

# **Evaluating the Effectiveness of Liquid Organic Anti-icing Chemicals for Winter Road Maintenance**

by

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## **AUTHOR'S DECLARATION**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final versions, as accepted by my examiners.

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## Abstract

Over five million tons of road salts are applied in Canada every winter to keep users of roads, parking lots and sidewalks safe. While effective for snow and ice control, salts at high concentrations are detrimental to the environment and corrosive to vehicles and infrastructure. As an alternative to the regular salt, new organic and semi-organic anti-icing and deicing products are increasingly available in the market; however, limited information on their performance is available for transportation agencies and maintenance industry to make informed decisions. In this study, a set of organic (Snowmelt) and semi-organic (Caliber M1000 and Fusion) products were selected and their performances were evaluated through a series of field tests conducted in parking lot C (surfaced with asphalt concrete) at the University of Waterloo, Ontario, Canada. Approximately 155 tests were conducted in a real world environment for over 14 test days. The performance of the alternatives was compared to the regular salt (brine) using friction improvement as a measure. The factors influencing the performance of the alternative salts were also identified through both data exploration and statistical analysis. The results showed that organic and semi-organic anti-icing chemicals performed very similarly to brine in melting snow and ice in almost all of the weather conditions. Only a slight performance advantage was observed for Snowmelt and Caliber M1000 in very cold temperatures (below  $-7^{\circ}\text{C}$ ) for the first one and in milder temperatures (above  $-7^{\circ}\text{C}$ ) for the second one. This finding suggests that these alternatives to the regular salt (brine) can be effectively used for anti-icing operations, consequently reducing the impacts of chloride salts on the environment. The study also concluded that an application rate as low as  $3\text{L}/1000\text{ft}^2$  should be applied for parking lots or low volume roads, which is 25% less than the current application rates used in industry for parking lot maintenance.

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*To*

*My Family*

## Table of Contents

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AUTHOR’S DECLARATION .....	ii
Abstract .....	iii
Acknowledgements .....	iv
List of Figures .....	viii
List of Tables .....	ix
List of Abbreviations and Notations .....	x
Chapter 1 Introduction .....	1
1.1 Background .....	1
1.2. Objectives and Scope .....	3
Chapter 2 Literature Review .....	5
2.1. Overview of Winter Maintenance .....	5
2.1.1 Winter Maintenance Methods .....	5
2.1.2 Snow and Ice Control Materials .....	7
2.1.3 Snow Melting Performance of Common Snow and Ice Control Materials .....	9
2.2 Organic Materials in Winter Maintenance .....	17
2.3 Environmental and Infrastructural Impacts of Snow and Ice Control Chemicals .....	19
2.3.1 Environmental Pathways .....	19
2.3.2 Effects on Water Resources .....	20
2.3.3 Effects on Soil .....	25
2.3.4 Effects on Vegetation .....	28
2.3.5 Effects on Air Quality .....	30
2.3.6 Comparison of the Environmental Impacts of Common Snow and Ice Control Materials .....	30
2.3.7 Effects on Infrastructure .....	32
2.4. Summary .....	34
Chapter 3 Evaluation of the Effectiveness of Liquid Organic and Semi-organic Anti-icers .....	36
3.1. Introduction .....	36
3.2. Data Collection .....	37
3.2.1. Test Site .....	37
3.2.2. Chemicals and Application Rates Tested .....	38
3.2.3. Data Collection Procedure .....	40
3.3. Exploratory Analysis .....	43
3.4. Data Analysis and Results .....	45
3.4.1 Effectiveness of Anti-icing Treatment with Organic and Semi-Organic Chemicals .....	45
3.4.2. Investigation of the Contributing Factors .....	54
3.5 Summary .....	63

Chapter 4 Estimation of the Effectiveness of Liquid Organic Anti-icers in Different Weather Conditions.....	65
4.1. Introduction.....	65
4.2. Data Collection .....	65
4.3 Methodology .....	65
4.3.1 Multivariate Linear Regression.....	65
4.3.2. Artificial Neural Network .....	67
4.4 Results.....	68
4.4.1 Multivariate Linear Regression Models.....	68
4.4.2 Neural Network Models.....	73
4.5 Summary .....	76
Chapter 5 Conclusions and Future Work.....	77
5.1 Major Findings.....	77
5.2 Limitations and Future Work.....	79
References .....	80

## List of Figures

Figure 2.1: Effective temperature and eutectic temperature of common Salts .....	9
Figure 2.2: Ice penetration speed of common deicing chemicals .....	10
Figure 2.3: Melting capacity of common deicing chemicals .....	11
Figure 2.4: Cost comparison of common deicing chemicals .....	12
Figure 2.5: Environmental Pathways (NCHRP-577, 2007).....	20
Figure 2.6: Increase in chloride and sodium concentrations in Nagawicka Lake, Wisconsin, USA (Garn, et al., 2006) .....	23
Figure 3.1: Test site.....	37
Figure 3.2: Field test procedure .....	41
Figure 3.3: Winter 2014 anti-icing events .....	44
Figure 3.4: Effectiveness of anti-icing treatments by different liquids.....	48
Figure 3.5: Comparison of the chemical's effectiveness in temperatures above $-7^{\circ}\text{C}$ .....	49
Figure 3.6: Comparison of the chemical's effectiveness in temperatures below $-7^{\circ}\text{C}$ .....	49
Figure 3.7: Contributing factors to coefficient of friction.....	55
Figure 3.8: Effect of application rate on the CoF in temperatures above $-7^{\circ}\text{C}$ .....	56
Figure 3.9: Effect of application rate on the CoF in temperatures below $-7^{\circ}\text{C}$ .....	56
Figure 3.10: Relationship between pavement temperature and air temperature .....	57
Figure 3.11: Effect of pavement temperature on the CoF.....	58
Figure 3.12: Effect of precipitation amount on the CoF .....	59
Figure 3.13: Effect of precipitation type on the CoF .....	59
Figure 3.14: Performances of concentrated Snowmelt vs. diluted Snowmelt .....	60
Figure 4.1: NN procedure .....	68
Figure 4.2: Chemical effectiveness comparison in different weather conditions .....	73
Figure 4.3: Chemical effectiveness comparison in different weather conditions .....	75



## List of Tables

Table 2.1: Common characteristics of deicing chemicals.....	13
Table 2.2: Solid and liquid salts application rates for highways (NCHRP, 2004).....	14
Table 2.3: Deicing solid salt application rates for parking lots (Hossain and Fu, 2014) .....	15
Table 2.4: Liquid anti-icing application rate guideline for parking lots (Fortin Consulting Inc, 2006) .....	16
Table 2.5: Chloride increase samples .....	24
Table 2.6: Impacts of the most common elements in snow and ice control chemicals on soil.....	31
Table 2.7: Impacts of the most common elements in snow and ice control chemicals on water.....	31
Table 3.1: Materials tested.....	39
Table 3.2: Descriptive statistics of the data .....	43
Table 3.3: Risk levels associated with coefficients of friction (Hossain, et al., 2014) .....	45
Table 3.4: Paired T-tests results for improvement of friction on anti-icing sections vs. control sections ..	50
Table 3.5: ANOVA results for improvement on friction at treated sections with anti-icing in temperatures above -7°C.....	51
Table 3.6: ANOVA results for improvement of friction on treated sections with anti-icing in temperatures below -7°C .....	53
Table 3.7: ANOVA Results for Improvement of Friction on treated sections with anti-icing in temperatures below -7°C.....	54
Table 3.8: Test Results on Jan 30, 2014 .....	62
Table 4.1: Multivariate linear regression results.....	69
Table 4.2: MLP-NN results.....	74

## List of Abbreviations and Notations

NaCl	Sodium Chloride
MgCl <sub>2</sub>	Magnesium Chloride
CaCl <sub>2</sub>	Calcium Chloride
KAc	Potassium Acetate
CMA	Calcium Magnesium Acetate
KFm	Potassium Formate
NaFm	Sodium Formate
NAAC	Sodium Acetate
DOT	Department of Transportation
DLA	Direct Liquid Application
BOD	Biological Oxygen Demand
DO	Dissolved Oxygen
PH	Potential Hydrogen
EPA	Environmental Protection Agency
EC	Electrical Conductivity
PCC	Portland Cement Concrete
TRCA	Toronto Region Conservation Authority
MSDS	Material Safety Data Sheet
iTSS	Innovative Transportation System Solutions
P/U	Propitiatory/Unknown
CoF	Coefficient of Friction
ANOVA	Analysis of Variance
BPRT	Bare Pavement Regain Time
ANN	Artificial Neural Network
MLP-NN	Multi-Layer Perceptron Neural Network
RMSE	Root Mean Squared Error
WEKA	Waikato Environment for Knowledge Analysis

# Chapter 1

## Introduction

### 1.1 Background

In cold regions such as North America, frequent snow events, coupled with freezing temperatures, cause pavement surfaces to become slippery and unsafe for both pedestrian and vehicular traffic during the winter seasons. Studies show that adverse weather conditions in winter significantly increase the number of crashes and the fatality rate (Knapp, et al., 2000; Eisenberg, et al., 2005; Qiu, et al., 2008). Winter road maintenance has an important role in providing safety for vehicles and pedestrians in winter. The objective of winter maintenance is to improve the pavement surface condition and thus provide safety in different transportation facilities such as roads, parking lots and sidewalks. As a result, to prevent pedestrians from slipping and falling and vehicles from skidding, a large amount of snow and ice control materials are used in winter. According to Transportation Association of Canada (2013), an average of 5 million tons of snow and ice control materials is used, and over \$1 billion is spent each year for winter maintenance in Canada. Developing a sustainable winter maintenance strategy largely depends on the type of the transportation facility considering that different facilities have different service requirements and traffic conditions. For instance, winter maintenance strategies applied on parking lots and sidewalk are planned differently from roads and highways as the traffic volume and traffic speed are much lower in parking lots and sidewalks.

Deicing and anti-icing are the most common techniques used for winter road maintenance (NCHRP 526, 2004). Deicing and anti-icing can be done separately or in a combination together based on the weather condition and the weather event characteristics. Deicing is a reactive strategy in which the snow and ice control materials are applied on the top layer of the snow after a snow event. In the reaction between the snow and the deicing material, a brine solution is created which breaks the bonds between snow and the pavement surface by penetrating and lowering the water's freezing point. Anti-icing, on the other hand, is a proactive method for winter maintenance. In this strategy, the snow and ice control materials are applied prior to a snow event (Ketcham, et al., 1996). In anti-icing, the emphasis is on preventing the ice from bonding to the ground rather than trying to break the bond afterwards. In other words, applied

materials form a bond breaking layer between the pavement and snow, thus decreasing the chance of ice formation. Literature shows that anti-icing results in less material and labor usage and lowers operational and environmental costs compared to deicing.

Chloride salts, the most common snow and ice control material for winter maintenance operations, have been widely used since the mid-nineteenth century (Ramakrishna, et al., 2005). Among the chloride salts, Sodium chloride is the most common material for winter maintenance operations because it is comparatively abundant, inexpensive, and effective in melting snow and ice in sub-zero temperatures (Paschka, et al., 1999). Both solid and liquid materials are used for winter maintenance but liquid materials are mostly used for anti-icing purposes rather than deicing.

Although the usage of salts is essential for the safety and mobility of our transportation facilities, an excessive amount of chloride salts may damage the environment and infrastructure. In fact, excessive chloride application causes vehicles to rust out and the infrastructures nearby to corrode (Shi, et al., 2009). Also, the salt used in winter maintenance operations has the potential to travel by wind, traffic, run-off and seepage, further transporting the salt to the environment and causing excess damage (Ramakrishna, et al., 2005). This damage includes soil contamination, plant deterioration and increased chloride levels in both surface and ground water, all of which can threaten marine life and contaminate drinking water. According to Environment Canada (2000), the chloride salt used for snow and ice control may have immediate or long-term negative impacts on the environment and infrastructure. Therefore, in order to alleviate the negative impacts while sustaining safe and functional transportation facilities, organic and semi-organic products with fewer harmful; effects on the environment and infrastructure have been sought by governments and the industry.

A limited number of studies have explored and evaluated the effectiveness of alternative organic products through field tests. However, due to a lack of comprehensive research on their effectiveness, the higher initial cost, and the perception of risk associated with their use, organic anti-icers have not been widely applied in maintaining transportation facilities. A survey conducted in North America and Europe (Fay, et al., 2008), reported that more than 75% of the surveyed contractors use chloride salts (i.e., road salts) for winter road maintenance. As indicated before, one of the main reasons that the road salt is widely used in the winter maintenance industry is its low cost. However, hidden costs due to the negative impacts of deicers should also

be considered to make the right choice of snow and ice control materials. For instance, reports show that there is about a \$469 loss in dollar value in using just one ton of road salts when its negative impacts on the environment and infrastructures are considered (Shi, 2005). Therefore, although cheaper in terms of purchase cost, labor, and equipment, road salt may be more costly when its long-term consequences on environment and infrastructure is taken into account. As a result, transportation agencies need to consider a holistic approach to the problem, a more environmentally friendly alternative to regular chloride salts.

In summary, winter snow and ice control operations are critical to insure transportation facilities' safety; however, not only immediate financial costs, but also the long term environmental and infrastructural damages should be considered as well. To reduce the long-term negative impacts and hazards to the environment, infrastructure, and human health, usage of emerging alternative organic and semi-organic products in winter maintenance operations should be considered.

Few past studies have evaluated the effectiveness of organic and semi-organic products in winter maintenance, so there are no evidence-based and defensible guidelines on the performance, costs, and benefits of these alternatives. Of the studies that are available, most were conducted in a laboratory environment, which has limitations in accounting for real world situations (Fay, et al., 2011; Nixon, et al., 2005). Also, none of the studies have assessed the effects of these specifically on facilities with low speed and low volume traffic such as parking lots and rural highways (Shi, et al., 2009; Muthumani, et al., 2015). Given this lack of research, this study is designed to evaluate the effectiveness of some of the emerging anti-icing organic and semi-organic products by conducting field tests.

## **1.2. Objectives and Scope**

This research is motivated by the problems associated with the use of chloride salts for snow and ice control operations in winter, and by the lack of the studies evaluating the effectiveness of organic and semi-organic products for winter maintenance of parking lots. The specific objectives pursued in the proposed research are as follows:

1. Conducting a comprehensive literature review on the environmental impacts and performance of the common deicing and anti-icing chemicals and conducting a field experiment to determine the performance of liquid organic and semi-organic anti-icers.

2. Evaluating the effectiveness of liquid anti-icing organic and semi-organic products for winter maintenance operations and investigating the factors that affect the performance of anti-icing with liquid organic and semi-organic products in parking lots.
3. Exploring the effectiveness of liquid ant-icing organic and semi-organic products in different weather scenarios by developing statistical estimation models.

## **Chapter 2**

### **Literature Review**

This chapter provides an in-depth literature review of the existing winter maintenance operations methods, standards and guidelines along with a review of the past studies conducted to evaluate the alternative semi-organic and organic snow and ice control materials. This is followed by a comprehensive review of the environmental impacts of the most commonly used snow and ice control materials.

#### **2.1. Overview of Winter Maintenance**

The main objective of winter maintenance is to provide a safer pavement condition for pedestrians and vehicles during the winter months. This goal can be achieved by optimizing the uses of a variety of methods, equipment, and materials. Many studies have been done related to winter maintenance, especially, for highway winter operations. Also, different deicing and anti-icing materials have been compared in terms of their performance and environmental effects. Therefore, a number of guidelines are developed to help practitioners maintain their facilities by using different materials, ranging from popular chloride salts to some semi-organic salts.

##### **2.1.1 Winter Maintenance Methods**

Winter maintenance operations include three general methods namely deicing, anti-icing and sanding which are briefly explained below (NCHRP, 2004):

###### **2.1.1.1 Deicing**

Deicing is a reactive strategy for winter maintenance. In this method, the deicing materials are applied on the top layer of the snow after a snow event. The reaction between the top layer of the snow and deicing material creates a brine solution that penetrates the ice and snow and lowering the water's freezing point and subsequently breaking the bonds between snow and pavement surface. As a result, snowplows can remove the snow and ice more easily. Deicing performance depends on the type of the material, application rate of the material, and the equipment used to spread the deicing materials (Chappelow et al., 1992). The materials used for deicing could be in both forms of solid and liquid salts. However, when solid salt is used for the deicing treatment, a

pre-wetting strategy is used to provide the minimum moisture required to initialize the reaction. This strategy improves the effectiveness of solid salts in the deicing treatment, also less salt bounces off the road surface (Fitch, et al., 2012). According to NCHRP-526 Report (2004), deicing is a suitable strategy for most weather conditions, sites, and traffic conditions, except when pavement temperatures drop below  $-7^{\circ}\text{C}$ . Past studies have shown that deicing is the most popular method due to its flexibility in the application time interval, high effectiveness, easy operation and low initial costs (MDOT, 1993; Ketcham, 1996; Williams and Linebarger, 2000).

#### 2.1.1.2 Anti-icing

Anti-icing is a pro-active method for winter maintenance. In this strategy, the snow and ice control materials are applied prior to a snow event. In anti-icing the emphasis is on the preventing ice from bonding to the pavement rather than reacting after it does so. In other words, applied materials form a bond breaking layer between the pavement and snow that causes the snow to melt faster thus lowering the chance of ice forming and bonding to the pavement. Anti-icing has some advantages over other winter maintenance techniques. It makes plowing easier and provides a higher level of friction after the snow event. Also, with a small accumulation of snow, the pre-applied chemical can melt the snow itself, and clear pavement can be reached in a shorter time (Hossain, et al., 2014). The amount of material used for deicing is approximately 5 times higher than that used for anti-icing (NCHRP-577, 2007). Overall, the anti-icing method requires less material and labor, resulting in lower operational costs and decreased environmental impacts than the deicing method. Both liquid and solid materials can be used for the anti-icing strategy; however, anti-icing with liquid is suitable for conditions where the pavement temperature is above approximately  $-7^{\circ}\text{C}$  before snowfall (Druschel, 2012; NCHRP-577, 2007). Anti-icing is also not effective when precipitation consists of freezing rain or sleet. Solid anti-icing materials are suitable when pavement temperature is above approximately  $-10$  degrees Celsius (NCHRP 526, 2004).



### 2.1.1.3 Sanding

Sanding, a technique that involves using sand or abrasives, is used to enhance traction on pavement surfaces. Sanding is usually practiced in very cold regions or in very cold temperatures. According to Nixon (2001) and Blackburn (2004), the main goal of using sand or abrasive is to improve the friction level on ice-covered roadways, especially when the temperature is too low for other deicing and anti-icing materials to function effectively. The situations in which deicing and anti-icing materials are not effective and sanding is required generally occur when the temperature is below  $-11^{\circ}\text{C}$  (Technology Transfer Center, 1996; Shi et al., 2004; Blackburn et al., 2004 and Environmental Canada, 2005). The materials used for sanding include natural sands, finely crushed rocks or gravels, bottom ashes, slags, ore tailings and cinders. The application rate for abrasives differs from one winter maintenance agency to the other, mainly due to the different and diverse weather conditions at each location.

## 2.1.2 Snow and Ice Control Materials

The most common solid and liquid materials used for winter maintenance include sodium chloride ( $\text{NaCl}$ ), magnesium chloride ( $\text{MgCl}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), potassium chloride, potassium acetate ( $\text{KAc}$ ), and calcium magnesium acetate ( $\text{CMA}$ ). All of the deicing and anti-icing materials melt the ice and snow through the same underlying concept of lowering the freezing point of water and thus breaking the bond between ice and pavement (Amsler D., 2006; Zhang J et al. 2009; Rubin J., 2010). Different groups of snow and ice control materials are briefly discussed below.

### 2.1.2.1 Chloride Salts

Chloride salts are the most common materials used for winter maintenance. Chloride salts are discharged through a variety of methods, including the mining of surface or underground deposits, extracting and fractionating well brines, industrial by-products, and solarizing saltwater (NCHRP-577, 2007). Among chloride salts, sodium chloride ( $\text{NaCl}$ ) is the most frequently used material for snow and ice control because it is not only inexpensive and abundant but also easy to store, handle, and disperse on the road surface. (Fischel, 2001; Ramakrishna, et al., 2005). It can also be used in both solid and liquid form (brine) for deicing and anti-icing purposes (Shi,

2005). Calcium chloride and magnesium chloride, other commonly used materials, are usually applied in colder temperatures when sodium chloride is not effective (Ketcham, et al., 1996).

#### 2.1.2.2 Organic Salts

As alternatives to chloride salts, organic deicing and anti-icing materials are less popular, representing only a small percentage of the deicing and anti-icing materials market largely because they have higher market price compared to chloride salts. Organic deicing and anti-icing materials are generally divided into two groups. Those in first group, including CMA and KAc, are completely synthesized. CMA is produced through the reaction of high grade acetic acid with limestone, and KAc is produced using same high grade acetic acid as CMA (NCHRP-577, 2007). The process to obtain a high grade of acetic acid consumes huge amount of energy and it is costly; therefore, these products are much more expensive than chloride salts. The second group of organic anti-icing and deicing materials are made from agricultural resources including by-products from grain processing, brewing, winemaking, etc (NCHRP-577, 2007). Organic products, used either alone or in combination with chloride salts, are considered to be more environmentally friendly because there is less or no chloride content in their composition. Other organic deicing and anti-icing materials, which are a combination of alcohols such as methanol and ethanol, are of concern due to their potential for flammability during storage and handling. Some other organic products are a combination of glycols such as ethylene and propylene glycol, which are used more in aircraft facilities than on roadways.

#### 2.1.2.3 Sand and Abrasives

In contrast to the previously discussed groups of snow and ice control materials, sand and abrasives do not melt the ice and snow. Instead, they enhance the friction level between the tires of vehicles and the icy road surface (Wisconsin Transportation Bulletin, 2005). Although sand and abrasive can be used in all temperatures and weather conditions, they are usually applied when the temperature is too cold for the deicing and anti-icing materials to work efficiently. The major sources of sand and abrasives are natural sources of stones, volcano deposits, metallurgical slag, clinker ash, and natural river sands (NCHRP-577, 2007).

### 2.1.3 Snow Melting Performance of Common Snow and Ice Control Materials

The five most common snow and ice control materials are Sodium Chloride (NaCl), Magnesium Chloride ( $MgCl_2$ ), Calcium Chloride ( $CaCl_2$ ), Calcium Magnesium Acetate (CMA) and Potassium Acetate (KAc). This section compares five aspects of these materials: effective temperature, eutectic temperature, ice penetration, melting capacity, and cost.

#### 2.1.3.1 Effective Temperature and Eutectic Temperature

Eutectic temperature is the temperature at which a snow and ice control solution freezes; effective temperature is the lowest temperature at which a snow and ice control material is effective. In Figure 2.1, the most common snow and ice control materials are compared in terms of their eutectic temperature and effective temperature (Ketcham, et al., 1996; Fischel, 2001). As shown in Figure 2.1, calcium chloride has the lowest eutectic temperature and effective temperature; thus, it is the most effective snow and ice control material in low temperatures. The same figure also shows that sodium chloride and CMA are not suitable for use under -10 degrees.

