextrose experiment from the top of the tank over 10 hours with photos taken every two minutes. The paler blue color indicates mixing zones.


Figure 46. The density equivalent dextrose experiment starting at the top of the tank from 0 to 2 hours, 2 to 5 hours, 5 to 10 hours, and 10 to 20 hours. Figure created through pixel by pixel subtraction. The dark color is the difference between the two images.

A density equivalent experiment of CsCl, a strong electrolyte, was conducted to look at the impacts of surface tension. The experiment also demonstrates a similar pattern of finger-like convective cells and color gradient, indicating concentration. However, the convective cells show less variation in size and shape but the solution progressed through the sand at a similar rate to that of the 1% NaCl solution (Fig. 47). Image analysis of this experiment shows the formation of fingers in the first 2 hours at a similar speed to the 1% NaCl experiment (Fig. 48). Over the next 18 hours, the fingers travel downward at varying rates until they reach the bottom of the tank (Fig. 48).



Figure 47. The progression of a 1% density equivalent CsCl experiment from the top of the tank over 10 hours with photos taken every two minutes. The paler blue color indicates mixing zones.



Figure 48. The density equivalent CsCl experiment starting at the top of the tank from 0 to 2 hours, 2 to 5 hours, 5 to 10 hours, and 10 to 20 hours. Figure created through pixel by pixel subtraction. The dark color is the difference between the two images.

5.2.2 Convection Experiments

Experiments initiated at the bottom of the tank have been conducted over three weeks using 1% NaCl solution and equivalent densities of dextrose and CsCl solutions as well as the blue dye with only deionized water and no other solutions. The blue dye with deionized water spread outward is all directions from its initial injection site at a steady pace to form an arc with the most concentrated color in the center and did not travel towards the bottom of the tank (Fig. 49). Image analysis of this experiment shows the progression of the solution during the first 12 hours from a spherical shape expanding out towards the side and the bottom (Fig. 50). Over the next 3 days, the solution continues to spread sideways (Fig. 50). From day 3 until day 7, the solution continues to spread laterally as well as upwards (Fig. 50). After day 7, the solution spreads upwards and outwards in an arc shape at a consistent rate (Fig 50).



Figure 49. The progression of the blue dye alone with deionized water injected at the bottom of the tank over three weeks with photos taken every ten minutes. The paler blue color indicates mixing zones.



Figure 50. The dye alone experiment starting at the bottom of the tank from 0 to 12 hours, 12 to 24 hours, 1 to 3 days, 3 to 7 days, 7 to 14 days, and 14 to 21 days. Figure created through pixel by pixel subtraction. The dark color is the difference between the two images.

The 1% NaCl solution rapidly dropped to the bottom of the tank within the first 24 hours before spreading laterally during the next 4 days and finally traveling at a steady pace back upwards to fill slightly more than half the tank (Fig. 51). Image analysis shows the progression of the solution during the first 12 hours from a spherical shape to more of a pyramid as it drops quickly to the bottom of the tank (Fig. 52). Over the next 3 days, the solution continues to spread laterally (Fig. 52). From day 3 to day 7 the solution starts to spread evenly around the central point in an arc pattern (Fig. 52). After day 7, the solution continues to progress evenly in all directions in the same arc pattern (Fig. 52).



Figure 51. The progression of the 1% NaCl solution injected at the bottom of the tank over three weeks with photos taken every ten minutes. The paler blue color indicates mixing zones.



Figure 52. The 1% NaCl experiment starting at the bottom of the tank from 0 to 12 hours, 12 to 24 hours, 1 to 3 days, 3 to 7 days, 7 to 14 days, and 14 to 21 days. Figure created through pixel by pixel subtraction. The dark color is the difference between the two images.

The dextrose solution also rapidly dropped to the bottom of the tank and started spreading laterally within the first twelve hours before traveling back upwards after 3 days at a steady pace to fill slightly more than half the tank (Fig. 53). ArcGIS analysis of this experiment shows the progression of the solution during the first 12 hours from a spherical shape to more of a pyramid as it drops quickly to the bottom of the tank (Fig. 54). Over the next 3 days the solution spreads laterally from the central point (Fig. 54). From day 3 to day 7 the solution starts to spread evenly upwards and sideways (Fig. 54). Past day 7, the solution continues to progress upward until it forms a nearly level surface across the tank (Fig. 54).



Figure 53. The progression of the dextrose solution injected at the bottom of the tank over three weeks with photos taken every ten minutes. The paler blue color indicates mixing zones.



