Draft Final Report NCHRP 25-25/Task 86: Toxicological Effects of Chloride-Based Deicers in the Natural Environment

Prepared for:

Association of American State Highway and Transportation Officials Standing Committee on the Environment

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Instructions to Panel Members (distribute to panel members at beginning of project and when report is distributed)

This project is being conducted for the AASHTO Standing Committee on the Environment as part of NCHRP Project 25-25, Toxicological Effects of Chloride Based Deicers in the Natural Environment. The report has not gone through the usual rigorous review process established and monitored by the Transportation Research Board Executive Committee or the Governing Board of the National Research Council, and should not be described as a "TRB Report." It should be described as a contractor's report conducted for the AASHTO Standing Committee on the Environment with funding provided through National Cooperative Highway Research Program Project 25-25.

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We would like to thank the project panel including the project Chair Mr. Kevin Walsh, technical panel members Mr. Mark Hemmerlein, Mr. G. Scott McGowen, Mr. Charles B. Pace, Ms. Mary Kay Solberg, Dr. Nicole Trahan, Mr. David C. Weider, and liaisons Mr. Marcel Tchaou and Mr. Mike Borst for their efforts to make this the best possible document. We would also like to thank Mr. Nanda Srinivasan for his coordination and management of this project. A special thank you goes to Mr. Scott Jungwirth, Mr. Stephen Mery, and Mr. Yongxin Li for their efforts researching and writing sections of this report. And a final thank you to Ms. Marie Venner of Venner Consulting and Mr. Eric Strecker of Geosyntech Consultants for their efforts.

ABSTRACT

This report documents and presents information on the toxicological impacts of chloride-based deicers to the environment. Chloride-based deicers have been the primary products used by road agencies since the 1960s for winter maintenance operations. Chloride-based deicers prevent or weaken the bond between ice and snow and the pavement, which facilitates ice and snow removal from roads. Once applied, chloride-based deicers easily migrate into the roadside environment as runoff, splash or spray from vehicles or plows, or are hauled off site to a melting location. Chloride-based deicers have been shown to impact soil, plants, wildlife, and aquatic ecosystems. To assess the toxicological impacts of chloride-based deicers to these environments, a comprehensive literature review was conducted to gain information on this topic and establish the current state of the practice. Information presented in the literature review includes background on chloride-based deicers and how they are used in winter maintenance practices; documented toxicological impacts of chloride-based deicers to soil, plants, wildlife, and aquatic ecosystems; information on how chlorides are regulated by federal and state agencies; current laboratory and field test methods used to quantify the toxicological impacts of chloride-based deicers; as well as a discussion of future research needs. The report then presents a set of guidelines for DOTs on state and federal chloride standards, and effective practices that can be used to reduce the toxicity of chloride-based deicers. The following themes are discussed: reducing the amount of chloride-based deicers applied, treatment of chloride laden runoff, mixing chloride laden runoff to reduce peak concentrations, and routing of deicing runoff away from sensitive receiving waters. A Scope of Work for a future research project is presented that addresses the need for a standardized analysis method to quantify the toxicological impacts of chloride-based deicers to the roadside ecosystem using laboratory and field test methods. In addition to the Scope of Work, suggestions for future research on this topic are presented.

EXECUTIVE SUMMARY

The goal of this research was to investigate the toxicological impacts of chloride-based deicers on the environment, specifically to waters, through a comprehensive literature review, in order to establish the current state of the practice. Information gained from the literature review was then used to develop guidelines for departments of transportation (DOTs) on relevant federal and state standards and effective practices that can be used to reduce the toxicity of chloride-based deicers, and develop a Scope of Work for a future research project on this topic.

State departments of transportation are continually challenged to provide a high level of service (LOS) on winter roadways and improve safety and mobility in a cost-effective manner, while at the same time minimizing adverse effects to the environment, vehicles, and transportation infrastructure. Level of service, cost-effectiveness, and corrosion have traditionally been considered more urgent priorities than other less well-characterized impacts, such as impacts to water quality. It is increasingly important to understand the environmental footprint of deicers, including their impacts on aquatic ecosystems.