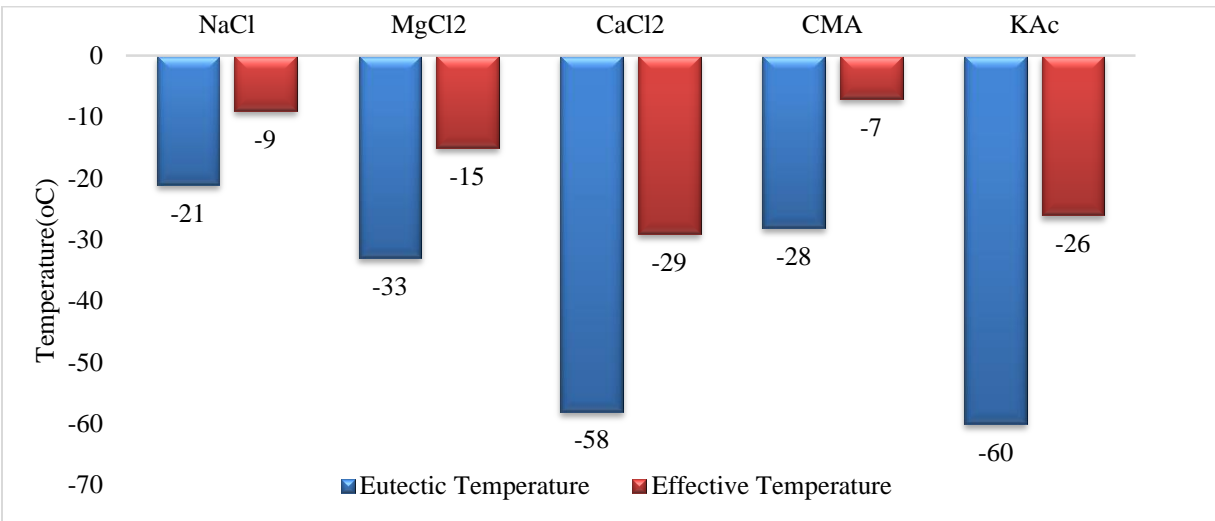


Figure 2.1: Effective temperature and eutectic temperature of common Salts

### 2.1.3.2 Ice Penetration

Ice penetration is a measure to determine the ability of a chemical to penetrate ice vertically which helps to identify the effectiveness of different snow and ice control products in terms of their ice de-bonding and ice undercutting capacity. One of the common test protocols to measure ice penetration ability involves dropping a dyed deicer chemical on a small part of the surface of the ice sample. At specific time intervals, the amount of penetration (in mm) is measured using a ruler affixed to the test apparatus (Nixon, et al., 2007). In Figure 2.2, the five most common snow and ice control materials are compared in terms of their ice penetration ability. Note that the ice penetration is shown in qualitative scale for easy understanding based on the results of the studies conducted by (Nixon, et al., 2005).

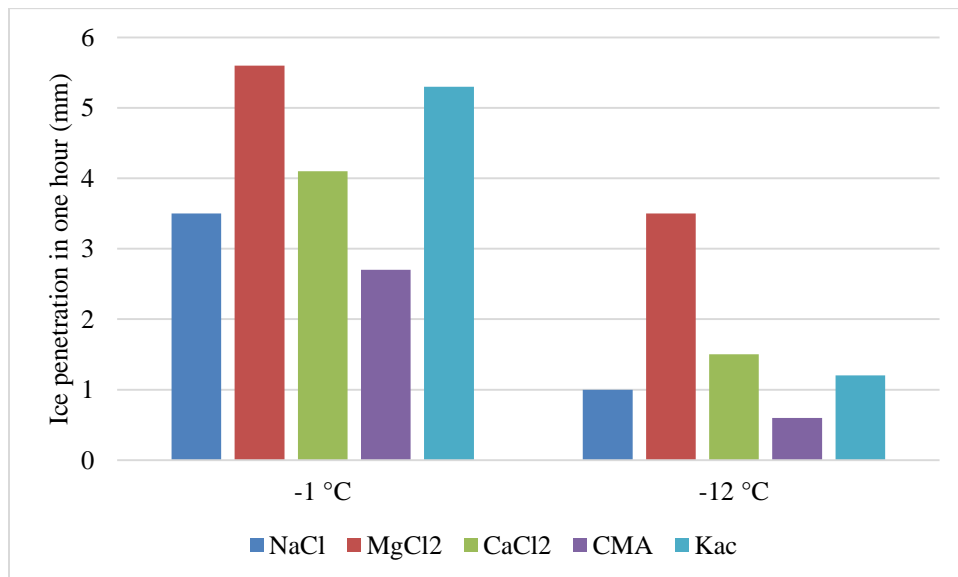


Figure 2.2: Ice penetration speed of common deicing chemicals

### 2.1.3.3 Ice Melting Capacity

The ice melting capacity is a measure which determines the melting capacity of different snow and ice control materials in different temperatures. To measure the melting capacity of a chemical a small amount of the chemical is applied in a uniform manner on the ice layer (Nixon, et al., 2007). At specific time intervals, the ice melted liquid is weighted and recorded. Studies show that the ice melting capacity has a direct relationship with temperature and that decreasing the temperature, also decreases the melting capacity decreases as well (Nixon, et al., 2007). In

Figure 2.3, the five most common snow and ice control materials are visually compared in terms of their melting capacity which shows the grams of ice melted by each chemical in one hour. From this figure, it is clear that in lower temperatures alternative materials (except CMA) outperform sodium chloride whereas in temperatures near 0°C all of these five chemicals perform similarly. This result agrees with the results from a study by Kelting (2010), which demonstrates that NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> perform similarly in temperatures above -4°C but that their performance is different in lower temperatures. For instance, he shows that 30% more NaCl by weight is required for melting the ice than when CaCl<sub>2</sub> is used as a deicing agent at a temperature of -12°C. His study also indicates that acetate based deicers require higher concentration than some chloride deicers such as CaCl<sub>2</sub> to melt the ice but that they still have better performance than conventional road salt (NaCl).

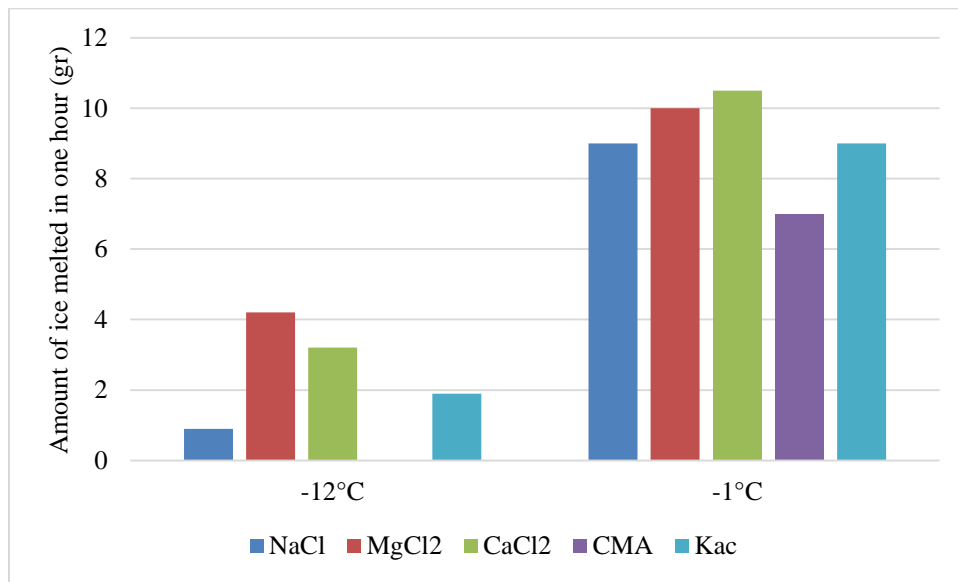


Figure 2.3: Melting capacity of common deicing chemicals

#### 2.1.3.4 Cost

Cost is one of the most important criteria for Department of Transportation (DOT) in choosing their snow and ice control materials. These materials have some direct costs, including the cost of materials, labor and equipment but also some indirect costs, those involving environmental burdens and corrosion to infrastructure and vehicles (Koch, et al., 2002). Figure 2.4 compares

the market price (purchasing price in year 2010) of the most common ice and snow control materials.

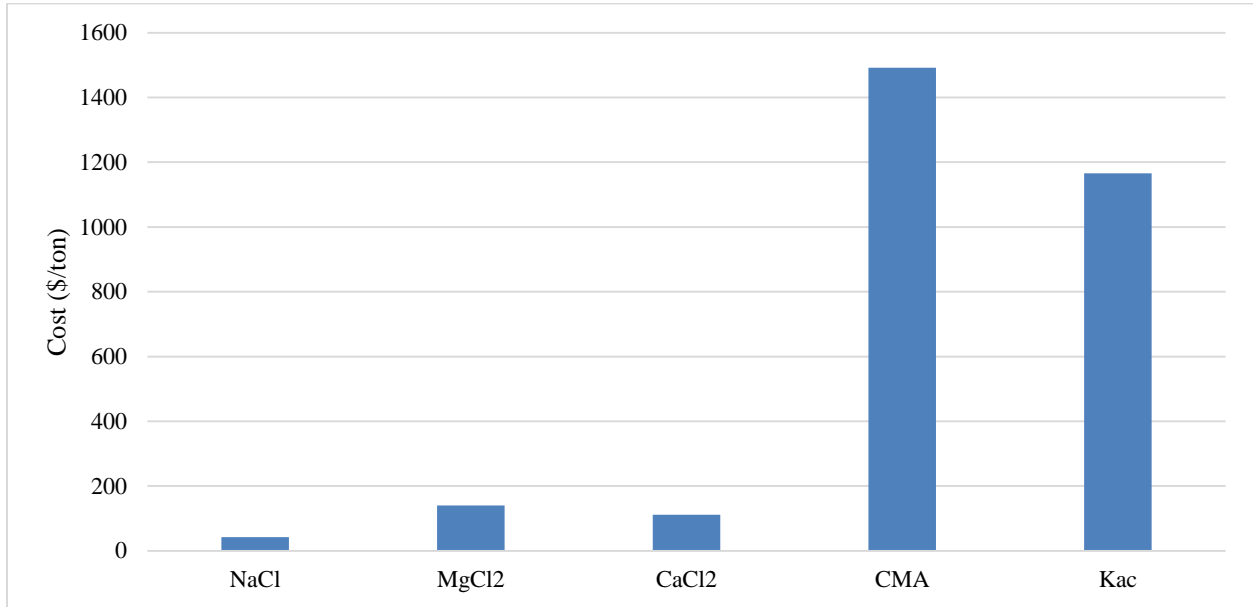


Figure 2.4: Cost comparison of common deicing chemicals

As shown in Figure 2.4, sodium chloride is the cheapest deicing agent; however, the effectiveness of materials in different temperatures also needs to be considered to accurately estimate the accompanying costs. According to Kelting (2010), among chloride salts, sodium chloride is the most cost-effective deicing and anti-icing material for temperatures above -4 degrees. However, in lower temperatures (less than -10°C), around 4 times more NaCl will be required to melt ice than MgCl<sub>2</sub>, resulting in a higher NaCl purchase price.

The indirect costs of using the deicing and anti-icing material should also be considered. Studies have confirmed that chloride based snow and ice control materials have negative impacts on the environment (Forman, 2004; Buckler, et al., 1999); also they damage vehicles and infrastructure due to their corrosive nature (Shi, et al., 2013). Another study shows that damage cost of approximately \$35 to \$57 dollars per each purchasing dollar have to be paid as a result of using road salt (D'Itri, 1992).

### 2.1.3.5 Material Characteristics Summary

The most commonly used materials in winter road maintenance are sodium chloride, magnesium chloride, calcium chloride, calcium magnesium acetate (CMA) and potassium acetate. Table 2.1 summarizes the performance characteristics along with the nominal cost of these materials. These data represents a quantitative summary of the information mentioned in the previous sections. By comparing the different performance characteristics of these material, it is clear that calcium chloride has the best performance in very low temperatures among the commonly used materials; therefore, it is recommended for the colder situations. Also, the performance of the sodium chloride and CMA drops significantly in low temperatures; thus, they are not recommended for the situations where air temperature is below  $-7^{\circ}\text{C}$ .

Table 2.1: Common characteristics of deicing chemicals

Salt Name	Eutectic Temp ( $^{\circ}\text{C}$ )	Practical Temp ( $^{\circ}\text{C}$ )	Melting Capacity at $-1^{\circ}\text{C}$ (gr/hr)	Melting Capacity at $-12^{\circ}\text{C}$ (gr/hr)	Ice Penetration at $-1^{\circ}\text{C}$ (mm/hr)	Ice penetration at $-12^{\circ}\text{C}$ (mm/hr)	Cost in 2010 (\$/ton)
Sodium Chloride	-21	-9	9	0.9	3.5	1	42
Calcium Chloride	-51	-29	10.5	4.2	4.1	1.5	111
Magnesium Chloride	-33	-15	10	3.2	5.6	3.5	140
CMA	-28	-7	7	0	2.7	0.6	1492
Potassium Acetate	-60	-26	9	1.9	5.3	1.2	1166

### 2.1.4 Application Rate

Application rate is the mass or volume of the deicing and anti-icing material applied per unit of area. In winter road maintenance, determines the right application rate depends on the material used and the temperature when applied. Tables 2.2, 2.3 and 2.4 show the recommended application rates for different facilities extracted from the literature for both liquid and solid salts.

Table 2.2: Solid and liquid salts application rates for highways (NCHRP, 2004)

Temperature °C	NaCl		CaCl <sub>2</sub>		MgCl <sub>2</sub>		KAc		CMA	
	Solid lbs/1000 ft <sup>2</sup>	Liquid gal/1000 ft <sup>2</sup>	Solid lbs/1000 ft <sup>2</sup>	Liquid gal/1000 ft <sup>2</sup>	Solid lbs/1000 ft <sup>2</sup>	Liquid gal/1000 ft <sup>2</sup>	Solid lbs/1000 ft <sup>2</sup>	Liquid gal/1000 ft <sup>2</sup>	Solid lbs/1000 ft <sup>2</sup>	Liquid gal/1000 ft <sup>2</sup>
0	1.6	0.7	1.7	0.5	1.4	0.5	2.5	0.5	2.5	1.1
-1	1.6	0.8	1.7	0.5	1.5	0.5	2.5	0.5	2.5	1.2
-2	1.6	0.8	1.7	0.5	1.4	0.5	2.4	0.5	2.4	1.3
-3	1.6	0.9	1.6	0.5	1.5	0.6	2.5	0.5	2.5	1.5
-4	1.6	1.0	1.7	0.6	1.6	0.6	2.6	0.6	2.6	1.8
-5	1.6	1.0	1.8	0.6	1.6	0.6	2.6	0.6	2.6	1.8
-6	1.6	1.1	1.7	0.6	1.6	0.7	2.4	0.6	2.4	2.0
-7	1.6	1.1	1.7	0.7	1.5	0.7	2.4	0.5	2.4	2.0
-9	1.6	1.4	1.6	0.7	1.5	0.7	2.2	0.5	2.2	2.7
-12	1.6	1.9	1.6	0.8	1.5	0.7	2.2	0.6	2.2	4.2
-15	1.6	2.6	1.6	0.9	1.5	0.8	2.2	0.6	2.2	9.9



Table 2.3: Deicing solid salt application rates for parking lots (Hossain and Fu, 2014)

Snow Depth (cm) (Snow Type= Regular snow with density of 100 kg/m <sup>3</sup> )	Average Pavement Temperature (°C)	Precipitation Duration + Desired Bare Pavement Regain Time (hours)							
		1	2	3	4	5	6	7	8
0.5	-7	85	70	55	45	30	15	0	0
0.5	-5	70	60	45	30	15	0	0	0
0.5	-3	60	45	30	15	0	0	0	0
0.5	-1	45	30	15	0	0	0	0	0
0.5	0	40	25	10	0	0	0	0	0
1	-7	90	75	60	45	30	20	5	0
1	-5	75	60	50	35	20	5	0	0
1	-3	65	50	35	20	5	0	0	0
1	-1	50	35	20	5	0	0	0	0
1	0	40	30	15	0	0	0	0	0
1.5	-7	95	80	65	50	35	20	10	0
1.5	-5	80	65	50	35	25	10	0	0
1.5	-3	65	50	40	25	10	0	0	0
1.5	-1	55	40	25	10	0	0	0	0
1.5	0	45	30	15	5	0	0	0	0

(Note: This application rate is for transit platforms, parking lots, sidewalks and any location where the effect of vehicular traffic is much less. The rates shown in lb/1000ft<sup>2</sup> can be converted to lb/lane-mile, kg/lane-km and gm/m<sup>2</sup> by multiplying with 63.3, 18.7 and 5.0 respectively.)

Table 2.4: Liquid anti-icing application rate guideline for parking lots (Fortin Consulting Inc, 2006)

Anti-icing Application Rate Guideline		
Condition	Gallons/1000 sq.ft.	
Regularly scheduled applications	MgCl <sub>2</sub>	Salt Brine (NaCl)
	0.1-0.2	0.25-0.3
Prior to frost or black ice event	0.1-0.2	0.25-0.3
Prior to light or moderate snow	0.1-0.2	0.2-0.4

## 2.2 Organic Materials in Winter Maintenance

The limited number of studies evaluating the organic and semi-organic materials for winter road maintenance purposes. The limited research and information available could be one of the potential reasons that organic and semi-organic materials are not widely used in winter road maintenance strategies. The results of a survey conducted by Fay (2008) in the North America and Europe show that the extent of the organic and semi-organic (i.e. CMA, KAc, KFo, etc) usage is less than 25% in the studied sample space. The results of a number of studies investigating the organic and semi-organic materials' performance and specifications are described in this section.

A study by Nixon (2005) the melting capacity of seven semi-organic and chloride based deicing chemicals (NaCl, CaCl<sub>2</sub>, KAc, CMA, MB, Caliber M1000 and Ice Ban Ultra) at four different temperatures (-18, -12, -6 and -1°C). Among the semi-organic materials, Ice Ban Ultra, Caliber M1000, and CMA were not effective at -18°C. Also, Ice Ban Ultra and CMA showed less effectiveness than the other materials by failing to work at even -12°C, thus suggesting that the semi-organic products were generally not as effective as chloride based materials tested in this study in very cold temperatures.

In another study done by Fay and Shi (2011), a series of lab tests were conducted to evaluate different chloride and organic based deicers in terms of their performance and their negative effects on metal and concrete. Among the performance measures considered in this study were ice melting capacity, ice penetration depth and rate of ice undercutting. The materials compared include solid or liquid chloride based, agricultural based, acetate-based, and formate-based deicers. The results of the three tests (ice melting, penetration and ice-undercutting) used to compare the deicers performance, showed that two MgCl<sub>2</sub>-based, one agro-based and, one KAc-based deicer outperformed the other deicers. It is worth mentioning that all these four materials were in liquid form. In terms of effective temperature, the results showed that the KAc-based and, following that, the MgCl<sub>2</sub>-based deicer outperformed the others. Also, the agro-based deicer provided less coefficient of friction whereas the solid NaCl-based deicer provided the highest coefficient of friction. In terms of corrosion, it has been found that acetate-based deicers are neutral to mild steel whereas all deicers, including acetate based, are corrosive to galvanized steel. It has to be mentioned that all these tests have been done in a lab environment which does not take into account external variables that may exist in real world situations. Therefore, they

may not represent real world results. Another study (Shi, et al., 2009) conducted a number of lab tests to evaluate the alternatives to chloride salts, including KFm, NaAc, NaFm-blend Geomelt C, Geomelt 55, NAAC, CF7, CMA and IceBan, in terms of their performance and negative impacts on the environment. The results of this study agree with the previously mentioned study. Another study was conducted to evaluate the use of organic materials versus regular brine for pre-wetting and anti-icing purposes (Fu, et al., 2012). The organic material used in this study was a combination of 30% beet juice with 70% salt brine. The performance of organic material and regular brine were compared using friction data collected in pre-wetting and Direct Liquid Application (DLA) experiments. In the pre-wetting experiment, none of the materials outperformed the others and overall showed similar performances. Also, in low temperatures, against expectation, the organic products did not show any superiority over conventional salt. However, due to limited data availability, it cannot be solidly concluded that organic products do not outperform other conventional salts in low temperatures. In DLA testing, the organic materials, although applied in lower application rates, outperformed brine by up to 30% higher averaged friction. This in turn suggests that organic products provide higher friction and maintain it for an extended period of time.

Hossain (2014) also conducted a series of field tests to investigate the effectiveness of anti-icing treatment and to optimize the application rate and material selection by testing two emerging semi-organic and organic alternatives of Caliber M1000 and SnowMelter2 along with regular brine. These two materials showed a performance similar to brine for anti-icing treatment in different weather conditions.

A recent study by Muthumani also explored the effectiveness of four agricultural based and two complex chloride/minerals (CCM) based deicing and anti-icing materials (Muthumani, et al., 2015). This study was conducted in a laboratory environment with a concentration of thermal properties, ice melting behavior, and corrosivity. In terms of ice melting capacity the agro-based additives did not cause any improvements at temperatures of  $-10^{\circ}\text{C}$  and  $-4^{\circ}\text{C}$ . However, the results showed that agro-based additives significantly lowered the freezing point of sodium chloride. Also CCM based materials did not lower the water's freezing point significantly but did improve the melting capacity slightly. In terms of corrosivity, agro-based additives significantly reduced the brine's corrosiveness.

## **2.3 Environmental and Infrastructural Impacts of Snow and Ice Control Chemicals**

In this section, first, the environmental pathways taken by snow and ice control materials to enter the environment are explained. Subsequently, the environmental and infrastructural impacts of the most common deicing and anti-icing materials are reviewed and compared; these include impacts on soil, water, air, animals and vegetation.

### **2.3.1 Environmental Pathways**

Snow and ice control materials discharge by means of transport, storage and application on the roads (NCHRP-577, 2007). The discharged material could be either in the form of liquid or solid. Solid discharged material, which can travel by wind and traffic, will deposit on the road-side vegetation, soil, and water bodies; it may also accumulate on vehicles and road surfaces. Liquid discharged material can leave the main roadway by splashing, spraying or gravity drainage. The run-off materials will enter the nearby water bodies and soil. The penetrating runoff, may either accumulate in the soil or enter the ground water and contaminate the microorganisms and roots of vegetation. Also, ground water is a pathway for the contamination to transfer to other water bodies. Based on the transport type, the discharged material could travel to different distances from the road (Lundmark, et al., 2007). For example, the run off can infiltrate near the main roadway, enter the ditches or drainage systems or, if close enough, enter the groundwater directly. If it travels through splashing, it usually deposits close to the road. However, transferring by spraying can result in depositing at further distances due to wind (Lundmark, et al., 2007). Figure 2.5 summarizes the environmental pathways that deicing and anti-icing materials take to enter the environment.