Figure 54. The 1% density equivalent dextrose experiment starting at the bottom of the tank from 0 to 12 hours, 12 to 24 hours, 1 to 3 days, 3 to 7 days, 7 to 14 days, and 14 to 21 days. Figure created through pixel by pixel subtraction. The dark color is the difference between the two images.

The CsCl solution dropped rapidly to the bottom of the tank and started spreading laterally within the first twelve hours. After the first three days, the solution continued to spread laterally slightly while starting to travel upwards. Over the next three weeks the solution gradually moved upwards, filling up the majority of the tank (Fig. 55). Image analysis of this experiment show the progression of the solution during the first 12 hours to a relatively linear shape at the bottom of the tank (Fig. 56). The next three days show a lateral spread at the bottom of the tank (Fig. 56). From day 3 to day 7 the solution begins to gradually spread upward evenly in an arc shape at a fairly constant rate (Fig. 56). After day 7, the solution continues to progress in the same pattern (Fig. 56).



Figure 55. The progression of the CsCl solution injected at the bottom of the tank over three weeks with photos taken every ten minutes. The paler blue color indicates mixing zones.



Figure 56. The 1% density equivalent CsCl experiment starting at the bottom of the tank from 0 to 12 hours, 12 to 24 hours, 1 to 3 days, 3 to 7 days, 7 to 14 days, and 14 to 21 days. Figure created through pixel by pixel subtraction. The dark color is the difference between the two images.

6.0 Discussion

6.1 Field Monitoring

6.1.1 Overall Patterns

The concentration of the brines measured in Bogle Brook, ranging from 200 to 450 mg/L (~500 ppm), are much lower than the highly concentrated brines leaving impervious surfaces during and slightly after snow storms (~30,000 ppm). As deicers are applied only a few months out of the year, a corresponding sharp increase in NaCl in surface waters followed by a slow decline would be expected. However, baseflow measurements have shown near constant levels of NaCl concentration throughout the year, with only slight variations due to precipitation and seasonal changes. Increases in stream discharge tended to result in lower concentrations. This trend indicates that there is a homogenous source of NaCl from groundwater entering the base of the stream. Homogenization and brine dilution has to be achieved in the subsurface, likely within a short period of time (few weeks to a month) and this could be a continuous process. The measurements from Bogle Brook confirm the pattern observed in other surface waters of elevated NaCl concentrations in the summer months despite road salt deicer application only occurring before and during winter storm events (Corsi et al. 2015; Kaushal et al. 2005; Demers and Sage 1990; Kelly et al. 2008).

6.1.2 Main Stream vs. Local Baseflow Discharge

The placement of two sensors in Bogle Brook shows that there is a consistent difference, ranging from 20 to 80 mg/L, between the NaCl concentration of the main streamflow and the local baseflow discharge throughout the year. The baseflow has a higher concentration than the main streamflow in a SpC ratio of 0.9. The main streamflow is diluted by fresh water from upstream as well as any precipitation. The baseflow must bring NaCl into the stream from a homogenous source in the subsurface, providing the elevated levels seen during all seasons.

6.1.3 Seasonal Response

The NaCl concentration generally increases steadily in the winter with application of deicers before and during winter storms, which can be observed in the sudden sharp increases in NaCl concentration following storm events. The road salt enters surface waters through surface runoff, causing the dramatic spikes. Even though the stream discharge also increases during winter precipitation events, the effect of dilution is not prominent. NaCl concentrations peak at the end of winter and early spring as the snow melts and any remaining road salt is swept into streams. The NaCl concentrations generally decrease towards the end of spring before leveling out. In the dry months of the summer, there is less dilution with precipitation so the NaCl concentration slowly increases over the course of the summer while stream discharge decreases. It is only during the summer months that the concentration of the streamflow sometimes exceeds

that of the local baseflow, which may be due to increased evaporation. In the fall months, precipitation increases, thus increasing stream discharge and dilution, and NaCl concentrations fall to their lowest levels.

6.1.4 Precipitation Response

Precipitation events can impact the NaCl concentration of the stream differently depending on the season and intensity of the storm. During the winter, there tends to be a sudden decrease in concentration as the stream is diluted, particularly the main streamflow, before a dramatic increase as deicers are washed directly into surface waters. During times when there are no deicers on the ground, precipitation events can actually cause an initial increase in NaCl before a sharp decrease as the stream is diluted. This trend may be due to the increased pace of groundwater movement that causes a pulse of saltier subsurface water to be released into the stream. The baseflow discharge shows a higher spike in concentration than the main streamflow. Typically, within a couple days of a storm, the NaCl concentrations will return to baseline levels. The more intense the storm, the longer the periods of dilution or elevated NaCl can last. The lowest NaCl concentrations measured in the stream occur in the fall when there is increased precipitation without the application of deicers.