Since the 1960s, chloride salts have been the primary products used by roadway agencies for deicing and more recently for anti-icing and pre-wetting. Due to their long term and widespread use, the environmental impacts of such deicers have been subject to significant research efforts (Hawkins 1971; Roth and Wall, 1976; D'Itri 1992; Paschka et al. 1999, Ramakrishna and Viraraghavan 2005; Levelton Consultants Limited 2007; Shi et al. 2009). Nonetheless, as identified by the NCHRP Report 512, "a clear need exists for more monitoring and characterization of snowmelt runoff from highways" to better understand deicer impacts to the environment, including aquatic ecosystems.

Chloride salts are readily soluble in water, difficult to remove from water, and tend to accumulate in water over time (Howard and Haynes 1993). Deicers have been found to negatively impact aquatic community structures. Elevated chloride concentrations have correlated with reduced species richness and food web dynamics (Sanzo and Hecnar 2006; Collins and Russell 2009; Van Meter et al. 2011). Laboratory and field studies in Canada found that in southern Ontario, Quebec and other areas of heavy road salt use, chloride concentrations found in ground and surface water are often sufficient to affect biota (Environment Canada 2001). Such toxicity can be associated with the direct effect of deicers and/or with the indirect effect via their interactions with runoff chemistry. Numerous studies have reported environmental risks of chloride-based deicers, indicating that the actual effects depend on individual site conditions as well as the type and amount of deicers applied (Dagher and Rouleau 1990; Winston et al. 2012; Fay and Shi 2012).

Toxicity testing has not been required of manufacturers or vendors producing chloride-based deicers and the associated additives (e.g., corrosion inhibitors and thickeners). As such, little toxicity data has been collected or published in the field of winter maintenance (Corsi et al. 2010a). Toxicity research has been conducted on similar products used in other fields including aircraft or airfield deicers (Corsi et al. 2006) and dust suppressants (Williams and Little 2011), but available data on toxicological impacts are still very limited.

The most commonly used tools to assess toxicity are the laboratory acute and chronic tests, which apply varying concentrations of a contaminant to a selected species. The information gained from these tests is specific to the species tested and can be used to assess damage at the cellular and subcellular level of organisms. For this reason, hundreds if not thousands of species have been tested in this fashion to gather as much information as possible. The U.S. Environmental Protection Agency (EPA) has utilized aquatic toxicity tests of pure chemicals to establish current water quality criteria. In contrast, stormwater, municipal, and industrial water discharges are regulated by whole effluent testing (US EPA WET program), which assesses the toxicological effects of all effluent pollutants to aquatic organisms (US EPA 2013a). Assessing the direct impacts of deicers to the ecosystem or higher levels of biological organization can be accomplished with bioassessements, or biological monitoring. Biological monitoring allows for a direct assessment of the aquatic biota and directly measures the biological health of the waterway.

Federal ambient water quality criteria for chloride are (US EPA 1988):

- 230 mg/L, maximum chronic exposure level, four-day average concentration
- 860 mg/L, maximum acute exposure level, one-hour average concentration

These criteria are not supposed to be exceeded more than once in a three year period. The drinking water standard for chloride is 250 mg/L. The Clean Water Act requires states to adopt water quality standards; these can be the established federal standards or states can develop site specific or pollutant specific standards if adequately justified. Identifying the designated use of a waterway using a Use Attainability Analysis (UAA) is one method to potentially justify whether an effluent limit is reasonably attainable or if a more or less stringent effluent limit should apply.

Chloride is a conservative substance; it does not degrade further once put into the environment. For this reason, chloride is difficult to remove once in solution. Methods that can be used to reduce the toxicity of chloride-based deicers include 1) reducing the amount of chloride-based deicers applied, 2) treatment of chloride laden runoff, 3) mixing chloride laden runoff to reduce peak chloride concentrations, and 4) routing chloride laden runoff away from sensitive surface and groundwater systems.