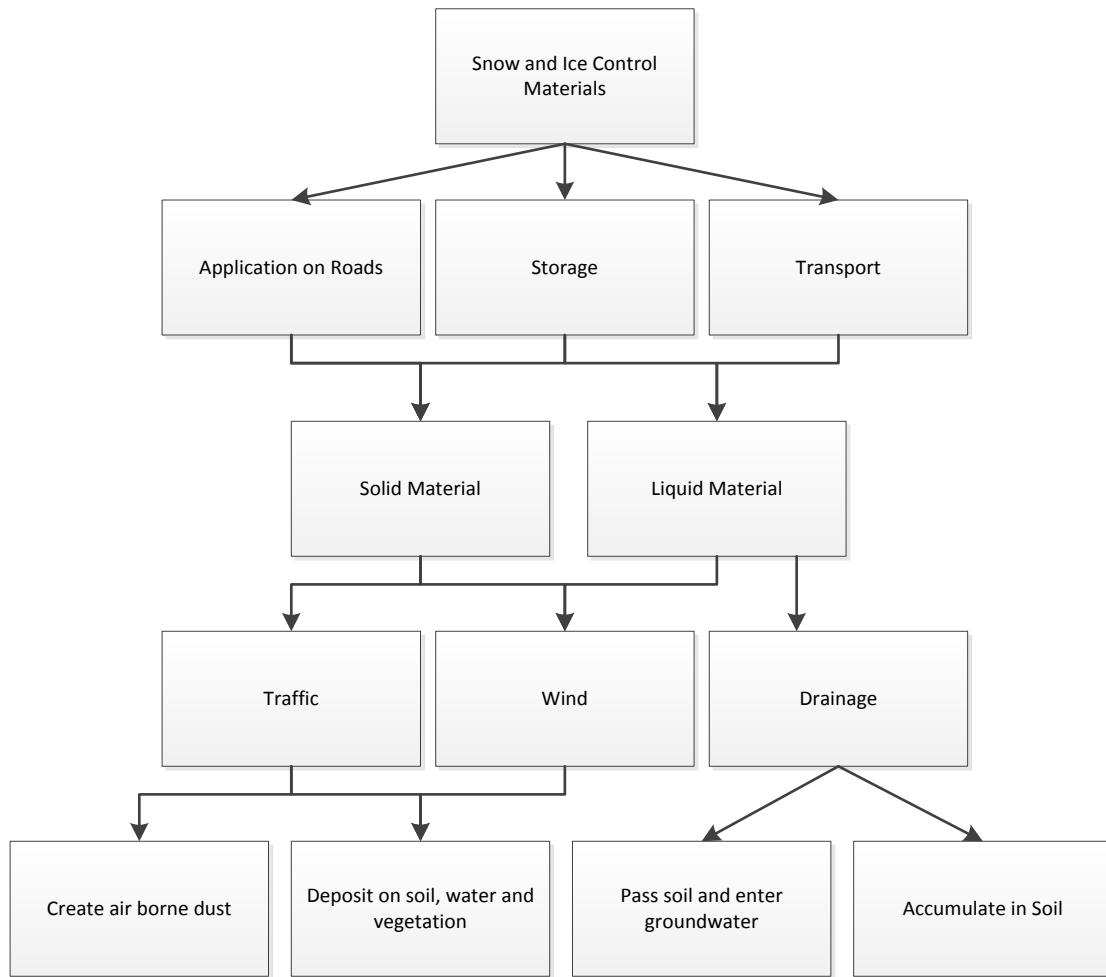


Figure 2.5: Environmental Pathways (NCHRP-577, 2007)

### 2.3.2 Effects on Water Resources

Numerous studies have researched the effects of deicing salts on water. The extent and distribution of water contamination depend on spatial and temporal factors, including the application rate of the salt applied on the nearby road, the salt pathway taken to enter the water body, the biodegradation level of the salt before reaching water, the drainage system, weather and soil conditions (McFarland, et al., 1992).

#### 2.3.2.1 Effects of Chloride Salts on Water Resources

The negative effects of chloride salts on water involve changing the density of the inflowing water, preventing the usual spring overturn (a natural process which ensures oxygen and nutrients distribution inside the lake), and altering the existence of its common aquatic species

(Ramakrishna, et al., 2005). In evaluating the effect of road salt (sodium chloride) on water streams in Michigan, Judd (1970) observed an increase in the water density of the lower lake caused by salt entering the First Sister Lake. The increased water density had led to incomplete spring overturn, which in turn caused oxygen and nutrients distribution disorders in the lake. In principle, salt load settles in a lake or pond due to its higher density, thus causing disorders in water circulation in the lower depths of the lake. This issue causes oxygen deficiency which in turn leads to organism mortality in the area and, over longer periods, increases nutrients at the bottom of the lakes and ponds that stimulate the algal growth (National Research Council (US), 1991). More algal growth leads to more oxygen consumption and less available oxygen in water.

Chloride salts also will increase the chloride concentration rates in water, which have been found to be much higher in smaller ponds and lakes (Ramakrishna, et al., 2005). Godwin (2003) studied the alterations in the ionic composition and solute flux of the Mohak river basin using data collected from 1952 to 1998. Analysis of this data indicated that the Na and Cl contents of the river basin have rose up to 130% and 243% respectively in the period under study. This dramatic increase is caused by the estimated 39kg/km per day of road salt used for winter maintenance. Lofgren also conducted a series of tests to investigate the effects of road salt on water by analyzing the dissolved salt content of storm water (Lofgren, 2001). The water streams under study were not directly influenced by the runoff from the road drainage system. Therefore, the contaminant likely first travelled through soil before reaching the ground water. The roads under study were deiced using salt between November and March each year with application rates of 5 to 10 gr/sqm per day. The test results indicate that the chloride ion concentration increased during the deicing period. In some of the streams, the chloride concentration levels were almost ten times higher than in other unaffected streams of the region. In another study in Otsego Lake an annual chloride concentration increase of 1 mg/Liters was observed due to the use of chloride salts for deicing purposes. In some cases, a chloride concentration of 1000mg/Liters was recorded in this lake during run-off events (Albright, 2005). The chloride concentration increase was also confirmed in similar studies (Backman, et al., 1995; Thunqvist, 2000; Crowther, et al., 1970). Shi (2009) also studied the impact of chloride based deicers in surface waters near highways in three locations where chloride based deicers were used. Several water quality parameters were monitored during the period of this study, including Ph, DO,

BOD, and chloride levels. All water quality parameters, except Greeley chloride concentration, complied with EPA standards since March 2008.

The chloride constituent of the chloride deicers, being easily soluble in water, is difficult to remove. Moreover, the recovery rate of chloride in water and soil is very low (Howard, et al., 1992). This issue was evaluated in a study on groundwater near a highway where potassium formate was used as a deicing agent, replacing chloride deicing agents used during previous years (Hellsten, et al., 2005). Several samples, taken from wells and at different soil depths, were analyzed in the lab for chloride, iron, potassium, and sodium formate concentrations, as well as for some other substances using a standard procedure. An interesting finding was that the chloride concentration levels were still high despite the use of the potassium formate deicer in the recent years, thus suggesting a slow recovery rate of chloride concentrations in water and soil.

The sodium element in sodium chloride has negative effects on water, and it has been reported that it could solute easily in water and increase the salinity and hardness of water (Forman, et al., 1998; Fay, et al., 2012; Peters, et al., 1981). Increased salinity can both decrease the growth and increase the abnormality of aquatic life (Karraker, 2007; Crowther, et al., 1977). Sodium also could stimulates algal growth (Fay, et al., 2012). Furthermore, calcium chloride and magnesium chloride both have twice the number of chloride ions as sodium chloride, so they increase chloride concentration more than sodium chloride in equal application rates (Bargo, 2004).  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  contents of calcium chloride and magnesium chloride are also soluble in water and thus increase its hardness.

Salt used for winter maintenance also can percolate through the soil and enter groundwater. However, the quantity of the ions entering the groundwater depends on the soil conditions such as soil porousness, plant cover, and moisture level of the soil (Ramakrishna, et al., 2005). Studies have indicated that sodium and chloride concentration in groundwater are increasing every year which could contaminate drinking water (Calabrese, et al., 1979; Watson, et al., 2002; Benbow, et al., 2004). A study in New York from 1986 to 2005 stated that sodium and chloride levels are increasing an average of 0.9mg/L and 1.5mg/Liter every year respectively (Kelly, et al., 2008). Figure 2.6 displays a sample of the increase in chloride and sodium concentration from 1975 to 2005 in Nagawicka Lake, Wisconsin, USA (Garn, et al., 2006). The main reason for the increase



in chloride and sodium levels is believed to be chloride deicers and some water softeners used in this area. The same trend in other lakes of the area has been observed.

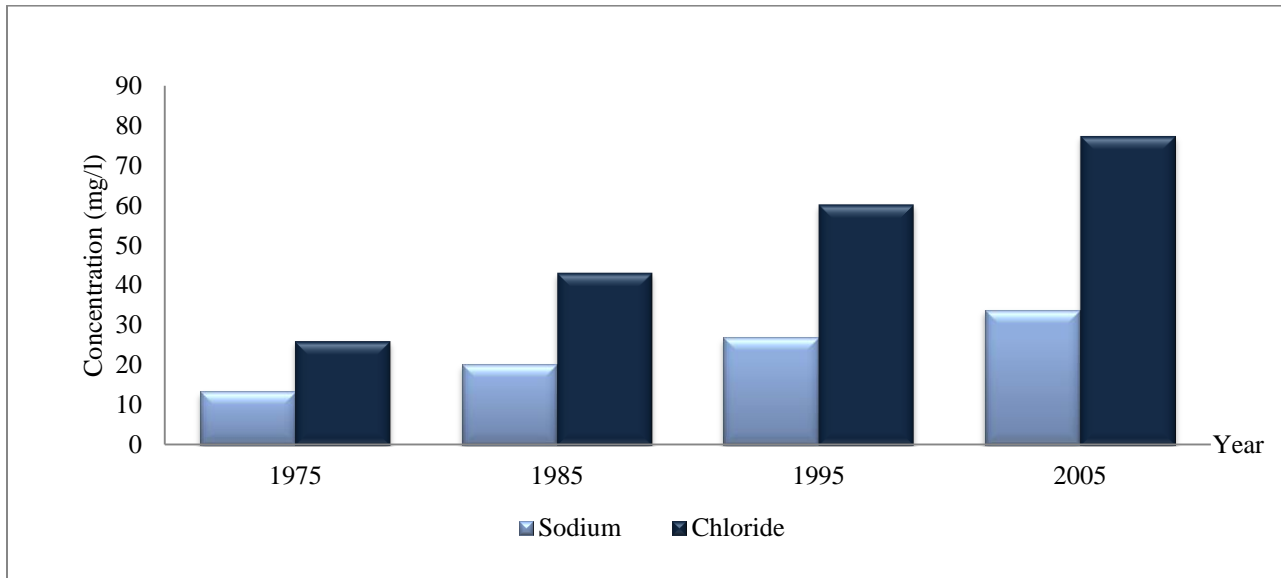


Figure 2.6: Increase in chloride and sodium concentrations in Nagawicka Lake, Wisconsin, USA (Garn, et al., 2006)

Studies indicate that the concentration of chloride is higher in shallow wells or groundwater closer to road salt application or storage locations (Transportation Research Board, 1991). In many cases, the chloride concentration of more than 250 mg/l, which is a secondary allowed concentration of chloride in drinking water, has been observed (Kelting, et al., 2010). In Table 2.5, four studies are brought which all indicate higher than standard (250 mg/l) chloride levels in drinking water reservoirs due to deicing applications. However, in some cases the deicers show less serious impacts on groundwater perhaps due to the type and designated use of reservoir or the drainage system used to discharge the runoff (Shi, et al., 2009).

Table 2.5: Chloride increase samples

Location	Years under study	Average chloride level (standard 250mg/l)	Maximum chloride level	Reference
G. Ross Lord Reservoir, Ontario, Canada	1974-1975	360 mg/l	1150 mg/l	(Scott, 1979)
Highland Creek, Ontario, Canada	1990-1993	316 mg/l	1390 mg/l	(Williams, et al., 2000)
Frenchman’s Bay watershed, Ontario, Canada	2002-2005	349 mg/l	1664 mg/l	(Meriano, et al., 2009)
Jamesville Road, New York, U.S.	1971-1972	445 mg/l	1696 mg/l	(Hawkins, et al., 1972)

### 2.3.2.2 Effects of Acetate Salts on Water Resources

An ongoing debate exists on the effect of acetate salts, such as CMA, on water. Some studies suggest that the acetate constituent decreases the level of dissolved oxygen in water, thus threatening the survival of fish and aquatic life (Horner, 1998; Harless, 2012; Bang, et al., 1998). However, other studies indicate no significant change in the dissolved oxygen level in streams with increased acetate concentration (Burkett, et al., 2004; Tanner, et al., 2000). For example, Burkett (2004) conducted a study in New Zealand where CMA was substituted for deicing salt in order to identify whether or not the former had a substantial effect on the DO (dissolved oxygen) levels of the water in the area’s streams. In the four year period of the study, CMA was applied in 30 snow events. The results showed no negative impact on the DO levels. However, it is important to note that the total mass of 23tons of CMA has been applied in each year may be significantly less than the amount of salt used in Northern America. Horner (1992) also evaluated the effect of CMA on water DO levels and observed that at near freezing temperatures CMA decomposition in soil can be delayed. Moreover, if the CMA reaches a waterbed, the decomposition takes place in the water and can decrease its dissolved oxygen level. In general it is recognized that decreased DO levels in water caused by acetate salts depend on factors such as

temperature, on the CMA transportation time from the road to the stream, and on the percentage of CMA applied to the road that reaches the stream (Burkett, et al., 2004; Horner, et al., 1992; IHS, et al., 1996). For example, it has been demonstrated that a high CMA concentration in water (15000mg/Liters in this study) will decrease the dissolved oxygen level and significantly impact fish survival (Horner, et al., 1992). CMA has also been reported to decrease the algal biomass in surface water and in terms of toxicity it is relatively harmless to fish and other aquatic species (McFarland, et al., 1992). In addition, the calcium and magnesium components of the CMA can also lead to hardening the water (Harless, 2012).

### **2.3.3 Effects on Soil**

Soil contamination as a result of deicing treatment with salts can harm nearby vegetation and cause water pollution, also damaging the road-side soil stability (National Research Council (US), 1991). The extent of deicing salt effects on soil depends on various influential site-specific factors: the road-side slope, the drainage system and configuration, salt type, vegetation, the presence of snow and ice, land topography, traffic conditions, soil's infiltration capacity, soil permeability and moisture content (Sorensen, et al., 1996). It is a challenge to specifically determine the impact zone of deicers on the soil due to several factors involved. For example, the distance that deicers discharge travel through splashing varies depending on traffic conditions. The amount of deicer penetration in the soil and the run off on the soil surface, both factors in the soil's infiltration capacity, depend on the soil permeability and moisture content. Another contributing factor, land topography, determines the travel route of surface and subsurface water flow. Moreover, in a study by Sorenson (1996), it was found that the effects of chlorides and their movement in soil depend on other factors such as road-side slope, the drainage system and configuration, salt type, vegetation and the presence of snow and ice. It has also been proven that the zone of impact varies both spatially and temporally (Kelting, et al., 2010).

Fischel (2001) confirmed that chloride concentration in soil decreases with distance from the edge of the roadways and observed that the highest concentration of chloride in the soil is found within 3 meters of the main roadway. This study also recorded chloride levels above normal up to 10 meters from the road. Another study (Lundmark, et al., 2007) found the greatest impact of deicers to be 6 to 9 meters from the road edge although residuals were observed up to 10 meters. This finding agrees with Backstorm (2003) which found that the major impact of salt was

constrained to 10 meters from the road-side. However, Hofstra (1984) found that measurable effects of chloride salts can be seen up to 30 meters from the road edge. Lofgren (2001) also observed that road-side soil samples containing abnormal Na content up to fifty meters from the main road section.

#### 2.3.3.1 Effects of Chloride Salts on Soil

One of the main concerns with soil contamination by chloride salts involves their potential to mobilize heavy metals. Soil clay particles and soil organic matter are both negatively charged (anions). The negative particles are neutralized by positively charged metals (cations), such as aluminum, calcium and magnesium, present in the soil. However, the bond between these anions and cations is weak enough that other cations can move through the soil, a process that helps supply soil with nutrients. When road salt (sodium chloride) enters the soil in high concentrations, sodium, which is positively charged, replaces the other cations being exchanged. This issue causes less soil fertility, decline in soil quality and structure, and passing trace metals to groundwater and other water bodies (Kelting, et al., 2010; Holmes, 1961). These trace metals can threaten aquatic life and also contaminate the drinking water, thus posing a hazard for human health. Furthermore, chloride ions are negatively charged and small enough to move through the soil, thus increasing the soil salinity (Ramakrishna, et al., 2005). Soil salinity will obstruct the roots' absorption of water and nutrients (Tester, et al., 2003).

A study by Cunningham et al. (2008) investigated the effect of chloride based deicing salts on soil in an urban environment where sodium chloride was the most widely deicing treatment used in the area. The concentration of deicing chloride salts in a semi-dense urban area in New York was studied in the fall season and it was found that sodium was the most abundant cation in the soil, after Ca and Mg, and that its level of concentration was high enough to damage the plants of that area. The Na concentration level was observed to be high up to ten meter from the road edge. Also Lofgren (2001) evaluated the effect of road salt (sodium chloride) on soil and observed that the ion exchange between Na and other cations in the soil, such as Ca and Mg, resulted in mobilizing  $H^+$  and trace metals in the region's streams. Increased soil salinity levels were also observed in this study. High sodium concentration scatters the soil bulk and changes its physical properties. This process leads to a finer soil structure and less soil permeability (Shi, 2005; Burtwell, 2001; Holmes, 1961 and National Research Council (US), 1991). In addition,

sodium constituent can also increase the alkalinity (Ph) and the Electricity Conductivity (EC) values of the soil and decrease the soil's oxygen level, thereby harming the roadside vegetation roots and making the plants more vulnerable to diseases (Bryson, et al., 2002).

The mobilization of a selected set of heavy metals (Cd, Cu, Pb and Zn) initialized by the chloride based deicing agents was investigated through a sampling process of soil quality on 2 test sites in Sweden (Backstorm, et al., 2003). In this study, soil samples obtained from soil depths of up to 50 cm were collected up to 30m from of the road's edge. Based on properties such as Ph and electrical conductivity, the concentrations of the metals were measured. It was found that the large amounts of heavy metals in the observed soils was due to the use of chloride based deicing materials. The major impact of salt was restricted to 10 meters from the roadside. This study also indicated that the chloride content due to deicing materials was at a very high level in the soil solution.

#### 2.3.3.2 Effects of Acetate Salts on Soil

The main concern with the impact of acetate salts on soil involves the metal mobilization caused by their magnesium, calcium and acetate constituents. A number of lab and field tests have confirmed this result (Ramakrishna, et al., 2005; Horner, 1998). However, compared to the chloride ion, acetate has proven to be less mobile in general (Ramakrishna, et al., 2005). In a study by Horner (1992) the mobility and transformation of CMA and its effects on soil were studied in a series of lab and controlled field tests. The lab tests showed that the calcium and magnesium components of CMA can trigger an ion exchange that results in the mobilization of certain metals in soil. However, the field tests indicated less metal mobility than the lab results. Armehin (1992) also observed that CMA could result in the mobilizing of heavy metals, even in organic soils. The amount of metal absorption increased in an approximately linear way with the concentration of CMA. Also it was observed that the concentration of Cu, Ni and Fe exceeded fresh water standards for aquatic life; however, the concentration of heavy metals in ground water were all beyond standard limitations.

Calcium and magnesium, on the other hand, can benefit the soil by forming more pore spaces, therefore increasing soil permeability and improving the soil structure (Gales, et al., 1992; Amrhein, et al., 1992). CMA can also enhance the soil fertility and increase its organic matter (Burkett, et al., 2004). In contrast to sodium chloride, CMA will not change the physical

properties of the soil and it is less toxic to the soil's germination and earth-worms' survival, and also improves soil fertility and increases its organic matter (Horner, 1998; Robidoux, et al., 2001; Burkett, et al., 2004). A study by Younge (2012) also observed that the soil samples treated with CMA have higher Ph than the control and NaCl samples; however, the soil samples treated with NaCl created higher EC than the control and CMA treated samples.

#### **2.3.4 Effects on Vegetation**

The negative effects of deicing and anti-icing materials on vegetation have been studied for many years. They include browning of foliage, premature defoliation, flower elimination, decreased regeneration and, increased mortality (Kelting, et al., 2010). The vegetation damage caused by snow and ice control materials occurs either through the deposit of salt in the soil and water or through salt deposit on shrubbery and tree branches, which is transferred through splashing and spraying (Kelting, et al., 2010).

Munchk (2010) conducted a study to quantify the long-term impacts of chloride deicing salts on nearby roadside conifers based on a two year study of Lake Thoe basin by using 176 control plots more than 300 meters away from the road and 137 plots near major roads. The effects on trees were studied through manual observation and based on standard procedures. The trees were also inspected for signs of damage caused by salts or other possible reasons (i.e. disease and insects). It was observed that around 15% of the trees nearby the roads were damaged by deicing salts. However, based on these observations, the trees damaged by salt were not vulnerable to further potential damage caused by insects or disease. The damage caused by salt were very obvious near the roadside due to the fact that the salt damage decreased with the distance from the road. Pine trees were found to be the most vulnerable to damage caused by salt than other trees. Downhill slope, high tree density and rocky soils were three factors contributing to the greater damage to the trees from salt. Also chemical tests on the roadside trees proved that they mainly contained more sodium and chloride than the control plots. It is important to mention that, in the study year, 863 ton salt was used for the Tahoe basin.

In another study by Bryson (2002), the effects of applying sodium chloride as a deicer on roadside plants was investigated by measuring the content of Na in plants and soil. The samples were taken from the leaves of the nearby trees which with visible salt damage and from trees without visible salt damage along with the soil samples in three meter intervals. Similar to the

results obtained in the previous study mentioned, pine trees were more damaged than other plant species based on the analyzed Na content, with Na content in the trees decreasing with the distance from the road. The Na concentration was high in samples of mixed grasses but no damage to them was observed. Oak and maple trees were found to be tolerant to salt even in cases where other trees nearby were visibly damaged. A high Na concentration was observed at a 5 meter distance from the road, apparently caused by the salt spray, a result also found in a study by Cunningham (2008). Thus Na ion concentration due to salt spray can remain high even further away from the road edge. A high Na concentration can reduce the oxygen level in soil, making plants more vulnerable to diseases.

Tarhan (2008) investigated the effects of chloride based deicing chemicals on roadside vegetation. Two types of pines, prior to and during the winter season, were studied in terms of the related soil quality, water pollution, mechanical damage and disease. Also, in a controlled experiment, the health effects of  $MgCl_2$  were compared to the solid sand and salt mixture. For this purpose, eight site studies on Colorado highways involved exposure to sand and salt and to  $MgCl_2$ -based liquid deicers. Four sites examined ponderosa pine and the other four examined lodgepole pine. Depending on the site, the selected trees were 45 to 95 meters away from the roadside. Prior to the deicing season, the overall health of the pine trees was investigated through a visual estimation and soil samples taken from the tree roots. A number of soil properties were assessed: Ph level, soluble salt levels, Na and Mg contents, and an assortment of heavy metals. It was evident from the results that the trees adjacent to the roadside, were subject to the worst damage of crown needle tissue death. The damage of deicing on the trees was clear due to a pattern of leaf damage of the tree side facing the roadway. Another interesting finding was that  $MgCl_2$  based deicers were caused more damage to the trees than the NaCl based sand and salt mixture. Controlled experiments on the effects of exposing the pine trees to  $MgCl_2$  and NaCl showed that the Mg component was neutral to plant life; therefore, the higher negative effects of  $MgCl_2$  could be due to its heavier concentration of chloride than in NaCl. Moreover, direct exposure to  $MgCl_2$  was observed to be more hazardous to plant life than exposure through the soil. The effect of direct exposure caused by spray was observed up to 20 meters from the roadside.  $MgCl_2$  was seen to have a more negative effect on photosynthesis rates than exposure to NaCl based sand and salt.

### **2.3.5 Effects on Air Quality**

The main concern with the effect of solid snow and ice control materials on air quality is the airborne salt dust produced mainly in the application phase. The tiny salt particles can penetrate deep inside the lungs and cause damage to vital human organs. A study by Idaho Department of Transportation found that substituting solid anti-icing or deicing material with liquid substances significantly enhances the air quality. However, limited information exists regarding the effects on air quality of using dry and liquid deicing anti-icing material together. Enhanced salt application methods such as anti-icing and pre-wetting reduce abrasive use, therefore enhancing air quality. On the other hand, there is also a possibility that liquid products may dry and cause air pollution, more so in working with NaCl than with other chemicals mainly due to the non-hygroscopic nature of this substance. Road salt spray has been observed to cause lung, skin and eye irritation but the extent of their impact has not yet been well explored (NCHRP-577, 2007).