6.1.5 Groundwater Deicer Transport

Once deicers are deposited on impervious surfaces, they infiltrate into the subsurface as a brine. As the brine moves through the subsurface, encountering fresh water as well as a variety of subsurface materials, it is diluted and homogenized. This homogenized, diluted NaCl brine eventually feeds into the baseflow discharge of streams, providing a constant contamination source even during the summer months when no deicers are applied. The concentration varies depending upon precipitation and season, but there is a constant input. Experiments provide insight into the processes that cause dilution and homogenization in the subsurface.

6.2 Experimental Observation

The benchtop experiments aid in the understanding of how high concentration contrast deicer brines enter the ground and produce homogenous output by the time the baseflow enters the stream. The experiments demonstrate the interactions of several important subsurface processes.

6.2.1 Infiltration Experiments

The results from the infiltration experiments provide insights into the percolation and flow mixing patterns of NaCl solutions. Gravitational forces exert the most influence. While patterns vary between simulations, the free convective behavior observed is the same as demonstrated by Xie (2012). The convective cells follow a Rayleigh-Taylor instability pattern, which is a fingering instability that occurs when a heavier fluid is pushes on a lighter fluid (Sharp, 1984). Portions of the higher density salt solution begin to sink, pushing aside the lower density freshwater. Lateral flow of the denser water then moves in to replace the sinking plume, further increasing the pressure there and decreasing the thickness of brine adjacent to the plume. This pressure exchange creates multiple small pockets of convection throughout the entire matrix. Interface irregularities increase in magnitude and cells elongate with time. Zones of mixing form within a matter of hours at the boundaries of the convective cells as well as at the surface of the tank indicating a pattern of rapid mixing. This rapid mixing could help to explain how the deicer brine becomes so diluted by the time it reaches surface waters and can do so in a short time period.

The comparison between the NaCl, dextrose, and CsCl density-equivalent solutions was designed to test the influence and role of surface tension/osmotic pressure in the progression of a deicer solution. As dextrose is non-polar and CsCl is a stronger electrolyte, any differences in the progression of the experiments could point towards the effect of surface tension. As the dextrose solution only took a few hours longer to reach the bottom of the tank and the CsCl solution performed similarly to the NaCl solution, surface tension/osmotic pressure does not seem to have a significant impact on the brine progression. If surface tension was a major factor, the CsCl solution, as a strong electrolyte, should have taken a longer time to progress through the tank. The greatest initial influence on the progression of the brine solution appears to be gravitational due to the density differences between the NaCl and the freshwater as well as flow

mixing/dispersion from the formation of the convective cells. As this was a static experiment with only quartz sand, the role of flow-mixing could be much greater in a natural environment with slope and a variety of subsurface materials. Given the small size of the tank and the limited run of the experiments, it is difficult to tell the initial influence of diffusion.

6.2.2 Convection Experiments

The comparison between the three different solutions revealed that the dextrose solution was the only solution that resulted in a level surface across the tank rather than an arc shape. The CsCl solution progressed slightly faster than the NaCl solution but otherwise followed the same pattern. These differences may indicate that surface tension/osmotic pressure may exert more of an influence once a brine solution is completely immersed in freshwater. As CsCl is a strong electrolyte, surface tension could cause it to progress more slowly through the tank. The greatest initial influence on the progression of the brine solution at the bottom of the tank also appears to be gravitational due to density differences. The solutions, except for the deionized water with the blue dye, first traveled to the bottom of the tank before spreading upwards. However, after the first few days, diffusion takes over as the primary process as the solution progresses upward in the tank. The experiment using deionized water with a few drops of dye clearly illustrates that any movement, once density differences are removed, is due almost entirely to the process of diffusion as the dye mainly progresses outward in an even arc pattern.

6.2.3 Subsurface Groundwater Transport

The infiltration and convection experiments demonstrate the effect that subsurface processes can have on the movement of deicer brines from infiltration to discharge in streams. Gravitational forces initially dominate and upon interaction with fresh water, there is rapid mixing. Once immersed in freshwater, the brine is influenced by diffusion and perhaps surface tension. The role of dispersion cannot be concluded from these experiments. The influence of these processes dilute the deicer brine to the levels observed in streams and result in a homogenous groundwater source.