One method that can be used to reduce chloride-based deicer toxicity is source control, using the minimum amount of chloride-based deicer needed to achieve the prescribed level of service. The following methods can be used by DOTs to reduce or minimize the amount of chloride-based deicer used or lost in their daily operations:

- Salt Management Plans
- Product substitution
- Snow removal
- Deicing, Anti-icing and Pre-wetting Practices that Optimize Salt Use
- Precision Application and Automatic Vehicle Location (AVL)/Global Positioning System (GPS) Technology
- Equipment Calibration
- Monitoring and Keeping Records
- Weather Information and Forecasting Services, including Road Weather Information System (RWIS) and Maintenance Decision Support System (MDSS)
- Staff training

Each of the technologies, tools, and methods discussed, when implemented correctly, has been shown to reduce the amount of chloride-based deicers needed by transportation agencies to achieve their prescribed level of service or reduce the amount lost to the environment.

Once chloride-based deicers have been applied, the following techniques can be used to minimize the toxicity of chloride in the environment. Phytoremediation has been shown to remove chlorides from runoff, but needs sufficient time for the biological process to work, and the plants that take up the chloride must be disposed of prior to die-off. Phytoremediation is most effective at sites with shallow subsurface contamination and works best as a polishing technique for treating soils and remaining salt laden pore water. Traditional stormwater structural Best Management Practices (BMPs) can be used to manage chloride concentrations in runoff by redirection or capture and mixing to dilute. This can reduce the potential toxicity of highway stormwater runoff. Only a few structural BMPs have shown promising results at capturing and managing chlorides in runoff. Ponds and wetlands can be used to store and release captured runoff. Detention, retention and evaporation ponds allow for mixing of chloride laden runoff with base flow or non-chloride runoff, reducing spike chloride concentrations and overall smoothing chloride concentrations. Wetlands and shallow marshes also reduce spike chloride concentrations, if they have sufficient storage capacity, and in most cases also utilize phytoremediation. In some cases chlorides have been shown to detrimentally impact wetlands. Infiltration of stormwater is an effective stormwater management technique, but with chloride laden runoff contamination of ground water is a concern. Infiltration trenches and basin can be used to reduce surface water volume, but the depth of groundwater and soil type may limit their use. Vegetated swales and filter strips utilize bioinfiltration to filter and reduce runoff velocity, and work best when combined with other treatments. Vegetated swales can be used for snow storage. Grass swales have been found to store chlorides from runoff and later re-release it acting like a chloride reservoir. Other methods to remove chlorides from runoff include reverse osmosis, filtration, and adsorption; however, these methods are only briefly discussed because they are costly, have functional constraints, or are in the development stage.

A scope of work for a Phase 2 research project was developed based on research needs and gaps identified from the literature review. The objective of the Phase 2 research project is to develop a guide that will establish procedures and methods for evaluating the aquatic toxicity of chloride-based deicers both in the laboratory and in the field; and provide quantitative information and insights regarding the toxicological effects of common chloride-based deicers used in snow and ice control operations on water bodies adjacent to highways.

Additionally research needs identified that fall outside of the proposed scope of work include: dilution volumes and impacts to stream biota; how cold temperatures and seasonal factors affect aquatic species tolerance to contaminants; cost-benefit analysis and identification of non-chloride-based deicers; identification of the water quality sampling locations for identification of contaminant exceedances; and development of a cost-effective methods for continuous in-situ monitoring of chloride in waters.

CHAPTER 1: Background

This report presents information on the toxicity of chloride-based deicers in the environment. It discusses commonly used chloride-based deicers and the toxicity of these chloride-based deicers quantified in the laboratory and field for various species, as well as documented impacts to water, soil, wildlife, and terrestrial and aquatic flora and fauna. Information is presented on chloride concentrations measured in aquatic environments, and how dilution affects these measured concentrations. Life cycle assessments, laboratory test methods, calculation methods, and other important variables are discussed. This is followed by a discussion of field test methods used to quantify chloride-based deicer toxicity, including sampling options, and bioassessments, and on-going and future research on this topic. Information is then presented on methods used to reduce the amount of chloride-based deicers used or lost on the following topics: use of alternative products, snow removal, anti-icing, pre-wetting, precision application and use of AVL and GPS technology, frequent and consistent staff training and equipment calibration, appropriate material storage, utilizing real-time weather and pavement condition data (including programs like MDSS), and creating detailed maintenance records. This is followed by a discussion of methods to remove chlorides from the environment once they have been applied including: filtration, phytoremediation, using traditional storm water BMPs, and new and alternative methods to remove chlorides.