### **2.3.6 Comparison of the Environmental Impacts of Common Snow and Ice Control**

#### **Materials**

As mentioned before, the most commonly used materials in winter maintenance are Sodium Chloride, Calcium Chloride, Magnesium Chloride, Calcium Magnesium Acetate (CMA) and Potassium Acetate. The common elements in these mentioned are Chloride, Sodium, Magnesium, Calcium and Acetate. Using the information explored in Section 2.2, from the literature, Tables 2.6 and 2.7 summarize and compare the impacts of these elements on different characteristics of the water and soil respectively. In these tables, an up direction arrow indicates increase whereas, the down direction arrow indicates decrease in the feature observed. As can be seen, Chloride and Sodium are the most destructive elements to the water and soil respectively; therefore, Sodium Chloride would have the most destructive effects to the water and soil among the most commonly used materials for winter road maintenance. This information could be beneficial in exploring the environmental impacts of any new material that contains at least one of these elements.



Table 2.6: Impacts of the most common elements in snow and ice control chemicals on soil

Elements	Soil Salinity	Oxygen Level	Soil Permeability	Soil Fertility	Soil Structure Quality	Metals Mobilization	Electrical Conductivity	Ph Level
Chloride	↑					↑		
Sodium		↓	↓	↓	↓	↑	↑	↑
Magnesium			↑	↑	↑	↑		
Calcium			↑	↑	↑	↑		
Acetate						↑		↑

Table 2.7: Impacts of the most common elements in snow and ice control chemicals on water

Elements	Water Salinity	Oxygen Level	Water Hardness	Metals Mobilization	Electrical Conductivity	Ph Level
Chloride	↑	↓	↑	↑	↑	↑
Sodium	↑	↓	↑			
Magnesium			↑	↑		
Calcium			↑	↑		
Acetate		↓	↑			

### 2.3.7 Effects on Infrastructure

Deicing and anti-icing materials are deleterious to concrete and metal, causing significant damage to vehicles and infrastructure. However there is some disagreement among the studies in the literature on this issue, perhaps due to the different test protocols used by researchers. Many factors involved in the corrosion process, such as the amount of moisture, and the quality of the cement in the concrete, influence the degree of corrosion. Some corrosion of metals is inevitable, but chloride deicing materials can increase the rate of this process. Therefore, using alternatives such as organic products will not solve the issue of metal corrosion but may delay the process.

In a study the effects of different deicers on concrete have been studied in a controlled laboratory environment (Darwin, et al., 2007). The approach involved exposing concrete specimens to wetting and drying in distilled water on a weekly basis and by exposing to deicing solutions including NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> and CMA; this process continued for 95 weeks. The result was that distilled water had no negative impact on the concrete properties but the deicing chemicals did. It was also observed that NaCl<sub>2</sub> in both low and high concentration levels had a relatively small negative effect. However, MgCl<sub>2</sub> and CMA, even at low concentration levels, caused considerable damage to the concrete. CaCl<sub>2</sub> had a small negative effect at low concentration but caused significant damage at high concentration levels. The main damages to concrete were a significant reduction in stiffness and strength of the specimen. Another study by Shi et al. (2009), also supported these findings and stated that MgCl<sub>2</sub> caused more significant deterioration to concrete than NaCl and CaCl<sub>2</sub> mainly because of the reaction between the Mg component and the cement hydrates.

In another study a much more comprehensive study on the effects of deicing chemicals on concrete materials is conducted (Wang, et al., 2006). Five deicing chemicals were studied: sodium chloride, calcium chloride (with and without using a corrosion inhibitor), potassium acetate, and an agricultural based deicer. The concrete specimens were exposed to freezing-thawing and wetting-drying conditions. The effects were studied in terms of several concrete properties, including compressive strength and chemical penetration; the study also used X-ray diffraction to study the micro-structure of the concrete exposed to the testing conditions. In this study it is found that CaCl<sub>2</sub> without a corrosion inhibitor resulted in the highest damage to concrete of the other materials in both testing conditions, a result which agrees with the findings of the previous studies mentioned. Another interesting finding was that CaCl<sub>2</sub> caused severe

damage to concrete material even with the use of corrosion inhibitors but at a slower corrosion rate. The non-chloride deicing chemicals (potassium acetate and agricultural based chemical) had an almost negligible negative impact on concrete material.

In another study, the effects of alternative deicers such as CMA, KFm, and KAc based products on concrete were compared to NaCl based products (Shi, et al., 2009). To reach this objective they conducted freeze/thaw lab tests following the SHRP205.8. They concluded that CMA solid deicer and CDOT MgCl<sub>2</sub> liquid deicer had almost no negative impact on PCC durability. However, KFm and NaAc/NaFm blend deicers had an almost moderate negative impact and NaCl and other NaCl-based deicer (IceSlicer) as well as KAc-based deicer (CF7) had the most negative impact on the durability of concrete. Therefore, one of the most important findings in their study is that almost all of the alternative deicers except CMA were highly deleterious to concrete.

Another study by Shi (2009), found that the effects of deicers on asphalt pavement in freeze-thaw situations highly depended on the aggregate material used. For example, quartzite aggregates were more susceptible to erosion than limestone aggregate asphalt. Overall, formate acetate based deicers have the most negative impact on asphalt pavement. It should be noted that the damage was not caused solely by the deicer whereas the combination of water, humidity, and heat along with the deicer contributed to the deterioration of the asphalt.

Report NCHRP-577 (2007) stated that all of the chloride deicers are highly corrosive to metal whereas CMA is non-corrosive. Also it was mentioned that CaCl<sub>2</sub> and MgCl<sub>2</sub> are more corrosive than NaCl. In another study through comparison of 3% deicer solutions under room temperature, it is concluded that CaCl<sub>2</sub> is the most corrosive chloride deicer followed by MgCl<sub>2</sub> and NaCl whereas CMA has negligible corrosive effects on metal (Shi, et al., 2009). In another study by Fay (2011), it is concluded that NaAc or KAc do not cause corrosion to mild steel but similar to chloride deicers, they are highly corrosive to galvanized steel. Evaluating corrosive effects of deicers on metals significantly depends on the test method and metal type. Overall, studies show that chloride salts compared to acetate salts, a subgroup of organic salts, are less corrosive to metal.

## 2.4. Summary

The major findings of the existing literature are summarized below:

- The most common snow and ice control method is de-icing (post-salting) and anti-icing (pre-salting) treatments. However, the anti-icing is beginning to be accepted as a more promising method in the industry.
- The most common material used for snow and ice control is chloride salt, specifically, sodium chloride. However, as this salt becomes less effective below  $-7^{\circ}\text{C}$ , the other chloride salts or alternative products (e.g.,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and abrasives) are also used in regions or situations where the temperature is very low.
- Transportation agencies are now more inclined to use a dependable cost effective alternative to chloride salts to reduce the negative environmental and infrastructural impacts of chloride salts. This inclination has motivated the search for and development of a viable alternative organic based product.
- Of the conventional semi-organic and organic products, a few chemicals, namely, CMA, KAc, Na-Fm, were the most common alternative chosen during the last decade until the recent evolution of various products. Among these, some trade names, for example, Caliber, Ice Ban, Geomelt, Sodium formate, Green salt, Pink salt, etc. were examined in some repeated studies. One of the major limitations is that there is scarcely any information on the chemical compositions of these products. Moreover, none of them has been reported in the independent research. For the recommended application rates of these chemicals, there are a few defendable guidelines; the situation is even worse for the organic chemicals, with no test results from any systematic study
- From the material costs perspective, road salts are less expensive than other inorganic or organic salts, whereas the former have the highest negative impacts on environment and infrastructures
- In regard to environmental concerns, the chloride part of any salt increases the chloride content in the drinking water source (ground water), and has thus identified as a health hazard
- In terms of the destructive effects of chloride salts on soil and water, they can decrease soil permeability and soil fertility depending on spatial and temporal factors. Chloride salts can also mobilize some types of heavy metals contaminating water and soil. The

chloride component could also reduce the dissolved oxygen levels in water resources and thus threaten aquatic life.

- The negative impacts of the chloride component in salts on plants and animal life include greater vulnerability of the plants to diseases, increased mortality of the nearby plants, and oral toxicity causing the premature death of birds and animals.
- Solid chloride salts, mostly sodium chloride, also cause air pollution through the airborne dust of the solid salt, which is hazardous to human health, causing skin and eye irritation also damaging the lungs.
- Based on the information available, chloride based materials are generally much more destructive to the environment and infrastructure than acetate salts when their various impacts on the environment are compared.

## Chapter 3

# Evaluation of the Effectiveness of Liquid Organic and Semi-organic Anti-icers

### 3.1. Introduction

As discussed previously, to reduce the adverse effects of chloride based materials on the environment and infrastructure, many government and environmental agencies are in favor of resorting to alternatives to conventional salts such as organic and semi-organic snow and ice control material. However, considering that safety is the main priority for all agencies, the effectiveness of these alternative in providing the required level of service must first be proven prior to putting new regulations in place. A few past studies evaluated the effectiveness of organic and semi-organic products for winter road maintenance; however results on their performance are still limited. Most of the available studies were conducted in a laboratory environment which does not take into account many external variables that may exist in real world situations (Nixon, et al., 2005; Shi, et al., 2009). Also none of the past studies have been conducted specifically for the facilities with low speed and low volume traffic (Muthumani, et al., 2015).

This chapter presents the results of field tests evaluating organic and semi-organic liquid salts for anti-icing treatment under different weather conditions in a low speed and low volume traffic transportation facility. The field test data are used to achieve the following two objectives.

- Evaluating and exploring the effectiveness of liquid anti-icing organic and semi-organic products for winter maintenance operations in parking lots compared to brine, a commonly used chloride based product.
- Exploring the factors that affect the performance of anti-icing with liquid organic and semi-organic products in parking lots.

## 3.2. Data Collection

A number of field tests were conducted under a range of weather conditions during the winter season of 2014. For each snow event, four different types of organic and semi-organic snow and ice control chemicals along with brine were applied to a set of test sections following specific test protocols. Two datasets of weather and surface condition were collected for each test, resulting in approximately 155 tests involving 14 anti-icing events.

### 3.2.1. Test Site

All the field tests were conducted in Parking Lot C at the University of Waterloo, Ontario, Canada (Figure 3.1), which has an area of approximately 25,540 m<sup>2</sup> (6.31 acres), with approximately 900 parking stalls and eight driveways.

The tests were conducted in multiple test sections (e.g., 3x6 m) possessing similar external conditions, such as pavement types, initial snow type and depth, and traffic conditions for any given snow event. Note that the pavement is asphalt concrete in good condition and with slight sloping throughout. This parking lot is busy during the day due to its convenient location next to the University.



Figure 3.1: Test site

### **3.2.2. Chemicals and Application Rates Tested**





After consultation with the Toronto Region Conservation Authority (TRCA), a regional environmental and conservation agency, a review was conducted to select the alternative anti-icing materials for testing. The criteria used to select the products included their organic contents, current usage, availability, price, and performance in low temperatures.

The materials selected for testing were as follows: brine, Snowmelt (organic), Fusion (organic with chloride content), and Caliber M1000 (organic with chloride content). In addition, Snowmelt was tested at two concentration levels: 100% concentrated Snowmelt, and Snowmelt diluted with brine at a ratio of 30:70 (Snowmelt to brine). This ratio was used for majority of the tests as recommended by the supplier. The brine used in the tests was regular brine (23% sodium chloride by mass) supplied from the City of Kitchener. It should be noted that the City of Kitchener filled the brine containers with an injecting pipe system, which was also used for providing other types of anti-icing materials (e.g., Fusion, beet juice). While there was a potential for cross contamination of the brine, the degree of this effect was considered to be relatively small. Information regarding the materials used for testing is summarized in Table 3.1.

Our test plan involved a fractional factorial experiment (i.e., investigating the response of some major influencing factors at their different levels) that enabled us to check the sensitivity of the major influencing factors, for example, ranging from the application rates of the materials to the response factors (i.e., the performance measure). Based on this design process and recommendations that were provided by the suppliers, three application rates for each of the product were tested for each day, i.e., 3, 6 and 9L/1000sft. Note that the application rates in the road industry vary from 3 to 10 L/1000ft<sup>2</sup> (Blackburn, et al., 2004), while 4L/1000ft<sup>2</sup> is the most common application rate used and recommended by suppliers for parking lots.



Table 3.1: Materials tested

Liquid Trade Name	Composition*	Cost (\$/L)	Appearance
Brine	23% NaCl 77% Water	0.15	
Fusion 2350	12% NaCl 50% Degraded Beet Juice 38% P/U	0.30	
Snowmelt	15-20% Glycerine 10-20% Polyether Polymer 3-8% Lactic Acid 2-4% Sorbitol 1-3% Formic Acid 1-3% Acetic Acid 1-2% 1,2-Butanediol Balanced with Water	0.29	
Caliber M1000	27% MgCl <sub>2</sub> 6% Carbohydrate 67% Water and P/U	0.45	

\*Note: The compositions are based on MSDS/Flyers provided by supplier or literatures.

### 3.2.3. Data Collection Procedure

The winter maintenance technique used in this study was anti-icing as it is one of the most common methods for snow and ice control as indicated in the literature. Anti-icing is a pro-active method for winter maintenance. This strategy involves applying the snow and ice control materials prior to a snow event, with the emphasis on preventing ice from bonding to the pavement rather than trying to break the bond later on. In other words, the anti-icing agent forms a bond breaking layer between the pavement and snow which helps the snow to melt faster and lowers the chance of ice forming and bonding to the pavement. Ultimately, the weak bond created by the anti-icing agent will make plowing less cumbersome, developing a higher level of friction after the snow event. Also, in small accumulations of snow, the pre-applied chemical can melt the snow itself and bare pavement can be reached in a shorter time (Hossain, et al., 2014).

As the method used in this study was anti-icing, liquids were applied prior to a snow event to prevent bonding, creating a safer friction level. According to weather forecasts from Environment Canada, the expected snow events were identified and anti-icing treatments were done beforehand. In general, in each snow event, the three semi-organic and organic anti-icers along with brine were applied in the designated parking stalls. To make the conditions uniform for all of the test sections, the parking stalls were coned off to prevent the pedestrian traffic. Some tests were also conducted in the driveways of the parking lot to assess and explore the effect of vehicle traffic on the performance of the anti-icers used in this study. In general, the anti-icing treatment was performed 2 to 12 hours in advance of snow events (Figure 3.2). The liquids were applied using a backpack liquid sprayer purchased from Canadian Tire. To ensure uniform application of the liquid salts by the liquid sprayer, a significant amount of training was conducted during the initial stage of field tests to ensure the best possible uniformity in application. Moreover, each test section was approximately 10'x20'- a relatively small area used to achieve a high degree of uniformity. It should be noted that, in practice, the uniformity of salt spreading depends on the characteristics of the sprayer (e.g., manual rate setting vs. automatic rate control) and truck operational constraints (e.g., speed fluctuation), both of which remain issues to investigate.

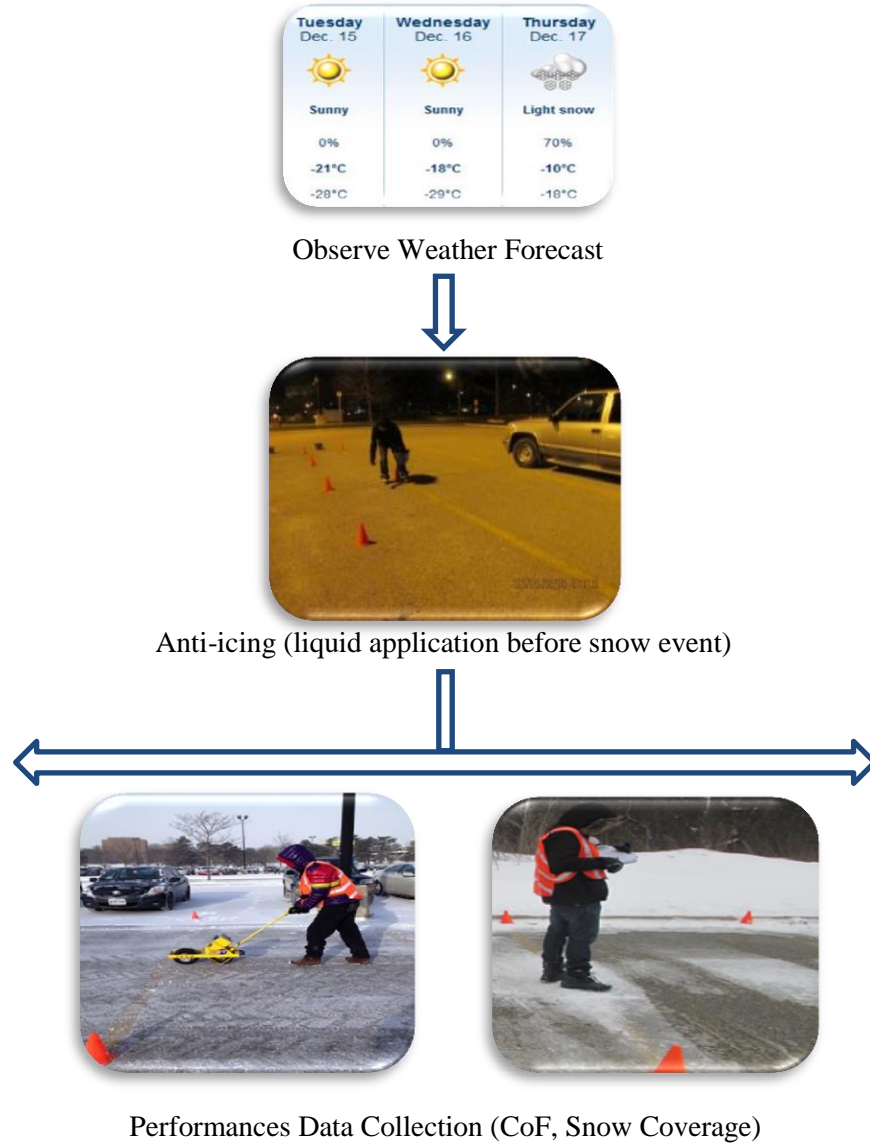


Figure 3.2: Field test procedure

To compare the performance of the treatments with the organic materials, the data including weather condition variables (e.g., precipitation amount, air temperature, snow type) and treatment performance (e.g., the coefficient of friction) were collected by filling out forms at a fixed time interval for each test section after the material had been applied. The data recorded included the initial and final conditions of the tests, total snowfall over the event, as well as some processed data from the day, such as average temperatures for the event and pavement condition. It is essential to emphasize that the data collection process continued until every test section reached the desired bare pavement (in general more than 70% bare). The interval of the data

collection runs varied depending on how fast the road surface conditions change. The performance metric used in this study was the coefficient of friction (CoF) level, a ratio value which shows the relationship between the force required to slide an object over another horizontally and the pressure force between the two objects. In other words, the coefficient of friction measures the slipperiness between two objects (in this study between the pavement and the wheels of the machine used for measuring the CoF). In summary two datasets were collected:

- **Weather Condition Data:** These data, including all the weather variables such as air temperature, wind speed and precipitation amount, were obtained from Environment Canada's website (region of Waterloo international airport station). At the beginning of a test, a master event log was filled out with information characterizing the event, including start and end of the snowfall, initial snow depth, snow type, density, and prevailing temperatures. Also in each section after the materials were applied, weather data were recorded at a time interval that varied depending on how fast the road surface conditions changed throughout the tests. The surface temperatures of the pavement and snow depths were measured on-site. The pavement temperature was measured after removing excess patches of snow using an infrared surface temperature reader. The snow depth was also measured with a standard ruler. To achieve higher accuracy, the average of 5 readings were recorded each time.
- **Surface Condition Data:** In this study, the performance measure was the coefficient of friction, a physical measure to represent the amount of frictional force available between a road surface and shoes or vehicle tires. The friction data were collected using portable friction measurement equipment called ASFT T2GO. Also, pavement surface states, a visual characterization of the pavement surfaces, were recorded to represent a driver's or pedestrian's perception of the surface condition of a parking lot or sidewalk. This characterization included two aspects: a) type of road surface cover such as loose snow, packed snow, slush and solid ice; and b) extent of snow and ice coverage. Digital cameras were used to collect these data.

### 3.3. Exploratory Analysis

Before proceeding with the statistical analysis, an exploratory data analysis was conducted to visualize the data characteristics. Table 3.2 summarizes the data collected in the 2014 winter season. It can be seen that the distribution of some variables varied for some of the products. For instance, the highest and lowest testing temperatures were similar for most of the products; however, there was a statistically significant difference in both kurtosis and skewness coefficients for some of the products, thus suggesting that the test temperatures were not distributed uniformly for all the products.

Table 3.2: Descriptive statistics of the data

Products Name	Variable	Salting Rates (lb/1000ft <sup>2</sup> )	Pavement Surface Temperature (°C)	Amount of Snow in kg/m <sup>2</sup> (Snow Depth in cm x Density in kg/m <sup>3</sup> )	% Improvement in CoF compared to control sections
Brine n=41	(Minimum, Maximum)	(3, 9)	(-14.8, -1.7)	(0.08, 4.74)	(-12.73, 87.5)
	Mean	5.93	-8.32	1.12	15.79
	Std. Dev.	2.46	3.97	1.30	21.69
	Variance	6.07	15.74	1.70	470.46
	Kurtosis	-1.51	-0.84	2.14	3.85
	Skewness	0.04	-0.43	1.71	1.75
Fusion n=35	(Minimum, Maximum)	(3, 9)	(-14.8, -1.7)	(0.08, 4.74)	(-12.73, 53.33)
	Mean	5.93	-8.52	1.15	16.04
	Std. Dev.	2.46	4.23	1.40	16.11
	Variance	6.07	17.90	1.96	259.68
	Kurtosis	-1.52	-1.15	1.41	0.07
	Skewness	0.05	-0.27	1.56	0.70
Snowmelt n=57	(Minimum, Maximum)	(3, 9)	(-14.8, -1.7)	(0.2, 4.74)	(3.7, 50)
	Mean	5.63	-7.04	2.16	19.84

	Std. Dev.	2.42	4.74	1.66	11.63
	Variance	5.85	22.45	2.75	135.31
	Kurtosis	-1.37	-0.78	-1.19	1.70
	Skewness	0.25	-0.79	0.34	1.15
Caliber M1000 n=21	(Minimum, Maximum)	(3, 9)	(-9, -4.4)	(0.08, 2.51)	(-16.67, 87.5)
	Mean	6.00	-6.66	0.60	13.05
	Std. Dev.	2.51	1.86	0.82	23.98
	Variance	6.30	3.44	0.67	574.90
	Kurtosis	-1.58	-1.84	2.48	3.49
	Skewness	0.00	-0.12	1.96	1.38

The data collected in the 2014 winter season clearly show that a wide variety of weather conditions were experienced, including a number of days with an average pavement surface temperature of below  $-10^{\circ}\text{C}$ . This winter season had more than 20 regular snow event (less than  $\sim 2\text{cm}$ ), 10 medium to heavy events (2 to 5cm snow) and five extremely heavy events (more than 5cm) while the pavement surface temperatures ranged from  $-15^{\circ}\text{C}$  to  $1^{\circ}\text{C}$ , and average air temperatures varied from  $-22^{\circ}\text{C}$  to  $-2^{\circ}\text{C}$ . Figure 3.3 shows the main weather features of the data collected. Note that, in order to closely simulate the way parking lot maintenance is performed in the real world, 70% of the tests started on or before 7am.