7.0 Conclusion

The purpose of this research is to understand how deicer contaminants are transported from sites of infiltration to discharge in surface waters. By combining the two approaches of field data and experimental simulations, a more complete picture of deicer contamination begins to emerge.

7.1 Field Observations

Field data from Bogle Brook confirms the pattern observed in other surface waters of elevated NaCl concentrations in the summer months despite road salt deicer application only occurring before and during winter storm events. The placement of two sensors in Bogle Brook shows that there is a consistent difference between the NaCl concentration of the main streamflow and the local discharge throughout the year and that the baseflow tends to have a higher concentration. Precipitation events generally result in brief decrease in NaCl concentration before a return to baseline levels with the exception of winter storms or snowmelt events in which the NaCl concentration dramatically increases for a brief interval before returning to the baseline levels. The consistent elevated concentrations indicate a homogenous source of NaCl that is diluted from the concentrations deposited on impervious surfaces. Processes in the subsurface must account for the rapid homogenization and dilution of NaCl concentrations.

7.2 Experimental Study

The experimental simulations were designed to help provide insight into the subsurface processes that influence deicer transport and groundwater homogenization. These processes include gravitational/convective forces, diffusion, surface tension/osmotic pressure, and dispersion. The experiments address the first three processes but do not entirely address the role of dispersion. The comparison of the NaCl solution to the density-equivalent solutions of dextrose and CsCl was designed to highlight any differences due to surface tension/osmotic pressure as dextrose is a non-polar solution and CsCl is a stronger electrolyte. The infiltration simulations starting from the top of the tank demonstrate that the brine solution deviates from planarity to form finger-like convective cells within the first few hours of contact with the freshwater surface, a Rayleigh-Taylor instability pattern. The convective cells move rapidly even with only a 1% NaCl solution and form active mixing zones at the tips of the cells.

The infiltration experiment with the dextrose solution formed similar convective cells, but took a longer time to progress through the tank. The infiltration experiment with the CsCl solution formed similar convective cells, and took the same about of time to progress through the tank as NaCl. Based on the results, surface tension/osmotic pressure does not seem to have significant influence on the progression of the brine solution as the CsCl solution did not progress more slowly despite being a strong electrolyte. The greatest initial influence on the progression of the brine solution appears to be gravitational due to the density differences between NaCl and freshwater and the formation of convective cells. Given the small size of the tank and the limited run of the

experiments, it is difficult to tell the initial influence of diffusion. Further top-down experiments would be required to gain more insight.

The convection simulations from the bottom of the tank demonstrate that the NaCl brine solution initially falls to the bottom of the tank before spreading laterally during the first few days forming a pyramid shape. The solution then spreads upward in an arc shape over the following weeks to fill most of the tank. The convection experiment with the dextrose solution showed a similar initial pattern as the NaCl solution, but formed a level surface across the tank rather than the shape of an arc. A convection experiment with the CsCl solution showed an overall similar pattern to the NaCl solution, but perhaps progressed slightly faster to the bottom of the tank. Surface tension/osmotic pressure may have a slight influence over how the solution progresses upwards from the bottom of the tank as CsCl did not move as rapidly or as easily through the tank. The greatest initial influence on the progression of the brine solution at the bottom of the tank also appears to be gravitational due to density differences as all the solutions except for the deionized water dropped immediately to the bottom of the tank before spreading outwards. However, after the first few days, diffusion takes over as the primary process as the solution progresses upward in the tank. The experiment with a few drops of blue dye in deionized water illustrates the primary role of diffusion as the dye mainly progresses outward in an even arc pattern.

7.3 Deicer Contaminant Transport

Based on the results, it seems that deicer contaminants are likely rapidly homogenized in a few weeks to a month within the upper few meters of the subsurface. The greatest initial influence is likely gravitational but the processes governing deicer transport may be highly variable depending on the nature of the watershed including subsurface material, topography, vegetation, hydraulic gradient, etc. As the brine moves further into the subsurface and interacts with the freshwater below the water table, the process of diffusion becomes of greater importance. The role of surface tension/osmotic pressure seems to be of the least importance but further experiments would be required to properly address this question. The experiments demonstrate how the processes in the subsurface result in the pattern of homogenized, diluted source that causes the elevated NaCl concentrations in surface streams year-round observed in the field data. As deicer use will likely not decrease in the near future, its presence as a contaminant in the environment and drinking water supplies will only increase. It is therefore crucial to better understand how it moves through the environment.

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