State departments of transportation are continually challenged to provide a high level of service on winter roadways and improve safety and mobility in a cost-effective manner, while at the same time minimizing adverse effects to the environment, vehicles, and transportation infrastructure. Level of service (or cost-effectiveness) and corrosion have traditionally been considered more urgent priorities than other less well-documented impacts, such as impacts to water quality, yet it is increasingly important to understand and mitigate the environmental footprint of deicers. Since the 1960s, chloride salts have been the primary products used by roadway agencies for deicing and more recently for anti-icing and pre-wetting. Due to their long-term and widespread use, the environmental impacts of such deicers have been subject to significant research efforts (Hawkins 1971; Roth and Wall 1976; D'Itri 1992; Paschka et al. 1999, Ramakrishna and Viraraghavan 2005; Levelton Consultants Limited 2007; Shi et al. 2009). Nonetheless, as identified by the NCHRP Report 512, "a clear need exists for more monitoring and characterization of snowmelt runoff from highways" to better understand the deicer impacts to the environment.

Information presented to date in the published domain on chloride-based deicer toxicity generally includes chemical composition and engineering properties of deicers. Additional information on their aquatic toxicity is needed to enable fully-informed decisions by stakeholders. Such toxicity could be associated with the direct effect of deicers or with the indirect effect via their interactions with runoff chemistry. Numerous studies have reported environmental risks of chloride-based deicers, indicating that the impacts depend upon site-specific conditions as well as the type and amount of deicers applied (Dagher and Rouleau 1990; Fay and Shi 2012; Winston et al. 2012). Increased chloride levels in surface water and groundwater have been found to be a function of highway density, percentage of urban area (as roadways), population density, traffic patterns, and road salting practices (Bowen and Hinton 1998). Environment Canada (2001) reported that "acute toxic effects of chloride on aquatic organisms are usually observed at relatively elevated concentrations (e.g., 4-day median lethal concentration (the percent of the effluent concentration that is lethal to 50% of the test organisms (LC_{50}) for the cladoceran *Ceriodaphnia dubia* at 1400 mg/L))" and "chronic toxicity occurs at lower concentrations (e.g., No-Observed-Effect Concentration for the 33-day early life stage test for survival of fathead minnow at 252 mg chloride/L)."

Toxicity testing has not been required of manufacturers or vendors producing chloride-based deicers and the associated additives (e.g., corrosion inhibitors and thickeners). As such, little toxicity data has been collected or published in the field of winter maintenance (Corsi et al. 2010a). Toxicity research has been conducted on similar products used in other fields including aircraft or airfield deicers (Corsi et al. 2006) and dust suppressants (Williams and Little 2011), but available data are still very limited. For roadway winter operations, deicers tend to have limited inclusion of additives, which are generally the more toxic component of the aircraft or airfield deicers (Pillard 1995; Corsi et al. 2009). Roadway deicers may have additives such as anti-caking agents, corrosion inhibitors, and dyes (Levelton Consultants Limited 2007; Shi et al. 2009). To appropriately determine the toxicity of the roadway deicers, identification of additives and/or chemical and biological testing of the deicer formulation is required.