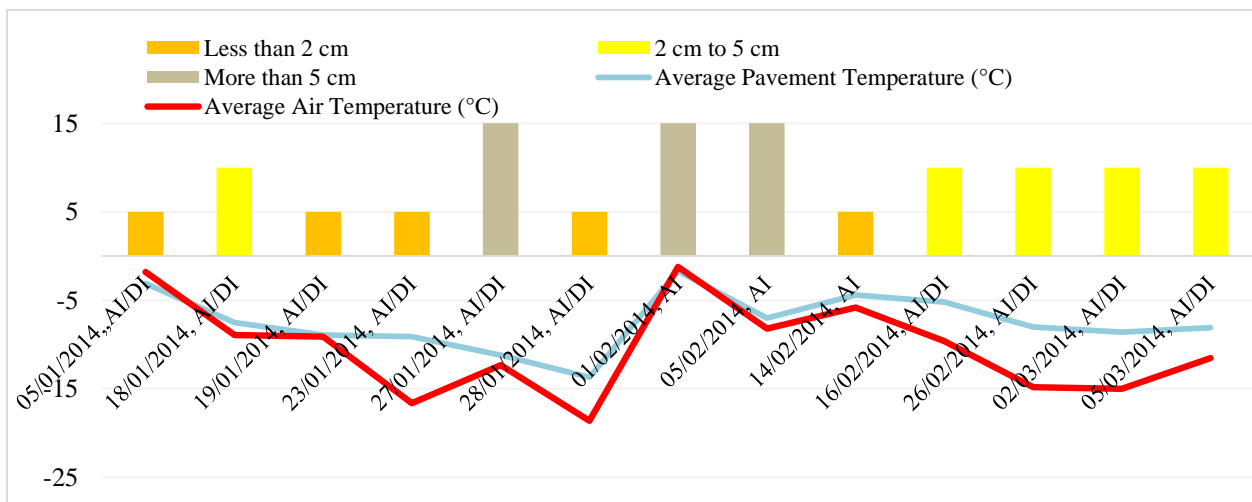


Figure 3.3: Winter 2014 anti-icing events

### 3.4. Data Analysis and Results

In this section, the effectiveness of anti-icing operations with the emerging liquid organic and semi-organic products is evaluated and compared to the effectiveness of the regular brine (the most commonly used anti-icing chemical in industry) specifically for the parking lot facilities. This is followed by an investigation of the factors contributing to the performance of the chloride (brine), semi-organic (Fusion and Caliber), and organic (Snowmelt) anti-icing chemicals.

#### 3.4.1 Effectiveness of Anti-icing Treatment with Organic and Semi-Organic Chemicals

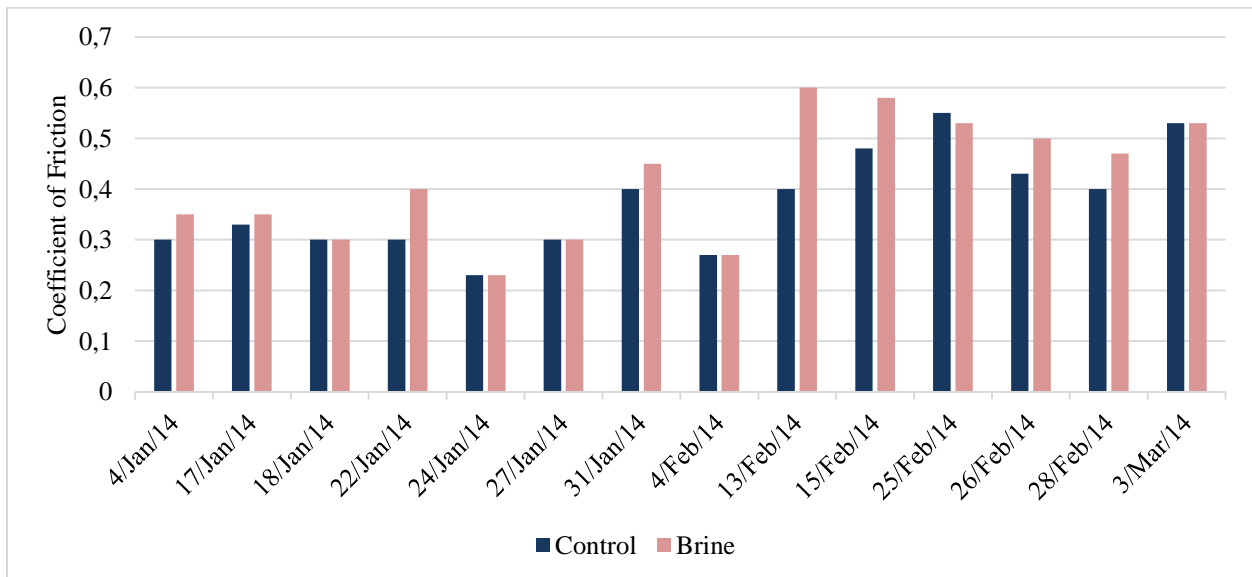
As mentioned previously, anti-icing effectively prevents the strong bond between snow and pavement surface by using chemicals to depress the freezing point of water. Field tests in previous studies have confirmed the effectiveness of anti-icing, proving that it increases the pavement surface friction level and leads to safer surface conditions (Hossain, et al., 2013). To investigate the effectiveness of anti-icing operations, the Coefficient of Friction (CoF) levels on the sections treated with anti-icing were compared to untreated sections (control sections).

Studies show that the coefficient of friction (friction level) is related to the slipping risk level. A coefficient of friction of 0.5 was determined to be safe for pedestrian in a study by Miller (1983). Another study was conducted specifically for the parking lots transportation facilities in which the slipping risk level was related to the coefficient of friction by dividing it into three groups of high, medium and low risk (Hossain, et al., 2014). A summary of this classification is displayed in Table 3.3.

Table 3.3: Risk levels associated with coefficients of friction (Hossain, et al., 2014)

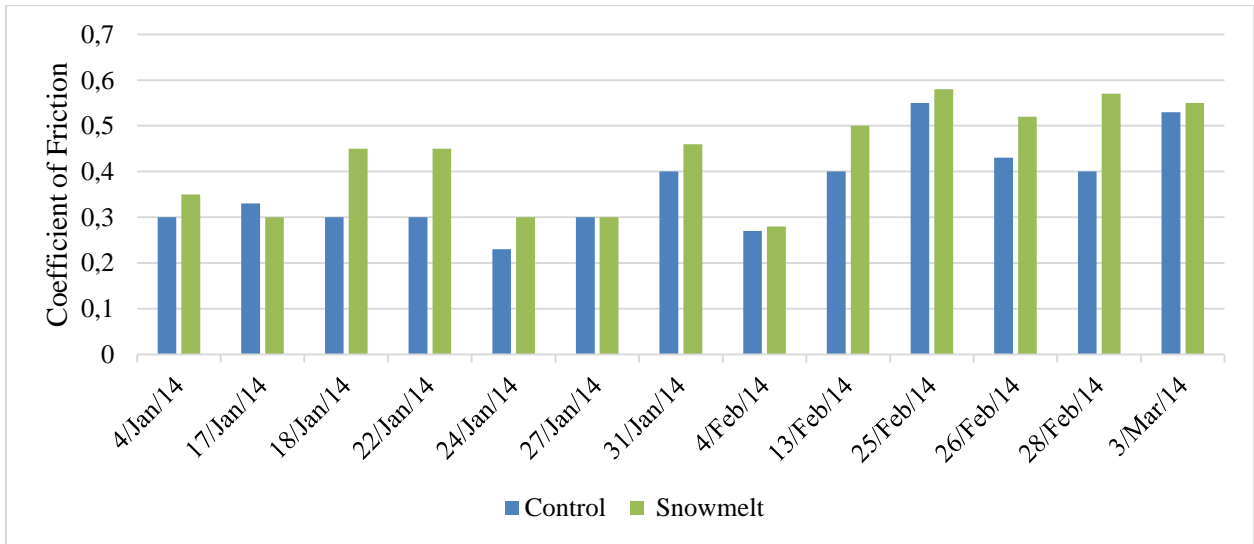
Risk Level	Coefficient of friction	Standard deviation	Contaminant type
High risk	0.22	0.08	Ice, slush, plowed-bonded snow/compacted snow
Medium risk	0.41	0.06	unplowed-unbonded snow and unplowed-bonded snow
Low risk	0.57	0.1	plowed-unbonded snow, wet, dry surfaces

In this study, to assess the effectiveness of the anti-icing treatments, the coefficient of friction of the pavement surface after a snow event was measured at a fixed interval until the pavement reached at least 70% bare and then was averaged. For this purpose, the accumulated snow was first removed by a snowplow or a shovel. The coefficient of friction was then measured in each section using a portable friction measurement equipment called ASFT T2GO, a device that calculates the kinetic coefficient of friction by measuring the friction between the pavement surface and the instrument's wheels. Figure 3.6 compares the measurements of the averaged coefficient of friction for sections treated with different liquids, namely, brine, Snowmelt (organic product), Fusion (organic with chloride content), and Caliber M1000 (organic and chloride contents) with an application rate of 3L/1000ft<sup>2</sup> to sections without anti-icing operations. It can be seen from Figure 3.6 that anti-icing operations with all of the materials used effectively prevented the bonding of snow and ice in general. The friction gain was positive in the most cases, except for a few days where the control section's CoF was almost equal or slightly higher than the treated section. It should be noted that this winter season was very cold and liquid salts become less effective in temperatures less than -7°C (Blackburn, et al., 2004). Also it should be noted that anti-icing can be conducted in situations where the pavement is bare and that it is not effective in situations where continuous snow events occur. This was the reason that limited this study to 14 anti-icing events.

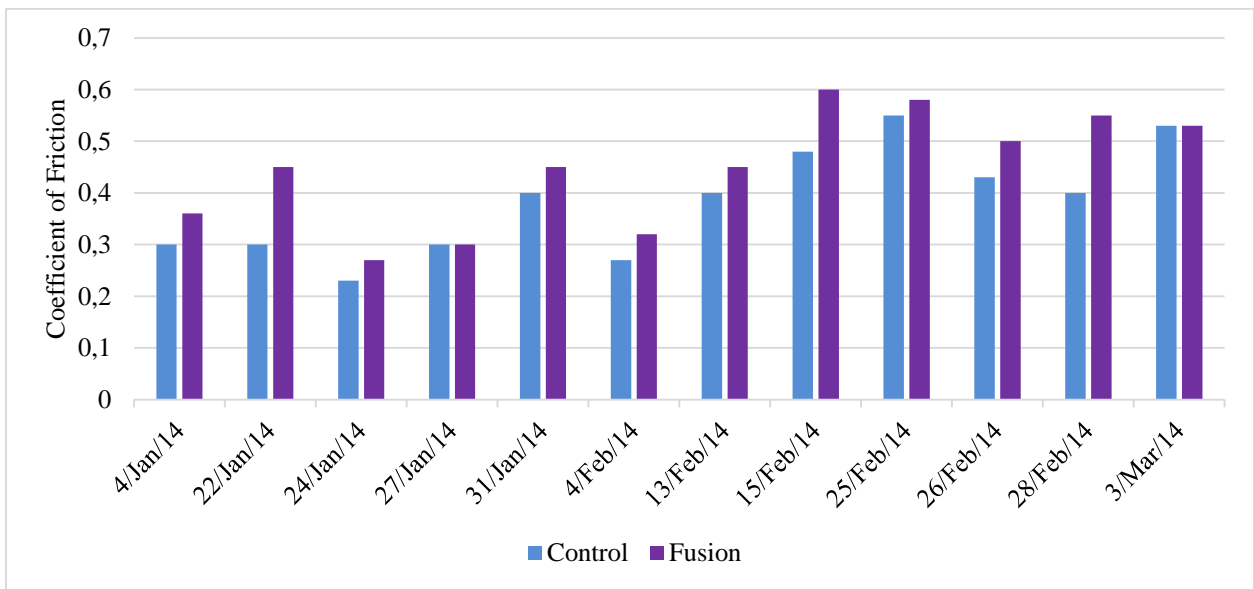


a: Effectiveness of treatment by brine

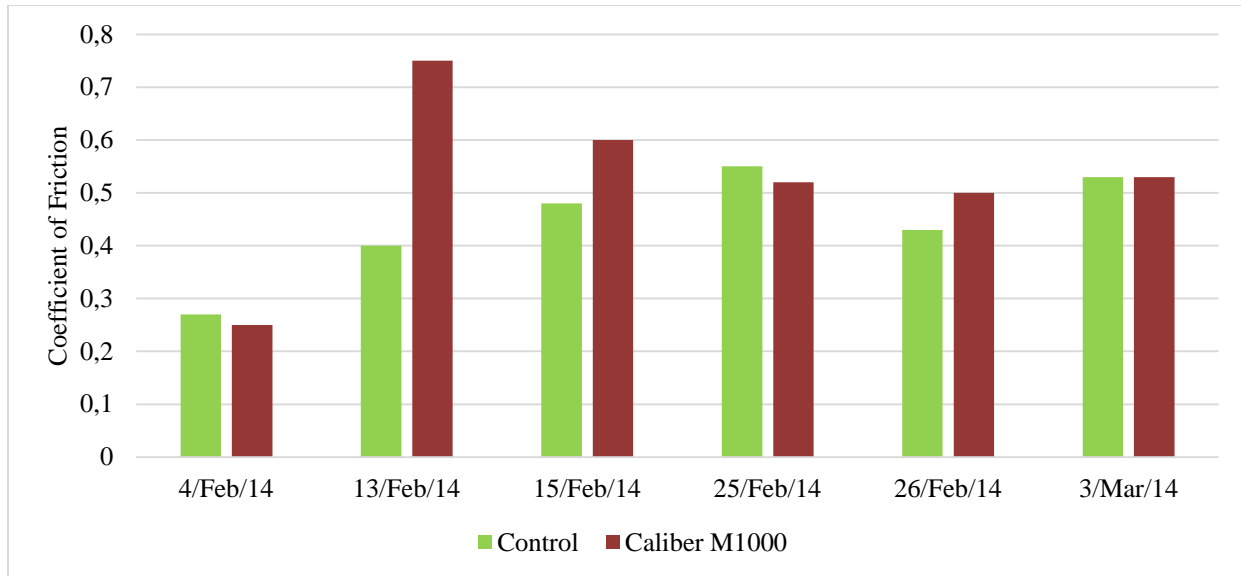




b: Effectiveness of treatment by Snowmelt



c: Effectiveness of treatment by Fusion



d: Effectiveness of Anti-icing Treatments by Caliber M1000

Figure 3.4: Effectiveness of anti-icing treatments by different liquids

Exploring and comparing the effectiveness of the anti-icing treatments with brine, semi-organic and organic products used in this study involved calculating the percentage of CoF improvement in the treated sites (with anti-icing) relative to the control sections (without anti-icing). Comparing the material's effectiveness in different weather conditions involved categorizing pavement temperatures into two groups: above  $-7^{\circ}\text{C}$  and below  $-7^{\circ}\text{C}$ , respectively. The basis for this threshold was studies that found anti-icing with liquid chemicals to be less effective in temperatures less than  $-7^{\circ}\text{C}$  (Blackburn, et al., 2004). Figure 3.7 and 3.8, which illustrate the results of this comparison, show that all the chemicals were effective in increasing the friction level, with improvements ranging from 2% to 40%. They also show that anti-icing with liquid chemicals was more effective in temperatures above  $-7^{\circ}\text{C}$ , with friction level improvements ranging from 17% to 40% with an average of 23%. However, in temperatures below  $-7^{\circ}\text{C}$ , the effectiveness was below 15% with an average of 11%. In summary, the results indicate that all the organic and semi-organic products performed very similarly to regular brine in temperatures above  $-7^{\circ}\text{C}$ , when anti-icing operations with liquid materials are effective (Blackburn, et al., 2004). However, in temperatures below  $-7^{\circ}\text{C}$ , organic and semi-organic products, except Caliber M1000, slightly outperformed the regular brine, especially with a lower application rate of  $3\text{L}/\text{ft}^2$ . Among the organic and semi-organic products, Snowmelt outperformed others in

situations where the pavement temperature was below  $-7^{\circ}\text{C}$ , a result which shows that it could be a better option for very cold temperatures. In general, it can be seen that all of the organic and semi-organic products performed as well as or better than regular brine. This result in turn suggests that these alternatives to brine can be effectively used for anti-icing operations, consequently reducing the impacts of chloride salts on the environment.

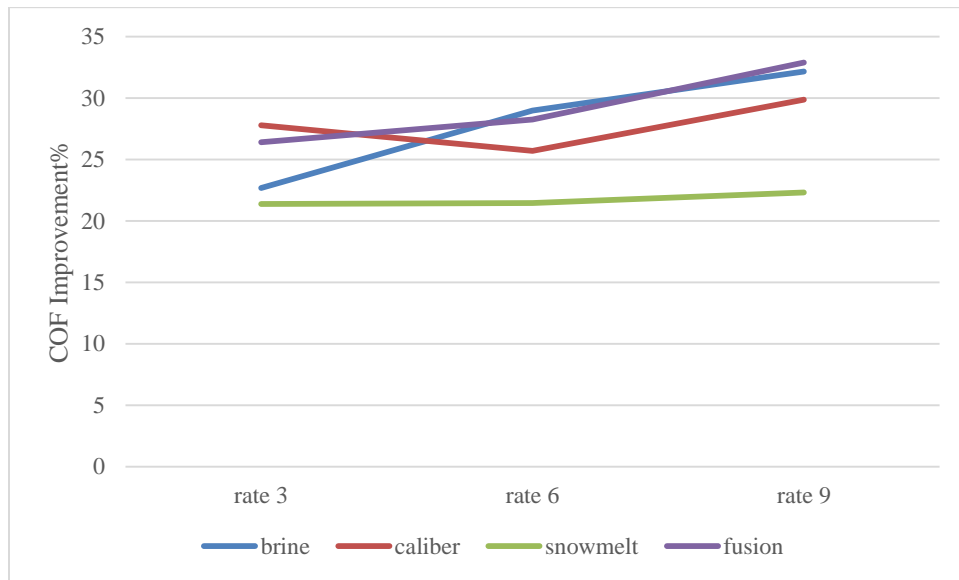


Figure 3.5: Comparison of the chemical's effectiveness in temperatures above  $-7^{\circ}\text{C}$

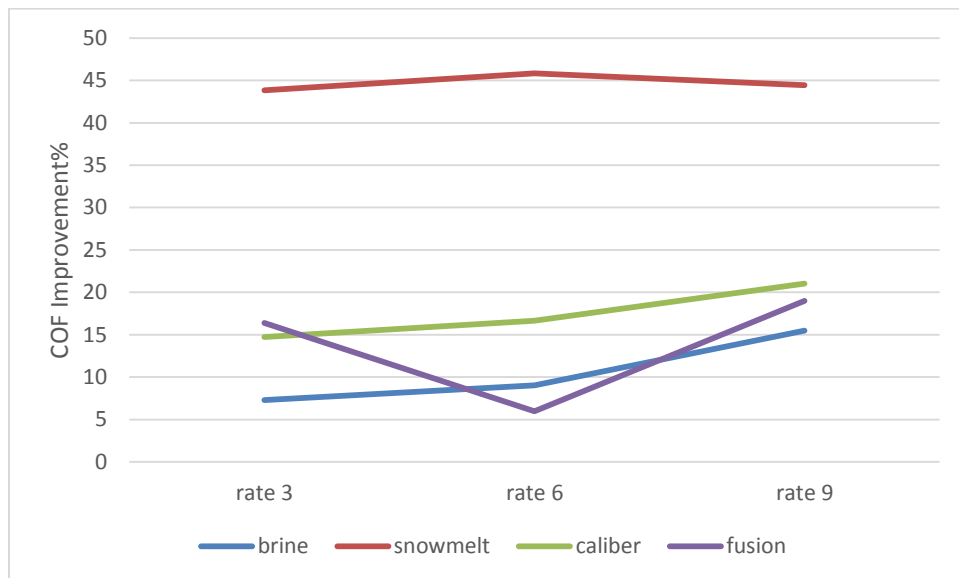


Figure 3.6: Comparison of the chemical's effectiveness in temperatures below  $-7^{\circ}\text{C}$

To confirm the results obtained from Figures 3.6, 3.7 and 3.8 statistically, a t-test and an ANOVA test were conducted using MS Excel software (Microsoft, 2013). A t-test statistically indicates whether there is a real difference between the averages of two groups of values in the population of a sample under study (Berenson, et al., 2012). Table 3.4 shows the results of the t-test conducted between the average coefficient of friction of the treated sections and control sections separately for each of the chemicals used in this study. The results confirmed that there was strong evidence to reject null hypothesis whereby the mean CoF in both treated and control sections are equal at the 95% confidence level. This finding confirms the result shown in Figure 3.6: that anti-icing with the chemicals tested in this study increased the friction level of the treated sections in the parking lot facility.

Table 3.4: Paired T-tests results for improvement of friction on anti-icing sections vs. control sections

Statistics	Brine	Snowmelt	Fusion	Caliber
Observed Difference in Mean CoF (Treated site over Control Site)	0.0575	0.0615	0.0571	0.0574
S.E	0.0124	0.0087	.0091	0.0208
Sample Variance	0.0071	0.0033	0.0036	0.0091
# Sample	44	57	38	21
Degrees of Freedom	43	56	37	20
Hypothesized Difference in Mean CoF (Treated site over Control Site)	0	0	0	0
t-calculated	4.63	7.06	6.27	2.78
t-critical (5% significance level)	1.68	1.68	1.68	1.72
P-value	2.4E-5	5.1E-9	5.6E-7	0.0061
Statistical Conclusion				

Similar to the t-test, analysis of variance (ANOVA) is also used to determine whether there is a significant real difference in the average value of the groups of the population where the sample is taken from; but between three or more groups; therefore it is an extension of the t-test that allows us to compare more than two groups together (Berenson, et al., 2012). To investigate and compare the effectiveness of the chemicals in different weather conditions, the data were categorized into two groups with pavement temperatures of above  $-7^{\circ}\text{C}$  and below  $-7^{\circ}\text{C}$  respectively. Table 3.5 shows the result of an ANOVA test conducted on the CoF improvements for four materials of brine, Snowmelt, Fusion and Caliber in situations where pavement temperature was above  $-7^{\circ}\text{C}$ . The result indicates that there is no evidence to reject the null hypothesis that the mean CoF in both treated and control sections are equal at the 95% confidence level, a finding which confirms the result outlined in Figure 3.7 whereby all of the four materials tested performed very similarly to each other in pavement temperature above  $-7^{\circ}\text{C}$ .

Table 3.5: ANOVA results for improvement on friction at treated sections with anti-icing in temperatures above  $-7^{\circ}\text{C}$

Source of Variation	Sum of Squares	Degree of Freedom	Mean Squares	F-Observed (5% significance level)	F-Critical (5% significance level)	P-Value	Conclusion form ANOVA
Between Treatments (Brine, Snowmelt, Fusion and, Caliber M1000)	0.017	3	0.006	1.035	2.718	0.381	No evidence to reject that the mean performances (CoF improvements) for all treatments are equal
Within Treatments (Brine, Fusion, Snowmelt and, Caliber M1000)	0.451	80	0.005				
Total	0.468	83					

To compare the material's effectiveness when the pavement temperature was below  $-7^{\circ}\text{C}$ , another F-test was conducted between the CoF improvements for four materials of brine, Snowmelt, Fusion, and Caliber with pavement temperatures above  $-7^{\circ}\text{C}$ . The result which is displayed in Table 3.6, rejects the null hypothesis that there is no significant difference among the average value of these groups; which means that at least one of them outperformed the others. As Figure 8 showed Snowmelt outperformed the other chemicals when pavement temperature was below  $-7^{\circ}\text{C}$ , so another ANOVA test was conducted among three chemicals of brine, Fusion, and CaliberM1000. The result of this ANOVA test is illustrated in Table 3.7 which shows there is no evidence to reject the null hypothesis that there is no significant difference between the average values of the mentioned three groups. Therefore, from the results in Table 3.6 and Table 3.7, one can conclude that Snowmelt outperformed the others when pavement temperature was below  $-7^{\circ}\text{C}$  whereas all of the chemicals performed very similarly at pavement temperatures above  $-7^{\circ}\text{C}$ .