Concerns associated with the use of chloride-based deicers include increased salinity in waterways and soils, infiltration of cations (e.g., Na^+, Ca^{2+}, and Mg^{2+}) and the chloride anion (Cl^-) into soils and drinking water, degradation of the environment along the roadside, and potential risk to biological diversity (TRB 1991; Environment Canada 2001). Studies have demonstrated that sodium chloride (NaCl) can pose significant risks to vegetation, soil, water, and aquatic life and mammals (Vitaliano 1992; Robidoux and Delisle 2001; Ramakrishna and Viraraghavan 2005; Fay and Shi 2012). Road salts have also been shown to impact flora and fauna in the near road environment, including water bodies (Crowther and Hynes 1977; Dickman and Gochnauer 1978; Molles 1980; Kersey 1981; Demmers 1992). According to Environment Canada (2001), “increased salt concentrations in lakes can lead to stratification, which retards or prevents the seasonal mixing of waters, thereby affecting the distribution of oxygen and nutrients.” Bowen and Hinton (1998) found elevated chloride concentrations in surface water affected the spatial patterns of total phosphorous concentrations and induced higher turbidity and bacteria growth, degrading the overall health of streams and making them potentially inhospitable for fish populations. Field research has found that elevated background and spike chloride concentrations in waterways have reduced species richness in some waterways (Turtle 2000; Houlahan and Findlay 2003; Collins and Russell 2009). Deicers have been found to negatively impact aquatic community structures, such that elevated chloride concentration are correlated with reduced species richness and food web dynamics (Sanzo and Hecnar 2006; Collins and Russell 2009; Van Meter et al. 2011). Laboratory and field studies in Canada found that in southern Ontario, Quebec and other areas of heavy road salt use, chloride concentrations in ground and surface water are often sufficient to affect biota (Environment Canada 2001). Changes in macroinvertebrate drift behavior and mortality caused by elevated salt concentrations are highly dependent on concentrations and exposure time, and vary among taxa (Blasius and Merritt 2002).

In addition to adding the major chemical constituents (Na^+, Ca^{2+}, and Cl^-) to aquatic systems, deicers can also be considered a source of other “major and trace” constituents in runoff (Granato 1996):

- NaCl deicer – sulfate, calcium, potassium, bromide, vanadium, magnesium, and fluoride
- Calcium chloride ($CaCl_2$) deicer - sodium, potassium, sulfate, bromide, silica, fluoride, strontium, magnesium

Chloride salts are readily soluble in water, difficult to remove, and tend to accumulate over time (Howard and Haynes 1993). Chloride anions are highly mobile, do not “significantly absorb into mineral surfaces,” and do not “biodegrade, volatilize, (or) easily precipitate” (Bowen and Hinton 1998). It has been shown that a high percentage of deicers can migrate from the road as surface runoff and then enter streams and rivers (Scott 1981; Crowther and Hynes 1977; Hoffman et al. 1981; Peters and Turk 1981; Demers and Sage 1990). Evidence shows that chloride salts can accumulate in aquatic systems, and are conservative (Environment Canada 2001; Mason et al. 1999; Kaushall et al. 2005). According to Environment Canada (2001), “research has shown that 10-60% of the salt applied enters shallow subsurface waters and accumulates until steady-state concentrations are attained." Road salt applied by the Swedish National Road Administration contributed to more than half of the total chloride load for the river basin of Sagan (Thunqvist 2004). Elevated concentrations are generally linked to spring flushing events. Of special importance is the study of snowmelt runoff from the first major snowmelt of the season due to high concentrations of pollutants contained in this "first flush." Elevated chloride concentrations have been observed in summer, due to recharge of surface water by ground water during times of low flow (Environment Canada 2001). Shallow wells, reservoirs, and low-flow surface waters adjacent to roadways or storage sites are most susceptible to contamination by deicers as they can infiltrate into groundwater aquifers (TRB 1991). The Pennsylvania Department of Transportation and some other northern state DOTs have had to purchase wells or provide replacement water where contamination has occurred (TRB 1991).