Table 3.6: ANOVA results for improvement of friction on treated sections with anti-icing in temperatures below  $-7^{\circ}\text{C}$

Source of Variation	Sum of Squares	Degree of Freedom	Mean Squares	F-Observed (5% significance level)	F-Critical (5% significance level)	P-Value	Conclusion form ANOVA
Between Treatments (Brine, Snowmelt, Fusion and, Caliber M1000)	0.031	3	0.010	3.717	2.743	0.015	Reject the null hypothesis that the mean performances (CoF improvement) for all treatments are equal
Within Treatments (Brine, Fusion, Snowmelt and, Caliber M1000)	0.186	66	0.002				
Total	0.218	69					

Table 3.7: ANOVA Results for Improvement of Friction on treated sections with anti-icing in temperatures below  $-7^{\circ}\text{C}$

Source of Variation	Sum of Squares	Degree of Freedom	Mean Squares	F-Observed (5% significance level)	F-Critical (5% significance level)	P-Value	Conclusion from ANOVA
Between Treatments (Brine, Fusion and, Caliber M1000)	0.002	2	0.001	0.351	3.214	0.705	No evidence to reject that the mean performances (CoF improvement) for all treatments are equal
Within Treatments (Brine, Fusion and, Caliber M1000)	0.128	43	0.002				
Total	0.130	45					

### 3.4.2. Investigation of the Contributing Factors

This section investigates the factors contributing to the variation in coefficient of friction observed in the previous section by exploring the data and conducting a multi-variable linear regression analysis. Due to the fact that the data was collected through field tests, many uncontrollable variables may have affected affect the coefficient of friction. Considering that not all of the factors are measurable and not all the data related to the existing factors are available, only the effects of the key contributing factors were investigated as illustrated in Figure 3.9.



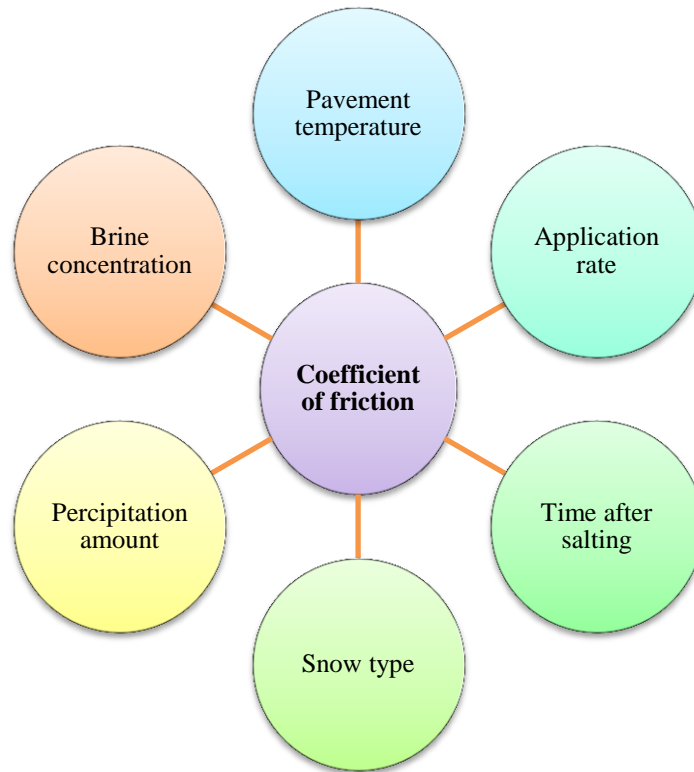


Figure 3.7: Contributing factors to coefficient of friction

#### 3.4.2.1. Effect of Application Rate

Studies indicate that the application rate has a positive relationship with the coefficient of friction (Hossain, et al., 2015). In this study, three application rates of 3, 6 and 9 L/1000ft<sup>2</sup> were tested for each of the products in each snow event to investigate their effect on the anti-icing performance (i.e., gained CoF). Note that the application rates in the road industry vary from 3 to 10 L/1000ft<sup>2</sup> (Blackburn et al, 2004), while the application rate of 4L/1000ft<sup>2</sup> is the most common rate for parking lots as instinctively recommended by the suppliers. Figures 3.10 and 3.11 show the CoF value for the four materials under the three application rates in two different temperatures ranges: below -7°C and above -7°C. The figures reveal only a negligible improvement in CoF by increasing the application rate by 100% and 200%, respectively. This finding suggests that the lower application rate of 3L/1000ft<sup>2</sup> is suitable for anti-icing with liquid organic and semi-organic products in parking lot facilities, an amount that is 25% less than the recommended application rate by the supplier and the current rates used in the practice. The achieved CoF value in temperatures above -7°C was close to 0.5, which is considered as a safe surface for pedestrians walking in any season (Pavement Guide, 2010). Also the CoF value in

temperatures below  $-7^{\circ}\text{C}$  was approximately 0.4, which is moderately safe under such cold weather conditions (Hossain et al.).

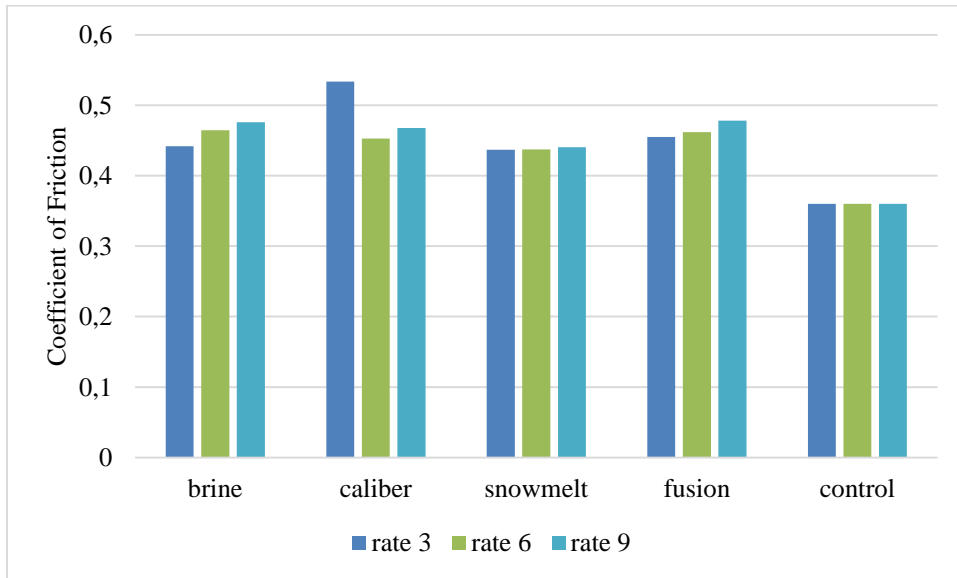


Figure 3.8: Effect of application rate on the CoF in temperatures above  $-7^{\circ}\text{C}$

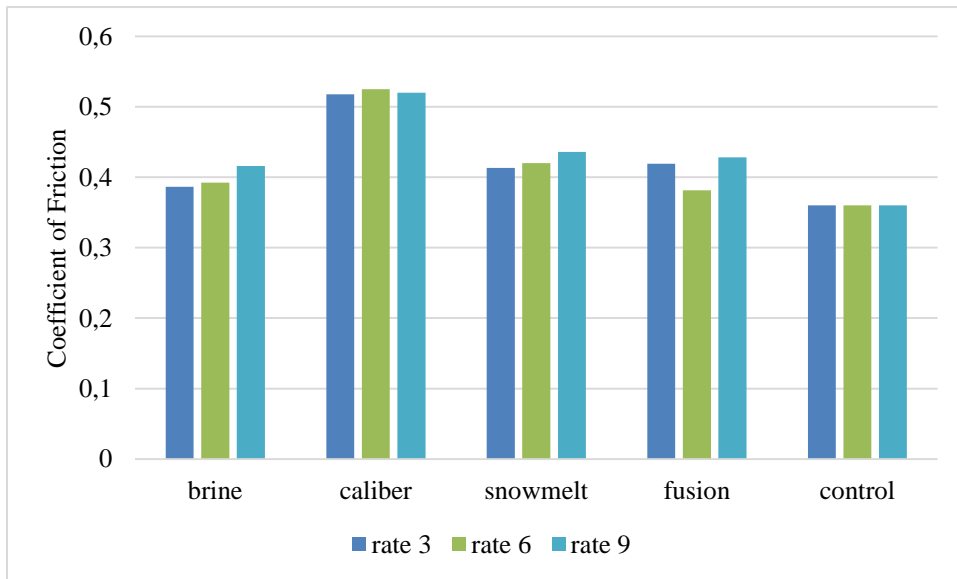


Figure 3.9: Effect of application rate on the CoF in temperatures below  $-7^{\circ}\text{C}$

### 3.4.2.2. Effect of Pavement Temperature

Pavement surface temperature and air temperature are other factors that affect the performance of any snow and ice control material (Blackburn, et al., 1994). As illustrated in Figure 3.12, air temperature is highly correlated with pavement temperature; therefore, only the effect of pavement surface temperature was investigated in this study. A wide range of pavement surface temperatures from  $-14.8^{\circ}\text{C}$  to  $-1.7^{\circ}\text{C}$  were observed. Figure 3.13 illustrates the relationship between CoF and pavement surface temperature for the anti-icing operation using brine in three different application rates of 3, 6 and 9L/1000sft. The chart clearly shows the positive relationship between the CoF value and pavement surface temperature in all the three application rates. It can be seen that, in temperature below  $-10^{\circ}\text{C}$ , the performance of brine drops significantly. This could suggest that, regardless of the application rate, anti-icing with liquid chemicals is less effective in pavement temperatures of below  $-10^{\circ}\text{C}$ . This was the case for all the materials used in this study.

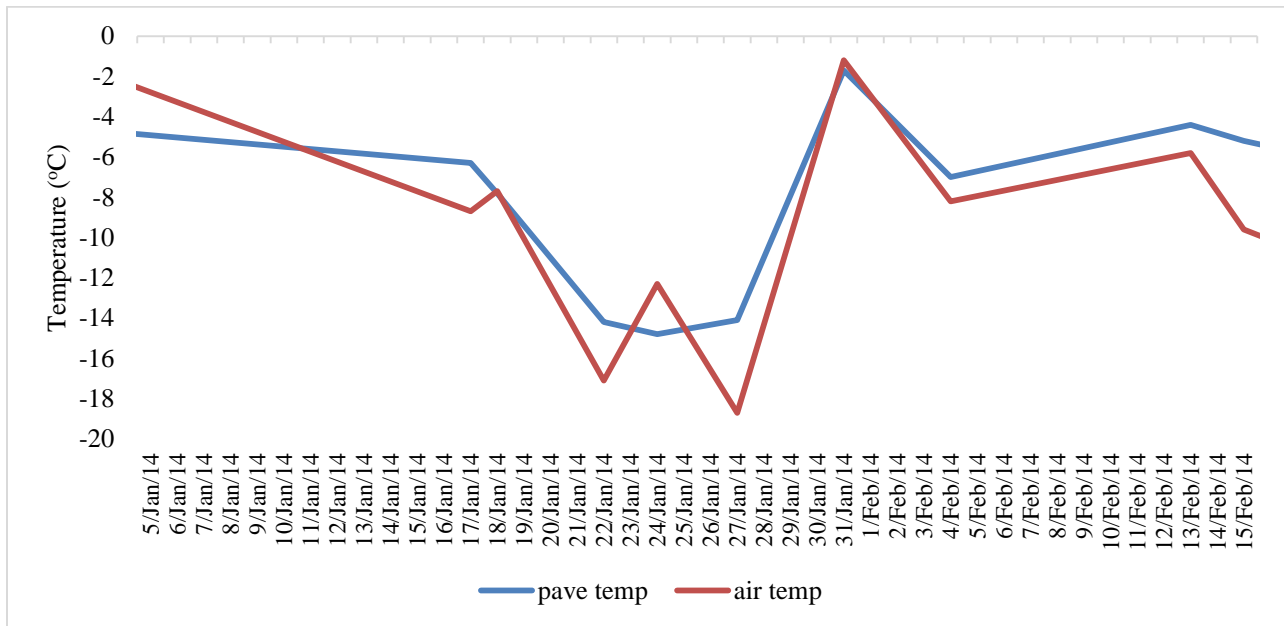


Figure 3.10: Relationship between pavement temperature and air temperature

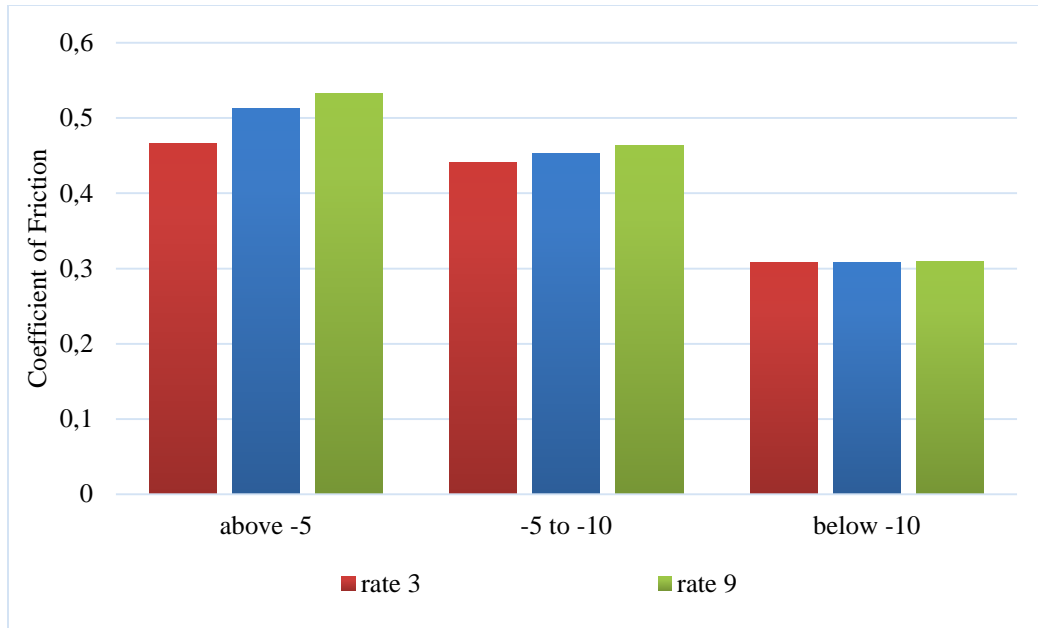


Figure 3.11: Effect of pavement temperature on the CoF

#### 3.4.2.3. Effect of Precipitation Type and Precipitation Amount

The total precipitation amount was expected to have a negative relationship with the performance of the liquid anti-icing chemicals. This is because higher total snow amount would have the potential to dilute the liquid salts making them less effective. Therefore, as illustrated in Figure 3.14, the data were categorized into three amounts of precipitation (less than 1cm, 1 to 3cm and more than 3cm) and the CoF values were compared for each of the chemicals. The results confirmed the hypothesis that a higher snow amount would lead to a lower CoF value. It was also observed that both salts with chloride content (brine and caliber) showed a shortfall in performance when there was a move from the light events to heavy events, thus suggesting that more dilution was taking place for chloride salts than for the organic alternatives. It should be noted that the anti-icing treatments were also conducted in heavy snow events with total amounts of over 10 cm to investigate their effectiveness in such conditions. The results showed that anti-icing was ineffective in preventing the bond between snow and the pavement surface.

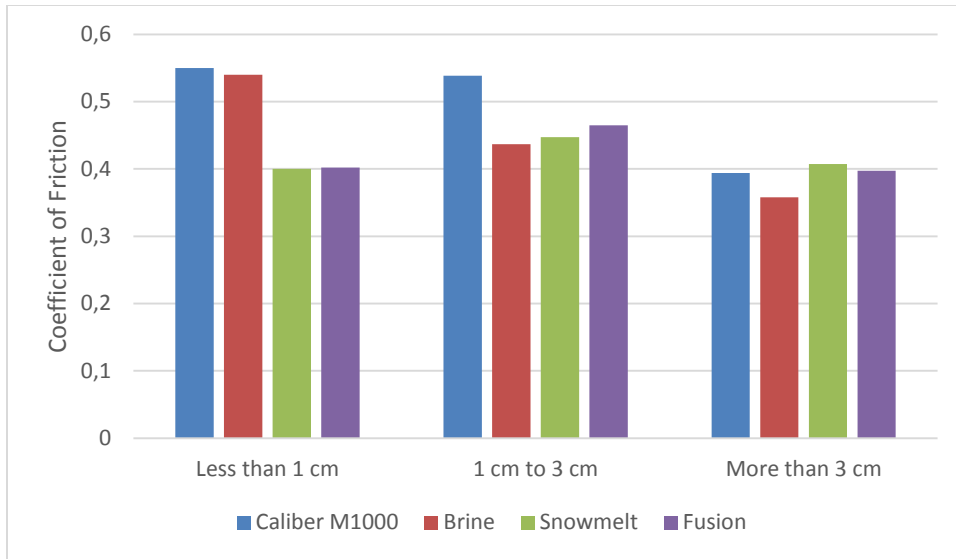


Figure 3.12: Effect of precipitation amount on the CoF

The effect of snow type on the anti-icing chemicals used in this study was also investigated. Through the data collection, four types of snow were observed: dry-loose, dry-packed, wet-loose, and wet-packed. Due to the low number of wet snow observations, only two types of dry snow were compared. Figure 3.15 displays the liquid anti-icing materials' performances under two different snow type conditions. It can be seen that packed snow made the anti-icing treatments less effective for all of the materials tested.

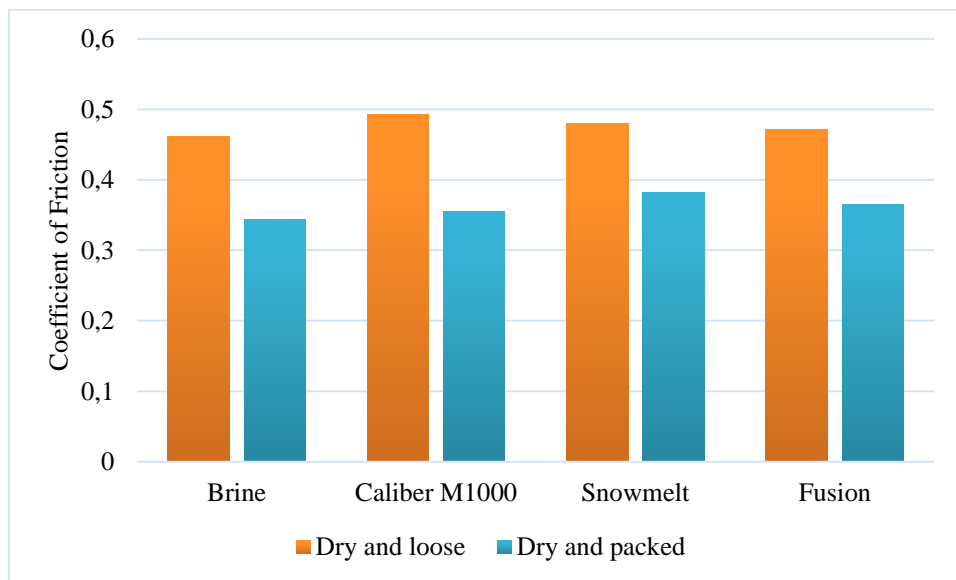


Figure 3.13: Effect of precipitation type on the CoF

#### 3.4.2.4. Effect of Brine Concentration on Anti-icing Performances (Snowmelt)

The data collection included a number of days of test to investigate the effects of mix-ratios (Snowmelt: brine) for diluting the concentrated snowmelt before anti-icing treatments were applied to the test sites. Note that concentrated Snowmelt is claimed to be a fully organic product with no chloride content.

Figure 3.16 compares the CoF value over the test sections treated by concentrated Snowmelt (100% Snowmelt) and diluted Snowmelt (30% Snowmelt and 70% brine). It can be seen that the diluted Snowmelt with brine did not improve the CoF more significantly than concentrated Snowmelt. This observation suggests that adding Chloride will mostly result in a significant amount of this chemical entering the environment but will not have a significant effect on performance.

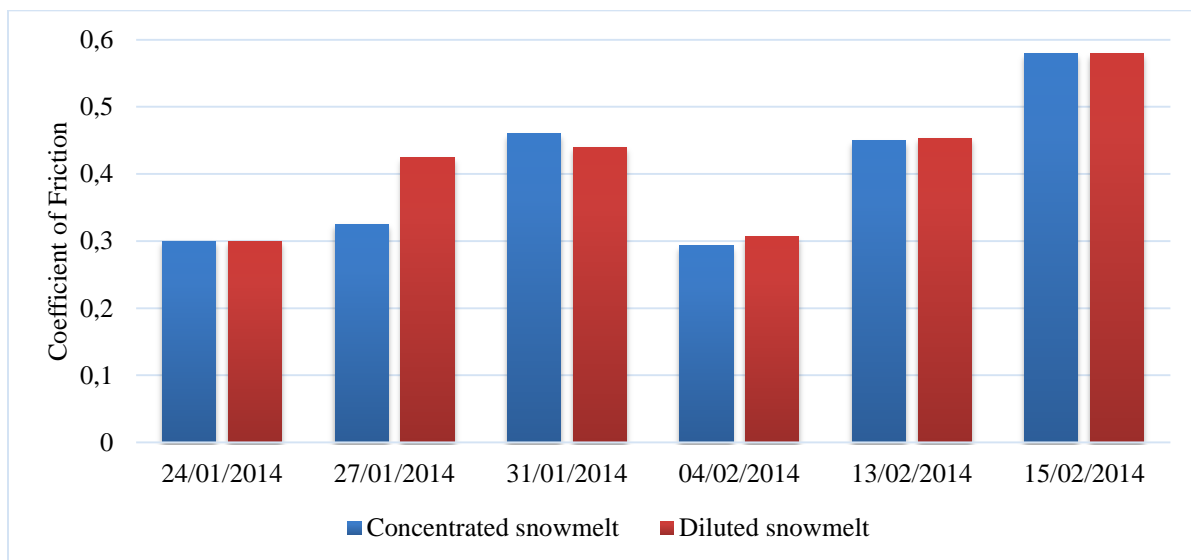


Figure 3.14: Performances of concentrated Snowmelt vs. diluted Snowmelt

#### 3.4.2.5. Effect of Traffic

The results provided in the previous sections were related to the tests conducted in the parking stalls without vehicular traffic. However, in order to investigate the effect of traffic on CoF, a total of five days of tests were conducted in the parking lot driveway. To explore the traffic effect on CoF, the test sections in driveways (trafficked) were compared to the cordoned off parking stall test sections (non-trafficked). The other objective of the tests in the parking

driveway was to evaluate and compare the effectiveness of organic and semi-organic products with brine in a surface under vehicular traffic as opposed to the cordoned off parking stalls without traffic which were studied in previous sections.









This parking lot has an average traffic volume of 30 to 40 vehicles/hr, on average obtained from manually collected data over seven week days from 7:00a.m. to 12p.m. In addition to manual counting, a web-camera was installed to count traffic during the earlier stage of the test season, but it eventually became non-functional due to the relatively cold ambient temperature surrounding it. The pavement condition data were collected on an hourly basis using a time stamped digital camera at the testing site. In this case, the effectiveness of the organic salts was evaluated by the final contaminant type (e.g., snowy, slushy or bare pavement) and the extent of the coverage in the testing sections. Friction data collection was not possible due to continuous passing traffic over the test sections at the driveway. These contaminant types have a CoF corresponding to that was reported by Hossain (2014). Therefore, the CoF and slipping risk, if required, could also be estimated from the contaminant conditions of the pavement.

An anti-icing treatment operation was conducted at 7p.m. on Jan 30<sup>th</sup>, 2014, for a snow event forecast for Jan 31<sup>st</sup>. This snow event started at 10p.m. and ended at 6a.m., with a total snow depth of 10cm. The tested materials (brine, Snowmelt, and Fusion) were applied of rates of 3 and 6L/1000ft<sup>2</sup>. After the snow event, all of the sections were plowed with a snow-plow, leaving a depth of snow of about 0.5cm. Hourly data collection started after the sections were plowed and continued until at least 80% bare pavement was reached. The data collection lasted 6 hours (from 7:20 a.m. to 1:20 p.m.) with an average air temperature of -1.7°C and average pavement temperature of -1.5°C. The visual condition of the pavement sections treated with the salts is shown in Table 3.8. Three hours after the plowing, the control section and brine applied section had more snow coverage than other sections. The snow coverage on other sections was relatively the same, showing that none of the organic and semi-organic materials significantly outperformed the others. In addition no significant difference, were observed between the application rates of 3 and 6 L/ft<sup>2</sup>. All of the sections with 3 and 6 L/ft<sup>2</sup> application rates for each material had the same Bare Pavement Regain Time (BPRT), also showing the same snow coverage based on the hourly observations.