Current standards used by the U.S. Environmental Protection Agency (US EPA) for chloride in surface waters are 230 mg/L maximum chronic exposure for a four-day average concentration of dissolved chloride associated with sodium, and 860 mg/L maximum acute exposure for a one-hour average concentration, occurring no more than once every three years on the average [US EPA 440/5-88-001] (US EPA 1988). The US EPA standard should apply to most locations except where more conservative values may be necessary, such as where locally important and sensitive species are present. When chloride concentrations in streams reach or exceed the acute and chronic standards, toxicity to aquatic species can result. In addition to toxicological impacts, elevated chloride concentrations can disrupt normal functions of surface water; e.g., cause density stratification and late vertical mixing in waters. A state can adopt the federal standards or develop a site-specific or pollutant specific standard if it is adequately justified, which can be higher or lower than the federal standard. Work completed by the Iowa Department of Natural Resources (DNR) and US EPA can be used as the basis to set site specific acute and chronic chloride criteria based on measured water hardness and sulfate levels (Iowa DNR 2009). The new chloride criteria "appear to provide a more accurate representation of the potential toxic effects of elevated chloride levels in freshwater streams and rivers" (MassDOT 2012).

Impaired or threatened waters (rivers segments, streams, lakes) identified by states, where the required pollution controls are not enough to maintain or reach applicable water quality standards are added to the 303(d) list maintained by the US EPA, and will have total maximum daily loads (TMDLs) established based on the severity of the pollution and the sensitivity of the waters (US EPA 2012b). Nationwide there are 977 303(d) listings for salinity, chlorides, and total dissolved solids (TDS). In 2004, New Hampshire added five chloride impaired waters along I-93, with a total of nine streams violating the state's standard for chloride. This occurred after elevated ground water chloride levels were detected and associated with years of heavy salt use (Fredrick and Goo 2006). The following parameters that are of interest to chloride toxicity and are covered by the 303(d) listing include chlorides, TDS, total suspended sediments (TSS), and biological oxygen demand (BOD).

The impetus for this project was the assessment of water bodies by US EPA and the designation of some of these water bodies as "impaired" because of chlorides and their potential effects on stream biota. This has in part led to the establishment of TMDL requirements restricting DOTs' use of chloride-based deicers.

The objective of this project was to find and summarize all the available information in the published domain on chloride-based deicers toxicity, present this information in a literature review, then use this information to develop guidelines for DOTs on relevant standards and effective practices for the use of chloride-based deicers, in order to reduce toxicity and minimize potential impacts. A second objective was to develop a scope of work for a larger project that addresses the identified research needs. The developed scope of work is intended to be submitted to the American Association of State Highway and Transportation Officials (AASHTO) Standing

Committee on the Environment (SCOE) for consideration as a larger National Cooperative Highway Research Program (NCHRP) project. The overarching goal of this project is to provide a foundation of information to support a larger NCHRP project that will determine the effects of chlorides to stream biota and consider the natural buffering capacities, changes in climate, flows, and other commonly occurring variables.

CHAPTER 2 Research Approach

A review of all available literature and interviews of professionals in this field of research were used to develop the content of the literature review, guidelines for DOTs, and scope of work for a larger project. This chapter presents details on how each of these tasks was conducted.

The summary of the state of the practice was developed from an exhaustive review of available literature on toxicological effects of chloride-based deicers in the environment. Information was sought on chemical and biological properties, environmental impacts, and toxicity information on the most commonly used chloride-based deicers, including sodium chloride, magnesium chloride, and calcium chloride. Information was also sought on past, current and ongoing laboratory and field testing of chloride-based deicer toxicity. Relevant information on non-chloride-based deicer toxicity is also presented, including information on acetates, formats, urea, and glycols. The information presented was found in peer reviewed publications, government and DOT reports, NCHRP reports, US EPA documents, as well as international peer reviewed publications. Information was also sought from fields outside of traditional water quality monitoring and transportation research.

Through the literature review process, researchers identified leaders in their field who could provide additional insight on chloride-based deicer toxicity; these experts were interviewed over the phone. Information gained from these interviews has been included in the report as personal communications. A draft literature review was developed and submitted to the project panel for review. Comments from the project panel were addressed and the literature was revised based on these comments.

The guidelines for DOTs on effective practices and relevant standards for the use of chloride-based deicers were developed based on information gained in the literature review process. Information presented includes relevant state and federal standards that apply to chloride-based deicer toxicity in the environment, including US EPA guidelines and recent changes based on additional research. Source control strategies that can be used to limit the amount of chloride-based deicers applied while allowing DOTs to maintain their prescribed LOS – mobility and safety are subsequently discussed, including: salt management plans, staff training, monitoring and keeping records, anti-icing, deicing, and pre-wetting, weather information, RWIS, and MDSS. Information is then presented on methods to remove chlorides from the environment once they have applied, which include water filtration; phytoremediation; and traditional storm water best management practices such as wetlands, detention and retention ponds, filter strips and bioswales; and new and alternative methods to remove chlorides. The discussion of each topic includes references to additional resources and information.

The draft Guidelines for DOTs document was developed and submitted to the project panel for review. Comments from the project panel were addressed and the guidelines were revised based on these comments.

A scope of work for a future research project was developed for laboratory and field testing of deicer toxicity, based on information gained from the literature review and Guidelines for DOTs documents. Building on identified research needs, the scope of work will form the basis of the next phase of research. The draft scope was submitted to the project panel for review and comments. After the incorporation of this feedback, the final scope of work was then submitted to the AASHTO SCOE by the project panel as a research idea.

The final report has been developed based on all the work completed, including the literature review, Guidelines for DOTs document, and scope of work. This report presents background information on chloride-based deicer toxicity, followed by a discussion of methods used to gather the information presented. The next section presents the findings and applications developed including the literature review, Guidelines for DOTs, Scope of Work. The last section of the report summarizes the major findings and makes recommendations for future research.

CHAPTER 3: Findings and Applications

Task 1 Literature Review

Chloride-based Deicers

Since the 1960s, due to their abundance and low direct costs, chloride salts have been the primary freezing point depressants in deicers used by roadway agencies; these salts include NaCl, magnesium chloride ($MgCl_2$), and $CaCl_2$ (Paschka et al. 1999; Fishel 2001). Deicers refer to all the chemicals used for anti-icing, deicing, or pre-wetting operations, aimed at preventing or breaking the bond between the snow/ice and pavement by reducing the freezing temperature of precipitation (Field et al. 1975; Murray et al. 1977; Novetny 1986; Buttle and Labadia 1999; Ramakrishna and Viraraghavan 2005). Road salt, NaCl, was first introduced for snow melting operations in the 1930s. A recent survey of highway maintenance agencies indicated that NaCl was most frequently used, followed by abrasives, $MgCl_2$, agro-based products, $CaCl_2$, and others (Shi et al. 2009). Less than 25% of the survey respondents used alternative deicers such as potassium acetate (KAc), sodium acetate (NaAc), calcium magnesium acetate (CMA), and potassium formate (KFm). NaCl is still the most commonly used deicer on roadways in North America, with approximately 4 to 5 million tons used each year in Canada and 15 million tons in the United States (Salt Institute 2003). In comparison, approximately 0.3 million tons of $CaCl_2$ are used each year in the United States (Ramakrishna and Viraraghavan 2005). $MgCl_2$ brines are becoming more commonly used, because they have shown better ice-melting performance than NaCl at cold temperatures (Ketcham et al. 1996). It has been demonstrated that $CaCl_2$ adheres to road surfaces better than NaCl and has better ice-melting performance at cold temperatures while showing reduced impacts to metal and concrete (McElroy et al. 1988; Cheng and Gunthrie 1998; Fay et al. 2009). In addition, the use of $CaCl_2$ as a pre-wetting agent for rock salt has been shown to significantly increase product performance (Nixon and Foster 1996). However, some agencies choose not to use $MgCl_2$ or $CaCl_2$ because of their ability to hold water (hygroscopic nature), which may cause roads to become slippery under certain conditions (Perchanok et al. 1991). It is well known that the performance of a deicer significantly decreases if the ambient temperature is below the deicer's effective temperature. NaCl has an effective temperature of 15°F, whereas $MgCl_2$ and $CaCl_2$ have effective temperatures of 5°F and -20°F, respectively (Fischel 2001).