The tests results from this experiment showed that first traffic significantly lowered the BPRT, thus suggesting its positive effect on increasing the material's performance (i.e. increasing CoF).

Also, the results indicate that organic and semi-organic products outperformed the brine in situations where there was vehicular traffic. Among the organic and semi-organic products, none outperformed the others. This study also suggests that an application rate of 3 L/ft<sup>2</sup> is sufficient to achieve the desired pavement conditions.

Table 3.8: Test Results on Jan 30, 2014

Time Material	Right after plow	Three hours after plow	Condition after 3 hr
Control Section			Mostly covered slushy snow
Brine			Mostly covered slushy snow
Snowmelt			50/50 covered/bare
Fusion			50/50 covered/bare



### 3.5 Summary

This chapter presents the results of field test conducted to evaluate and compare the effectiveness of organic and semi-organic liquid salts with brine for anti-icing treatment in the low speed and low volume traffic of the parking lot facilities. This chapter also explored the effect of the contributing factors on the performance of the organic and semi-organic anti-icing chemicals. For this purpose, the data collected in winter 2014 in parking lot C at the University of Waterloo, Ontario, Canada were used. The organic and semi-organic anti-icing chemicals tested were Snowmelt, Fusion and Caliber M1000. Both data exploration and statistical analysis were conducted to achieve the mentioned objectives.

This study found that organic and semi-organic anti-icing chemicals performed very similarly to brine in melting snow and ice when the pavement temperature was above  $-7^{\circ}\text{C}$ . However, the results indicated that, in temperatures below  $-7^{\circ}\text{C}$ , Snowmelt (a completely organic product), outperformed the other chemicals used in this study. In general, organic and semi-organic products performed as well as or better than regular brine in all of the tests conducted in this study. This result in turn suggests that these alternatives to brine can be effectively used for anti-icing operations for reduced impacts on the environment. A number of tests were also conducted to evaluate the effectiveness of the chemicals in parking driveways with vehicular traffic. The results showed that the organic and semi-organic chemicals outperformed brine only slightly under vehicular traffic.

Three application rates of 3, 6 and  $9 \text{ L/ft}^2$  were used to identify the best application rate to use for organic and semi-organic products in the parking lot facilities. Only a negligible improvement in CoF was observed by increasing the application rate by 100% and 200% respectively. This finding suggests that the lower application rate of  $3\text{L}/1000\text{ft}^2$  is suitable for anti-icing with liquid organic and semi-organic products in parking lot facilities, which is 25% less than the recommended application rate by the supplier and the current rates used in practice.

The results also showed that pavement temperature had a positive relationship with CoF improvement. Also it was observed that in temperatures below  $-10^{\circ}\text{C}$  the performance of the chemicals drops significantly, thus suggesting, regardless of the application rate, the effectiveness of anti-icing with liquid chemicals will be less effective in very low pavement temperatures of below  $-10^{\circ}\text{C}$ , a finding which is in line with past studies (Blackburn, et al., 2004).

The investigation of the precipitation type and precipitation amount showed that the chemicals tested in this study were more effective in situations where the snow was loose compared to situations where it was packed. Also a negative correlation with snow amount was observed, and anti-icing, regardless of the type of the chemical, was found to be ineffective in situations with snow amounts higher than 10cm. However, it is essential to mention that these results are limited to the tests conducted in the winter of 2014, which experienced unseasonably below average temperatures.

## **Chapter 4**

### **Estimation of the Effectiveness of Liquid Organic Anti-icers in Different Weather Conditions**

#### **4.1. Introduction**

The main purpose of this study is to evaluate the organic and semi-organic liquid salts used for anti-icing treatment under a wide range of weather conditions in the low traffic environment of parking lots. In Chapter three, using the field data collected, the performance of the alternative organic and semi-organic products was evaluated and compared to the regular brine under the observed weather conditions. This chapter first develops statistical models are developed to estimate and compare the effectiveness of the organic, semi-organic and chloride based (brine) products in different scenarios of weather conditions, it then recommends the suitable material for each weather condition. The analysis applies two different techniques: multivariate linear regression and Artificial Neural Networks.

#### **4.2. Data Collection**

As explained in the data collection section in Chapter three, field tests were conducted during a number of snow events in the winter of 2014 in parking lot C at the University of Waterloo. For each snow event, three different types of anti-icing materials, including fully organic and semi-organic, along with brine, were applied to a set of test sections following the test protocols. In the field tests, weather and surface condition data were collected for each test, resulting in approximately 220 tests involving 14 anti-icing events. The dataset used in this chapter is the same used in Chapter three; therefore, to avoid repetition, the test protocol and tested materials are not further explained in this chapter.

#### **4.3 Methodology**

##### **4.3.1 Multivariate Linear Regression**

In order to quantify and compare the effectiveness of the anti-icing materials in different weather conditions and to investigate the factors (e.g., temperature, application rate) that influence the performance (i.e., improvement in CoF) of a given material, a multivariate linear regression

analysis has been conducted. The main goal of linear regression is to predict the dependent variable based on the independent variables. In this process the coefficients of the independent variables in a linear equation will be estimated in a way that best predicts the dependent variable (Alexopoulos, 2010). Linear regression can also describe and explore the influencing extent of the considered variables on the dependent variable. Linear regression analysis should be conducted in addition to exploratory data analysis and t-test, because they fail to consider the effect of multiple factors and their interactions. Moreover, they are not quantitative and do not have prediction power to estimate the output in the data's gaps.

To investigate the effect of the anti-icers used in this study (Brine, Snowmelt, Caliber M1000 and Fusion), a multivariate linear regression analysis was conducted to estimate the CoF improvement value for each of the materials separately. For this purpose, the CoF improvement of the treated sites (with anti-icing) relative to their control sites (without anti-icing treatment) was calculated and used as the dependent variable for each observation. The independent variables were application rate and all weather factors, including air temperature, wind speed, snow type (Wet/Dry and Packed/Loose), total snowfall, snow density and pavement surface temperature. Four multivariate regression models were developed separately for each of the anti-icers: Brine, Snowmelt, CaliberM1000, and Fusion. In order to calibrate the models, all of the weather variables were included and different combinations of these independent variables were tested to find the combinations of the weather variables that would best estimate the CoF improvement. The goodness of the fit measures of the estimated models was the adjusted coefficient of determination ( $R^2$ ) and Root Mean Square Error (RMSE). The coefficient of determination is useful in evaluating the performance of a linear model as it determines the percentage of the data which is the best fit for the estimated linear line (Devore, 2012). In other words, it is a measure to determine how well data are represented by the estimated linear equation. RMSE, another useful measure in evaluating a model's performance, calculates the average of the squared errors, in which the error value is the difference between the estimated value and the observed value (Devore, 2012). In this study, to determine the RMSE, a random ten-fold cross validation was applied using the R statistical software (R Core Team, 2012). In k fold cross validation, the data is randomly divided into k folds, for k-times, a model is developed with the k-1 section of the data and tested on the one fold of hold-out data (Russeau, et al., 2013). The RMSE is a report of the average RMSE of each cross validation sequence. It is essential to

mention that, once the validation is complete, the model is developed and reported with all of the data available. The main reason for using cross validation was that it has lower variance than a single hold out data especially for the situations where there are limited number of observations.

The significance of each contributing variable was tested using a p-value at a 5% level of significance. The coefficient values determine how strongly the CoF improvement is impacted and whether the impact is positive or negative. A binary variable was also used to represent snow mass condition (packed snow=0, loose snow=1) to quantify its effects on the performance.

#### **4.3.2. Artificial Neural Network**

Artificial Neural Network (ANN) is a non-parametric method that detects the complex patterns and relationships in data through a training process (Martin, et al., 1995). Compared to other estimation methods, ANN has the advantage of learning from the observed dataset in order to best estimate the output.

In this study, in addition to a linear regression analysis, a multi-layer perceptron neural network (MLP-NN) was conducted to model the improvement of the coefficient of friction in the treated sites with anti-icing. This is because a linear regression analysis is not able to detect non-linearity and complex relationships in data. It also fails to consider interaction that may exist between the variables. Therefore, to estimate the Cof improvement more accurately in different weather conditions, a MLP-NN model was also conducted. The independent variables used to estimate the output were application rate and weather factors, including air temperature, wind speed, snow type (Wet/Dry and Packed/Loose), total snowfall, snow density and pavement surface temperature. As shown in Figure 4.1, MLP-NN consists of an input layer, one or more hidden layers, which estimate the output layer based on the input layer through activation functions and weights, and one output layer. The input layer consists of independent variables (in this study, the application rate and weather factors) and the output layer consists of dependent variables (in this study CoF improvement).

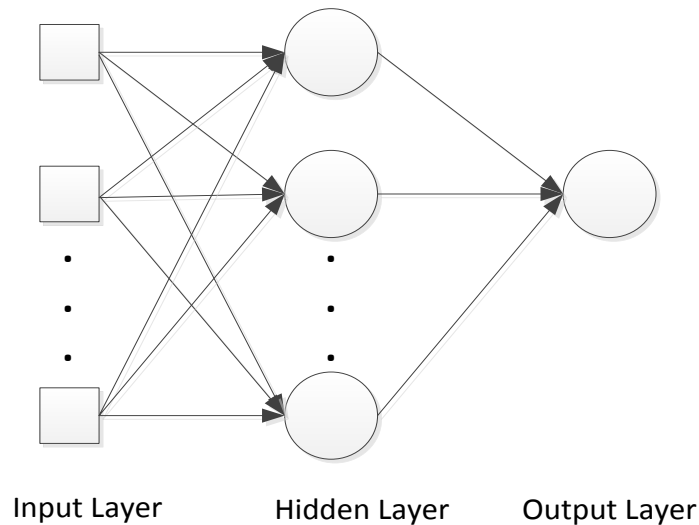


Figure 4.1: NN procedure

Similar to multivariate linear regression analysis, four models were developed separately for Brine, Snowmelt, Fusion, and Caliber. In order to calibrate the models, a learning rate of 0.3 and a momentum of 0.2 is considered for the weights of the MLP-NN. This calibration was done by a back and forth algorithm aiming at minimizing the RMSE through the 10 fold cross validation method. Also the sigmoid function is selected for the output layer. For the input layer, different combinations of the independent variables were tested, and the best combination was chosen based on the RMSE.

## 4.4 Results

### 4.4.1 Multivariate Linear Regression Models

Four multivariate linear regression were conducted for Brine, Snowmelt, Fusion and CaliberM1000 separately. The statistical software of Excel (Microsoft, 2013) was used to calibrate the models. Table 4.1 shows the results of the linear regression analysis for each of the materials. Among the weather variables, the combination of snow amount, snow type and pavement surface temperature was the best combination, resulting in the highest coefficient of determination ( $R^2$ ) and the lowest root mean squared error (RMSE).

Table 4.1: Multivariate linear regression results

Product	Sample Size	R <sup>2</sup> , RMSE	Variable Name	Coefficient	P-Value
Brine	41	0.29, 0.08	Intercept	0.191	3.65E-03
			Application Rate (L/ft <sup>2</sup> )	0.005	0.28
			Pavement Temp (°C)	0.011	7.97E-03
			Snow Amount (kg/m <sup>2</sup> )	-0.007	1.22E-02
			Snow Type (Loose=1, Packed=0)	-0.055	0.10
Fusion	35	0.5, 0.04	Intercept	0.255	1.37E-06
			Application Rate (L/ft <sup>2</sup> )	0.002	0.48
			Pavement Temp (°C)	0.013	3.11E-05
			Snow Amount (kg/m <sup>2</sup> )	-0.003	4.35E-02
			Snow Type (Loose=1, Packed=0)	-0.119	1.89E-05
Snowmelt	57	0.36, 0.04	Intercept	0.174	1.12E-06
			Application Rate (L/ft <sup>2</sup> )	0.0005	0.81
			Pavement Temp (°C)	0.005	0.01
			Snow Amount (kg/m <sup>2</sup> )	-0.002	0.10
			Snow Type (Loose=1, Packed=0)	-0.089	8.01E-06

Caliber M1000	21	0.52, 0.08	Intercept	0.376	3.08E-04
			Application Rate (L/ft <sup>2</sup> )	-0.006	0.34
			Pavement Temp (°C)	0.025	0.01
			Snow Amount (kg/m <sup>2</sup> )	-0.010	0.07
			Snow Type (Loose=1, Packed=0)	-0.073	0.12

#### 4.4.1.1 Investigation of Contributing Factors to the CoF Improvement

The statistical modeling results displayed in Table 4.1 clearly confirm the explanatory analysis conducted in Chapter three, which qualitatively explored the effect of the different factors on the improvement in the coefficient of friction. This section analyzes of the estimated relationships between CoF improvement and influencing factors in the linear regression.

##### *Intercept*

The intercept of the regression model, can be interpreted as the expected mean in the friction improvement for sections treated with ant-icing over untreated sections in the context of experiment being conducted. As previously mentioned, the testing season was extremely cold; however, the regression results showed that the intercept coefficients for all products were positive, thus indicating that the coefficient of friction improved with the use of these products. This overall improvement of coefficient of friction found in this analysis reconfirms the t-test results obtained in the previous section for all the products.

##### *Application Rate*

Intuitively, the application rate should have a positive effect on improving the effectiveness of anti-icing operations. However, the statistical tests could not confirm this expected effect; in fact, the application rate was not found to be statistically significant at a significance level of 5%. The coefficient for all of the products is positive suggesting positive effects in general. It should, however, be cautioned that this finding should not be extrapolated beyond the range of the



application rate being covered (i.e., 3, 6 and, 9 L/ft<sup>2</sup>). While the rates being tested were selected on the basis of practicality, theoretically the anti-icing effect could change dramatically when the rate increases or decreases beyond this range. Since there was only small improvement in the coefficient of friction for a large increase in material usage, the lowest application rate should be used for anti-icing purposes in parking lots. Recall that, in the current industry of parking lot maintenance, the recommended application rate is 4L/1000ft<sup>2</sup>. Therefore, the lower application rate of 3L/1000ft<sup>2</sup> represents a 25% reduction in material usage.

### *Pavement Temperature*

Pavement temperature is another factor considered to significantly affect the performance of the chemicals used for snow and ice control, including anti-icing. As such, lower pavement temperatures may render liquid salts ineffective, as the water in the mixture may simply freeze. A decrease in pavement temperature means that a higher concentration of salt needs to be used to create a liquid salt-snow mixture and break snow-pavement bonding. Thus, an increase in pavement temperature should result in a comparative increase in performance of the liquid salt over the control.

As expected, the regression analysis showed that pavement temperature was positively associated with the performance of all of the materials which was found statistically significant at the level of significance of 5%. The positive coefficients associated with the pavement temperature suggest that they performed significantly better under warmer events than colder events.

### *Amount of Snow*

The amount of snow that had accumulated on the test sections by the end of the event (before being plowed for friction measurement) was another factor being examined. The more snow covering the pavement surface, the more quickly the anti-icing liquids may be diluted, and thus the less effective they will be. This result was confirmed, as all of snow amount coefficients obtained were negative. However, only in the sections where brine and Snowmelt were used as anti-icing materials, the effect of snow amount found to be statistically significant at a level of significance of 0.05. The dilution effect for the other materials was found to be insignificant,

suggesting that the performance of the other liquid salts did not change significantly with snow amount.

#### *Snow Type*

Before plowing, the snow on each test section was checked and classified as either loose or packed. To examine the effect of snow type on the anti-icing performance of the materials, snow type was included in the regression analysis. Anti-icing operations with both chloride and organic materials were found to be more effective for packed snow than loose snow. This finding does not agree with the result obtained from exploratory analysis which could be because of interactions or complex relationships between variables which linear regression could not explain.

#### 4.4.1.2 Performance Comparison

Anti-icing can only be conducted when the pavement is initially bare. As a result, anti-icing cannot be performed during a chain of continuous snow events. This fact limited the tests to a total of 14 anti-icing events in winter 2014. Therefore, as the number of observations is limited, the data exploration itself could not be solely used to compare the effectiveness of the materials in different weather conditions. For this purpose, using the models developed, the effectiveness of the materials were estimated in different weather scenarios and then compared to identify the best material for each of the weather scenarios. The dataset used for estimating purposes included four different weather scenarios: “very cold air temperature with high amount of snow”, “very cold air temperature with low amount of snow”, “mild cold air temperature with high amount of snow”, and “mild cold air temperature with low amount of snow”. This dataset consisted of 5 different records for each scenario to decrease the estimation bias. The synthesized scenarios were developed based on real weather events using Environment Canada’s website to provide more realistic results. Note that very cold air temperature and mild cold air temperature refers to temperatures below  $-7^{\circ}\text{C}$  and above  $-7^{\circ}\text{C}$ , respectively. High amount of snow and low amount of snow also represents the events with more than 4cm of snow and less than 4cm of snow, respectively. Also  $3 \text{ L/ft}^2$  was used as the application rate for all of the records. This application rate was selected based on the results obtained in Chapter three confirming that application rates more than  $3\text{L/ft}^2$  do not affect the CoF improvement significantly. Figure 4.2

displays the results of this comparison. As shown in Figure 4.2, the performance of the materials improves with the increase in air temperature, however, their performance do not change significantly with increase in snow amount (precipitation). This finding suggests that pavement temperature has much more power in affecting the CoF improvement rather than the precipitation amount. Overall, the results indicate that all of the materials performed very similarly in all of the weather conditions, suggesting that organic and semi-organic products can be suitable alternatives to the chloride based material of regular brine almost in all weather conditions. This finding agrees with the results obtained in Chapter three. Also it can be seen from Figure 4.2 that Snowmelt and Caliber M1000 slightly outperformed other materials in very cold temperatures (below  $-7^{\circ}\text{C}$ ) and in less cold temperatures (above  $-7^{\circ}\text{C}$ ), respectively, confirming the results obtained in Chapter 3.

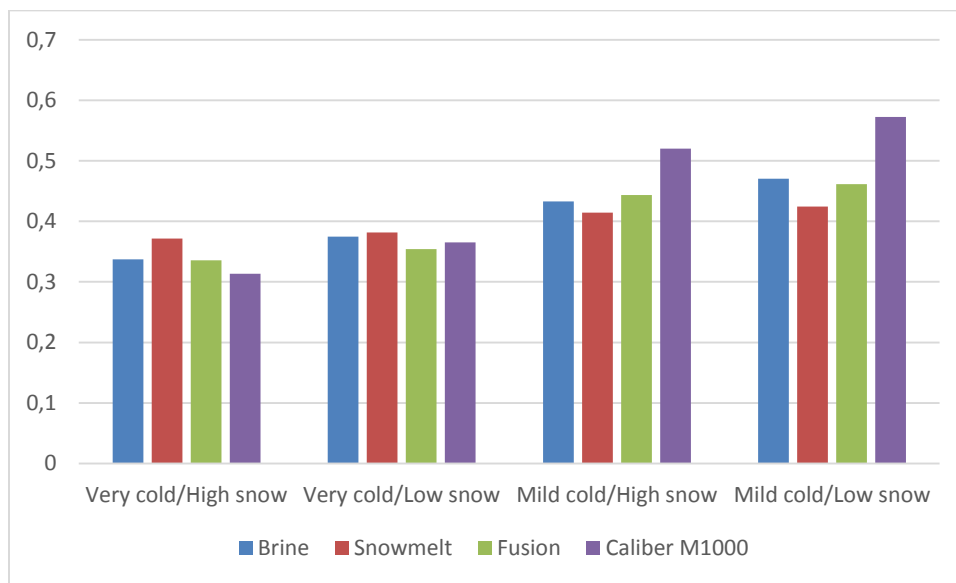


Figure 4.2: Chemical effectiveness comparison in different weather conditions

#### 4.4.2 Neural Network Models

Four MLP-NN models were developed for Brine, Snowmelt, Fusion, and CaliberM1000 separately. WEKA (Hall, et al., 2009), a machine learning software, was used to calibrate the models. Table 4.2 shows the results of the calibrated models for each of the materials. Among the weather variables, the combination of snow amount, snow type and pavement surface temperature proved to be the best, resulting in a lower RMSE than other combinations.

Table 4.2: MLP-NN results

Model	Number of Hidden Layers	Number of Nodes	Root Mean Square Error
Brine	1	2	0.07
Snowmelt	1	2	0.05
Fusion	1	2	0.06
CaliberM1000	1	2	0.08

Similar to the multivariate linear regression model, in order to compare the effectiveness of organic and semi-organic anti-icers in different weather conditions, four different weather scenarios were considered. The results of this comparison are presented in Figure 4.3. Overall, the results agree with the results obtained from linear regression analysis and show that, in very cold temperatures (below  $-7^{\circ}\text{C}$ ) all of the materials performed very similarly; however, in less cold temperatures (above  $-7^{\circ}\text{C}$ ) CaliberM1000 outperformed other materials significantly. It can be seen from Figure 4.3, that in conditions where pavement temperature is moderately mild and the precipitation amount is low, Brine outperforms Fusion and Snowmelt. It should be noted that the performance of Caliber M1000 improved significantly with an increase in pavement temperature whereas it did not change significantly with increasing the snow amount. This finding shows that in the calibrated model for Caliber M1000, pavement temperature was much more effective in determining the CoF improvement than the precipitation amount. Similar to CaliberM1000, the performance of Brine improved significantly with higher temperatures and with low snow accumulation.

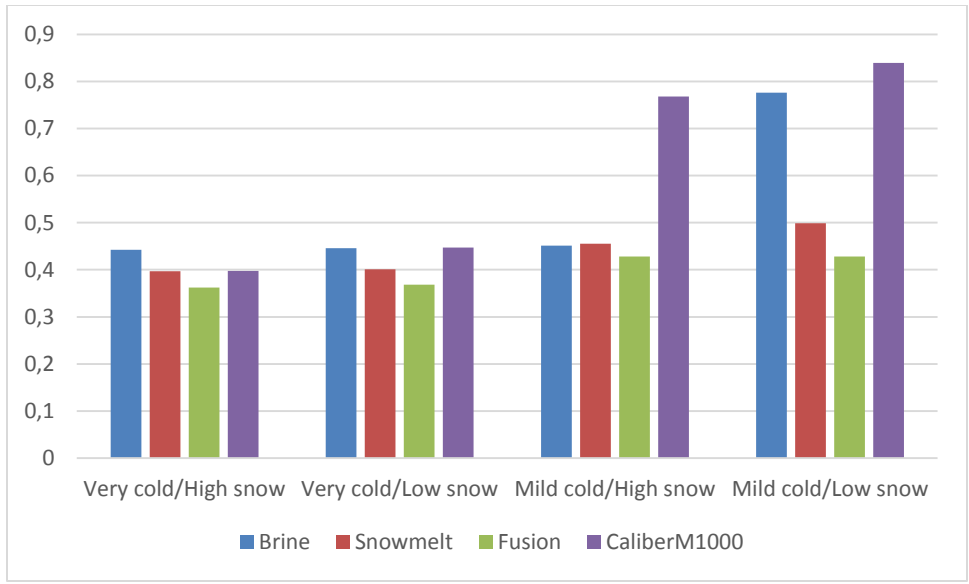


Figure 4.3: Chemical effectiveness comparison in different weather conditions

## 4.5 Summary

This chapter presents a modelling effort to estimate and compare the effectiveness of the organic, semi-organic and chloride based (brine) products in different weather condition scenarios. Also it investigates the impact of influencing factors on the CoF improvement. To calibrate the models, the data collected in winter 2014 in parking lot C at the University of Waterloo, Ontario, Canada was used. The organic and semi-organic anti-icing chemicals tested in this study are Snowmelt, Fusion, and Caliber M1000. Also a synthesized dataset was created that included four different weather scenarios to estimate and compare the chemicals performance in different weather scenarios. Two alternative approaches were applied: multivariate linear regression and Neural Networks.

Through this analysis it was found that organic and semi-organic anti-icing chemicals perform very similarly to brine in melting snow and ice in almost all of the weather conditions, a result which suggests that these alternatives to brine can be effectively used for anti-icing operations, and thus help reduce impacts on the environment. The results of the linear regression model showed a slightly better performance for Snowmelt and Caliber in very cold temperatures (below  $-7^{\circ}\text{C}$ ) and mild cold temperatures (below  $-7^{\circ}\text{C}$ ) respectively. The results of MLP-NN model shows a significant outperformance for the Caliber M1000 in mild cold temperatures. In general, the results of both estimation models were very similar with very similar accuracy in terms of RMSE values.

The investigation of the contributing factors to the CoF showed that application rate, snow amount, snow type (Packed/Loose) and pavement temperature were the best combination for estimating the CoF improvement. This investigation also found that only small improvements are observed in the CoF for a large increase in material usage; therefore, the lower application rate of  $3\text{L}/\text{ft}^2$  should be used for anti-icing purposes in parking lots, which is 25% less than the current application rate recommended by the industry for parking lot maintenance. It was also observed that both the snow amount and snow type (Loose/Packed) variables showed a negative correlation with CoF, which means that the tested materials performed better in light snow events and in conditions where the snow was packed.

## **Chapter 5**

### **Conclusions and Future Work**

The study was set out to investigate and compare the effectiveness of organic and semi-organic anti-icers alternatives to regular salt (brine) for winter maintenance operations. This chapter summarizes the main findings of this study, followed by highlighting the limitations associated with this research and future work.

#### **5.1 Major Findings**

- A comprehensive review of the literature was conducted to synthesize the findings of the past studies on the effect of chloride based materials on the environment and infrastructure as compared to organic (Snowmelt) and semi-organic (Fusion and Caliber M1000) materials. The consensus is that chloride based materials have negative impacts on the environment, including soil contamination, drinking water contamination, mobilization of heavy metals in soil and water, and an increase in the vulnerability of plants to diseases, all of which are hazardous for both humans and marine life. Among the most common constituents of the snow and ice control materials, Chloride (Cl) and Sodium (Na) was found to have the most detrimental effects on water and soil respectively.
- The field test results showed that organic and semi-organic anti-icing chemicals performed very similarly to brine in melting snow and ice in the observed weather conditions in the winter of 2014. Only a slight performance advantage was observed for Snowmelt and Caliber M1000 in very cold situations (with pavement temperatures below  $-7^{\circ}\text{C}$ ) for the first one and in milder temperatures (above  $-7^{\circ}\text{C}$ ) for the second one.
- In this study using the estimation models, it was found that organic and semi-organic materials perform very similarly to brine in almost all weather conditions. This finding in turn suggests that these alternatives to brine can be effectively used for anti-icing operations, consequently reducing the impacts of chloride salts on the environment. Both linear regression and MLP-NN estimation models provided very similar results and accuracy in terms of the RMSE value.

- Investigation of the factors contributing to the CoF improvement showed that pavement temperature, snow amount and snow type (packed/loose) were the most important weather factors in determining the CoF improvement. Pavement temperature showed a positive relationship with CoF improvement, meaning that both chloride and organic materials used in this study perform better in higher temperatures. Snow amount and snow type also showed a negative correlation with CoF improvement, suggesting that anti-icing, with the materials used in this study, is more effective when there is lower amount of snow and snow is packed.
- In terms of optimal application rates, the CoF improved only negligibly despite large increases in the application rate; therefore, the lower application rate of 3L/1000ft<sup>2</sup> is recommended for anti-icing with liquid organic and semi-organic products in parking lot facilities, which is 25% less than the recommended application rate by the supplier and the current rates used in practice.
- The field observations also showed that the anti-icing effectiveness with organic and semi-organic products used in this study, drops significantly when pavement temperatures was below -10°C or when the snow amount was higher than 10 cm. Therefore, they are not recommended for these temperature ranges. However, it should be mentioned that the results obtained in this research were limited to the tests conducted in the winter of 2014, which may be categorized as much colder winter compared to normal winter conditions for Southern Ontario.



## 5.2 Limitations and Future Work

Some limitations are associated with this research and following improvements can be made to better understand the effectiveness of liquid organic and semi-organic anti-icing materials in different weather conditions.

- This study is conducted based on the data collected only in one winter season (2013-2014). As anti-icing can be conducted only in situations where the pavement is bare and it is not effective in situations where continuous snow events occur, this study was limited to 14 anti-icing events
- The 2013-2014 winter season was cold and most of the tests were conducted in the temperature ranges which anti-icing with liquid salts is less effective. Therefore, the results may not be generalized to warmer winter seasons.
- In order to better stimulate the real world conditions, the data used for this study was collected through field tests which involved many uncontrollable variables. A series of lab-tests along with the field test could fill the gaps and reduce the variations that may exist in field tests.
- The measuring equipment used in this study could produce some extent of error, especially when used in very cold temperatures.
- This study does not evaluate the impact of the pavement type (asphalt vs concrete) on the performance of the products and it has concentrated on the evaluation of the products on asphalt pavement.
- This study does not contain a comprehensive cost-benefit analysis which quantifies the environmental and infrastructural benefits in monetary values and compares with the associated costs.

## References

- Albright, M. (2005). Changes in water quality in an urban stream following the use of organically derived deicing products. *Lake and Reservoir Management*, 21(1), 119-124.
- Alexopoulos, E. C. (2010). Introduction to multivariate regression analysis. *Hippokratia*, 14(Suppl 1), 23.
- Amrhein, C., Strong, J. E., & Mosher, P. A. (1992). Effect of deicing salts on metal and organic matter mobilization in roadside soils. *Environmental Science & Technology*, 26(4), 703-709.
- Bäckman, L., & Folkesson, L. (1995). The influence of de-icing salt on vegetation, groundwater and soil along Highways E20 and 48 in Skaraborg County during 1994. *VTI Meddelanden*, (775A).
- Bäckström, M., Karlsson, S., Bäckman, L., Folkesson, L., & Lind, B. (2004). Mobilisation of heavy metals by deicing salts in a roadside environment. *Water Research*, 38(3), 720-732.
- Bang, S. S., & Johnston, D. (1998). Environmental effects of sodium acetate/formate deicer, Ice Shear™. *Archives of environmental contamination and toxicology*, 35(4), 580-587.
- Baroga, E. (2004, June). Washington State Department of Transportation's 2002-2003 Salt Pilot Project. In *Transportation Research Circular Number E-C063, Proceedings of the Sixth International Symposium on Snow Removal and Ice Control Technology* (pp. 282-295).
- Benbow, M. E., & Merritt, R. W. (2004). Road-salt toxicity of select Michigan wetland macroinvertebrates under different testing conditions. *Wetlands*, 24(1), 68-76.
- Berenson, M., Levine, D., Szabat, K. A., & Krehbiel, T. C. (2012). *Basic business statistics: Concepts and applications*. Pearson Higher Education AU.
- Blackburn, R. R. (2004). *Snow and ice control: Guidelines for materials and methods* (Vol. 526). Transportation Research Board.
- Blackburn, R. R., McGrane, E. J., Chappelow, C. C., Harwood, D. W., & Fleege, E. J. (1994). *Development of anti-icing technology* (No. SHRP-H-385). Strategic Highway Research Program, National Research Council.
- Bryson, G. M., & Barker, A. V. (2002). Sodium accumulation in soils and plants along Massachusetts roadsides. *Communications in Soil Science and Plant Analysis*, 33(1-2), 67-78.
- Buckler, D. R., & Granato, G. E. (1999). Assessing biological effects from highway-runoff constituents.

- Burkett, A., & Gurr, N. (2004, June). Icy roads management with calcium magnesium acetate to meet environmental and customer expectations in New Zealand. In *Transportation Research Board (Ed.), Proc. 6th Intl. Symposium on Snow Removal and Ice Control Technology. Transportation Research Circular E-C063: Snow and Ice Control Technology. SNOW04-050* (pp. 267-277).
- Burtwell, M. (2001). Assessment of the performance of prewetted salt for snow removal and ice control. *Transportation Research Record: Journal of the Transportation Research Board*, (1741), 68-74.
- Tuthill, R. W., & Calabrese, E. J. (1979). Elevated sodium levels in the public drinking water as a contributor to elevated blood pressure levels in the community. *Archives of Environmental Health: An International Journal*, 34(4), 197-203.
- Cheng, K. C., & Guthrie, T. F. (1998). Liquid road deicing environment impact.
- Costanza, R., Wilson, M. A., Troy, A., Voinov, A., Liu, S., & D'Agostino, J. (2006). The value of New Jersey's ecosystem services and natural capital.
- Crowther, R. A., & Hynes, H. B. N. (1977). The effect of road deicing salt on the drift of stream benthos. *Environmental Pollution (1970)*, 14(2), 113-126.
- Cunningham, M. A., Snyder, E., Yonkin, D., Ross, M., & Elsen, T. (2008). Accumulation of deicing salts in soils in an urban environment. *Urban Ecosystems*, 11(1), 17-31.
- Darwin, D., Browning, J., Gong, L., & Hughes, S. R. (2008). Effects of deicers on concrete deterioration. *ACI Materials Journal*, 105(6).
- Demers, C. L., & Sage Jr, R. W. (1990). Effects of road deicing salt on chloride levels in four Adirondack streams. *Water, Air, and Soil Pollution*, 49(3-4), 369-373.
- Devore, J. (2015). *Probability and Statistics for Engineering and the Sciences*. Cengage Learning.
- D'Itri, F. M. (1992). *Chemical deicers and the environment*. CRC Press.
- Druschel, S. J. (2012). *Salt Brine Blending to Optimize Deicing and Anti-Icing Performance* (No. MN/RC 2012-20).
- Eisenberg, D., & Warner, K. E. (2005). Effects of snowfalls on motor vehicle collisions, injuries, and fatalities. *American Journal of Public Health*, 95(1), 120-124.
- Level, L. L. O. A. E., Level, L. L. O. E., & Level, N. N. O. E. Canadian Environmental Protection Act, 1999.
- Eyles, N., Chow Frazer, P. (2003) *Remediation of an Urban-impacted Watershed and Lagoon, Frenchman's Bay, City of Pickering*. Ontario Innovation Trust and the City of Pickering.

Fay, L., & Shi, X. (2012). Environmental impacts of chemicals for snow and ice control: State of the knowledge. *Water, Air, & Soil Pollution*, 223(5), 2751-2770.

Fay, L., & Shi, X. (2010). Laboratory investigation of performance and impacts of snow and ice control chemicals for winter road service. *Journal of Cold Regions Engineering*, 25(3), 89-114.

Fischel, M. (2001). Evaluation of selected deicers based on a review of the literature.

Fitch, G., Smith, J. A., & Clarens, A. F. (2012). Environmental life-cycle assessment of winter maintenance treatments for roadways. *Journal of Transportation Engineering*, 139(2), 138-146.

Forman, R. T. (2004). Road Ecology's Promise: What's Around the Bend?. *Environment: Science and Policy for Sustainable Development*, 46(4), 8-21.

Forman, R. T., & Alexander, L. E. (1998). Roads and their major ecological effects. *Annual review of ecology and systematics*, 207-C2.

Fortin Consulting Inc. (2006). Winter Parking Lot and Sidewalk Maintenance Manual.

Fu, L., Omer, R., & Jiang, C. (2012). Field test of organic deicers as prewetting and anti-icing agents for winter road maintenance. *Transportation Research Record: Journal of the Transportation Research Board*, (2272), 130-135.

Gales, J. E., & VanderMeulen, J. (1992). Deicing chemical use on the Michigan state highway system. *IN: Chemical Deicers and the Environment. Lewis Publishers, Boca Raton, Florida. 1992. p 135-184. 7 fig, 8 tab, 93 ref.*

Garn, H. S., Robertson, D. M., Rose, W. J., Goddard, G. L., & Horwath, J. A. (2006). *Water Quality, Hydrology, and Response to Changes in Phosphorus Loading of Nagawicka Lake, a Calcareous Lake in Waukesha County, Wisconsin*. U. S. Geological Survey.

Godwin, K. S., Hafner, S. D., & Buff, M. F. (2003). Long-term trends in sodium and chloride in the Mohawk River, New York: the effect of fifty years of road-salt application. *Environmental pollution*, 124(2), 273-281.

Granato, G. E., Church, P. E., & Stone, V. J. (1995). Mobilization of major and trace constituents of highway runoff in groundwater potentially caused by deicing chemical migration. *Transportation Research Record*, 1483, 92-104.

Hall, M., Eibe, F. (2009). The Weka Data Mining Software. - University of Waikato : SIGKDD Explorations.

Harless, M. L. (2012). Effects of Chemical Deicers on Amphibian Communities.

- Hawkins, R. H., Judd, J. H. (1972). Water Pollution as Affected by Street Salting<sup>1</sup>.
- Hellstén, P. P., Salminen, J. M., Jørgensen, K. S., & Nystén, T. H. (2005). Use of potassium formate in road winter deicing can reduce groundwater deterioration. *Environmental science & technology*, 39(13), 5095-5100.
- Hofstra, G., & Smith, D. W. (1984). Effects of road deicing salt on the levels of ions in roadside soils in southern Ontario. *J. Environ. Manage.:(United States)*,19(3).
- Holmes, F. W. (1961). Salt injury to trees. *Phytopathology*, 51, 712-18.
- Horner, R. R. (1988). *Environmental monitoring and evaluation of calcium magnesium acetate (CMA)* (No. 305).
- Horner, R. R., & Brenner, M. V. (1992). Environmental evaluation of calcium magnesium acetate for highway deicing applications. *Resources, conservation and recycling*, 7(1), 213-237.
- Hossain, S. K., Fu, L., & Olesen, A. J. (2014). An Experimental Study on the Effectiveness of Anti-Icing Operations for Snow and Ice Control of Parking Lots and Side Walks. In *Transportation Research Board 93rd Annual Meeting* (No. 14-4398).
- Hossain, S. K., Fu, L., & Law, B. (2014). Parking Lots and Sidewalks under Winter Snow Events: Classification, Friction Characteristics, and Slipping Risk 2. In *Transportation Research Board 93rd Annual Meeting* (No. 14-4909).
- Hossain, S. K., Fu, L., & Olesen, A. J. (2014). Effectiveness of anti-icing operations for snow and ice control of parking lots and sidewalks. *Canadian Journal of Civil Engineering*, 41(6), 523-530.
- Hossain, S. K., Fu, L., & Lu, C. Y. (2014). De-icing Performance of Road Salt: Modelling and Applications. *Transportation Research Record: Journal of the Transportation Research*, 2440, 10.
- Howard, K. W., & Beck, P. J. (1993). Hydrogeochemical implications of groundwater contamination by road de-icing chemicals. *Journal of Contaminant Hydrology*, 12(3), 245-268.
- Ihs, A., & Gustafson, K. (1996). Calcium Magnesium Acetate (CMA)-An Alternative Deicing Agent. A Review of the Literature. *VTI Meddelanden*, (789A).
- Judd, J. H. (1969). Lake stratification caused by runoff from street deicing, Milwaukee, Wisconsin. *Center for Great Lakes Studies*.
- Karraker, N. E. (2007). *Investigation of the amphibian decline phenomenon: novel small-scale factors and a large-scale overview*. STATE UNIVERSITY OF NEW YORK COL. OF ENVIRONMENTAL SCIENCE & FORESTRY.

- Karraker, N. E., Gibbs, J. P., & Vonesh, J. R. (2008). Impacts of road deicing salt on the demography of vernal pool-breeding amphibians. *Ecological Applications*, 18(3), 724-734.
- Kelly, V. R., Lovett, G. M., Weathers, K. C., Findlay, S. E., Strayer, D. L., Burns, D. J., & Likens, G. E. (2007). Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. *Environmental science & technology*, 42(2), 410-415.
- Kelting, D. L., & Laxson, C. L. (2010). Review of effects and costs of road de-icing with recommendations for winter road management in the Adirondack Park. *Adirondack Watershed Institute, Paul Smith's College, Paul Smiths, NY, Adirondack Watershed Institute Report# AWI2010-01*.
- Ketcham, S. A., Minsk, L. D., Blackburn, R. R., & Fleege, E. J. (1996). *Manual of practice for an effective anti-icing program: a guide for highway winter maintenance personnel* (No. FHWA-RD-95-202).
- Knapp, K. K., Smithson, L. D., & Khattak, A. J. (2000). The mobility and safety impacts of winter storm events in a freeway environment, mid-continent transportation symposium 2000 proceedings. *Iowa, USA*.
- Koch, G. H., Brongers, M. P., Thompson, N. G., Virmani, Y. P., & Payer, J. H. (2002). *Corrosion cost and preventive strategies in the United States* (No. FHWA-RD-01-156,).
- Löfgren, S. (2001). The chemical effects of deicing salt on soil and stream water of five catchments in southeast Sweden. *Water, Air, and Soil Pollution*, 130(1-4), 863-868.
- Lundmark, A., & Olofsson, B. (2007). Chloride deposition and distribution in soils along a deiced highway—assessment using different methods of measurement. *Water, Air, and Soil Pollution*, 182(1-4), 173-185.
- Martin, H. T., Demuth, H. B., & Beale, M. H. (1996). *Neural network design*(pp. 2-14). Boston: Pws Pub.
- McFarland, B. L., & O'Reilly, K. T. (1992). Environmental impact and toxicological characteristics of calcium magnesium acetate. *IN: Chemical Deicers and the Environment. Lewis Publishers, Boca Raton, Florida. 1992. p 194-227. 9 fig, 6 tab, 50 ref.*
- Meriano, M., Eyles, N., & Howard, K. W. (2009). Hydrogeological impacts of road salt from Canada's busiest highway on a Lake Ontario watershed (Frenchman's Bay) and lagoon, City of Pickering. *Journal of contaminant hydrology*, 107(1), 66-81.
- Microsoft. (2013). Redmond, Washington : Computer Software.
- Murray, D. M., & Ernst, U. F. (1976). *An economic analysis of the environmental impact of highway deicing* (No. EPA-600/2-76/105 Final Rpt.).

- Muthumani, A., & Shi, X. (2015). Effectiveness of Liquid Agricultural By-Products and Solid Complex Chlorides for Snow and Ice Control. In *Transportation Research Board 94th Annual Meeting* (No. 15-5815).
- National Research Council (US). Committee on the Comparative Costs of Rock Salt, & Calcium Magnesium Acetate (CMA) for Highway Deicing. (1991). *Highway Deicing: Comparing Salt and Calcium Magnesium Acetate* (No. 235). Transportation Research Board.
- NCHRP 526. (2004). *Snow and ice control: Guidelines for materials and methods* (Vol. 526). Transportation Research Board.
- NCHRP 577. (2007). *Guidelines for the Selection of Snow and Ice Control Materials to Mitigate Environmental Impacts* (Vol. 577). Transportation Research Board.
- Nixon, W. A., Kochumman, G., Qiu, L., Qiu, J., & Xiong, J. (2007). Evaluation of Using Non-Corrosive Deicing Materials and Corrosion Reducing Treatments for Deicing Salts.
- Nixon, W. A., Qiu, J., Qiu, L., Kochumman, G., & Xiong, J. (2005). Ice melting performance for ice-control chemicals. In *84th Annual Meeting of the Transportation Research Board, Washington, DC*.
- Peters, N. E., & Turk, J. T. (1981). Increases in Sodium and Chloride in the Mohawk River, New York, from the 1950's to the 1970's Attributed to Road Salt<sup>1</sup>.
- Qiu, L., & Nixon, W. (2008). Effects of adverse weather on traffic crashes: systematic review and meta-analysis. *Transportation Research Record: Journal of the Transportation Research Board*, (2055), 139-146.
- R Core Team R. (2012). A language and environment for statistical computing. - Vienna : R Foundation for Statistical Computing.
- Ramakrishna, D. M., & Viraraghavan, T. (2005). Environmental impact of chemical deicers—a review. *Water, Air, & Soil Pollution*, 166(1), 49-63.
- Robidoux, P. Y., & Delisle, C. E. (2001). Ecotoxicological evaluation of three deicers (NaCl, NaFo, CMA)—Effect on terrestrial organisms. *Ecotoxicology and Environmental Safety*, 48(2), 128-139.
- Russeau, J., Cohn, R. (2013). Cross Validation (Statistics) : Book on Demand LTD.
- Robidoux, P. Y., & Delisle, C. E. (2001). Ecotoxicological evaluation of three deicers (NaCl, NaFo, CMA)—Effect on terrestrial organisms. *Ecotoxicology and Environmental Safety*, 48(2), 128-139.
- Scott, W. S. (1979). Road de-icing salts in an urban stream and flood control reservoir [Canada]. *Water Resources Bulletin (USA)*.

- Shi, X., Fay, L., Yang, Z., Nguyen, T. A., & Liu, Y. (2009). Corrosion of deicers to metals in transportation infrastructure: Introduction and recent developments. *Corrosion reviews*, 27(1-2), 23-52.
- Shi, X., Akin, M., Pan, T., Fay, L., Liu, Y., & Yang, Z. (2009). Deicer impacts on pavement materials: Introduction and recent developments. *Open Civil Engineering Journal*, 3, 16-27.
- Shi, X., Fay, L., Gallaway, C., Volkening, K., Peterson, M. M., Pan, T., Nguyen, T. A. (2009). Evaluation of Alternate Anti-icing and Deicing Compounds Using Sodium Chloride and Magnesium Chloride as Baseline Deicers. In *A Final Report Prepared for the Colorado Department of Transportation*.
- Shi, X., Veneziano, D., Xie, N., & Gong, J. (2013). Use of chloride-based ice control products for sustainable winter maintenance: A balanced perspective. *Cold Regions Science and Technology*, 86, 104-112.
- Shi, X. (2005, July). The use of road salts for highway winter maintenance: an asset management perspective. In *2005 ITE District 6 Annual Meeting* (pp. 10-13).
- Sorensen, D. L., Mortenson, V., & Zollinger, R. L. (1996). *A review and synthesis of the impacts of road salting on water quality*. Utah Department of Transportation.
- Sucoff, E. (1975). *Effect of deicing salts on woody vegetation along Minnesota roads* (No. Technical Bull-303 Final Rpt.).
- Tanner, D. Q., & Wood, T. M. (2000). *The effects of calcium magnesium acetate (CMA) deicing material on the water quality of Bear Creek, Clackamas County, Oregon, 1999* (No. 2000-4092). US Department of the Interior, US Geological Survey; Branch of Information Services [distributor].
- Thunqvist, E. L. (2000). Pollution of groundwater and surface water by roads-with emphasis on the use of deicing salt. *TRITA-AMI-LIC*, (2054).
- Wang, K., Nelsen, D. E., & Nixon, W. A. (2006). Damaging effects of deicing chemicals on concrete materials. *Cement and Concrete Composites*, 28(2), 173-188.
- Watson, E. R., Buszka, P. M., & Wilson, J. T. (2002). *Effects of highway-deicer application on ground-water quality in a part of the Calumet Aquifer, Northwestern Indiana*. US Department of the Interior, US Geological Survey.
- World Health Organization. (2004). *Guidelines for drinking-water quality: recommendations* (Vol. 1). World Health Organization.
- Young, J. P., Rallings, A., Rutherford, P. M., & Booth, A. L. (2012). The Effect of NaCl and CMA on the Growth and Morphology of *Arctostaphylos uva-ursi* (Kinnikinnick). *Journal of Botany*, 2012.