Recommended Application Rates

The appropriate application rates of deicers vary based on the type of deicer being used, pavement and air temperatures, amount of snow and ice present, and topography. In the past, application rates for salt ranged from 400 to 800 pounds per lane-mile (lbs/l-m), causing some roads to receive around 50 tons of salt per mile over the winter season (Field et al. 1975). Current application rate guidelines are much more conservative with recommended application rates in the range of 250 lbs/l-m (Salt Institute 2007). Commonly used application rates for chloride-based deicers are:

NaCl

- Solid Salt - 200 to 800 lbs/l-m (Salt Institute 2007)
- 23% Liquid salt brine - 20 to 80 gallons per lane mile (gal/l-m) (Peterson et al. 2010)

$MgCl_2$ and $CaCl_2$

- Solid – 100 to 400 lbs/l-m (Fischel 2001)
- Liquid for anti-icing – 30 to 45 gal/l-m (Fischel 2001)
- Liquid for deicing – 40 to 60 gal/l-m (Fischel 2001)
- Liquid for pre-wetting – 10 to 12 gal/l-m (Blackburn et al. 2004)

Laboratory tests have shown that the use of $CaCl_2$ would introduce five times fewer chloride anions and 10 times fewer calcium and magnesium cations for comparable deicing performance at 0 - 10°F within 1 hour, relative to NaCl (Brandt 1973). Therefore, when considering the toxicological effects of chloride-based deicers, utilizing $CaCl_2$ or $MgCl_2$ based deicers at colder temperatures can potentially aid in reducing the amount of anions and cations released into the environment.

Other Sources of Chlorides

Winter highway maintenance operations are considered the predominant source of anthropogenic chlorides introduced into the natural environment, even though there are other sources of chlorides such as parking lots, private roads, industrial effluents, agricultural runoff, landfills and water softeners (Panno et al. 2002), as well as dust suppressants. Principal sources of chloride depend on watershed characteristics. Researchers in New Hampshire determined that 50% of salt introduced into the Policy-Porcupine watershed was from parking lots and 36% was contributed by state and municipal roads (Burack et al. 2008). High levels of Na^+ and Cl^- have also been detected near multiple landfill sites (Panno et al. 2002). Major contributing sources of chlorides depend on land uses within a specific area. Road salt and industrial effluents are the most common sources of chloride-based products in urban areas. A 20-year study in upstate New York found a doubling in salt concentrations in the watershed, with 91% attributed to road salt application and 9% to sewage and water softeners (Kelly et al. 2008).

Chloride Transport in the Environment

Road salts can enter the roadside environment through a wide variety of pathways, such as runoff, splash and spray from vehicles, or from snow that has been plowed or hauled off site (Zinger and Delisle 1988; Ramakcrishna and Viraraghavan 2005). Figure 1 outlines the pathways of deicer movement in the environment (Cheng and Guthrie 1998; Fischel 2001). Once applied, deicers can become a part of road runoff or be dispersed aerially. Once in runoff, deicers can impact soil, water, flora and fauna. If distributed aerially, deicers can impact the soil, water, flora, and air quality. Because the chloride ion is conservative and will not break down further, once in runoff it can affect multiple systems (e.g., soil, water, flora, and fauna) or flow from one system to another (e.g., soil to water, or surface to ground water). Environment Canada (2001) reported that field measurements revealed elevated chloride concentrations in lakes a few hundred meters from rural roadways. A two-year study monitored chloride levels in runoff from a New York State Highway and found that all four streams that were monitored showed significant increases in chloride concentrations up to 100 m from the highway, and chloride concentrations were up to 31 times higher than comparative upstream samples (Demers and Sage 1990). The elevated chloride levels were found in the streams up to six months after the roads had stopped being treated with road salt. The fours streams terminate in a lake and chloride concentrations at lower depths (18 m, ~60 ft) were 2.5 times higher than at 2 m (~6.5 ft). In addition to road salts, the runoff from snowmelt may also carry other pollutants, all of which may end up in soil, water, or roadside vegetation (Bryson and Barker 2002; Munck, et al. 2009; Nelson et al. 2009; Findlay and Kelly 2011).

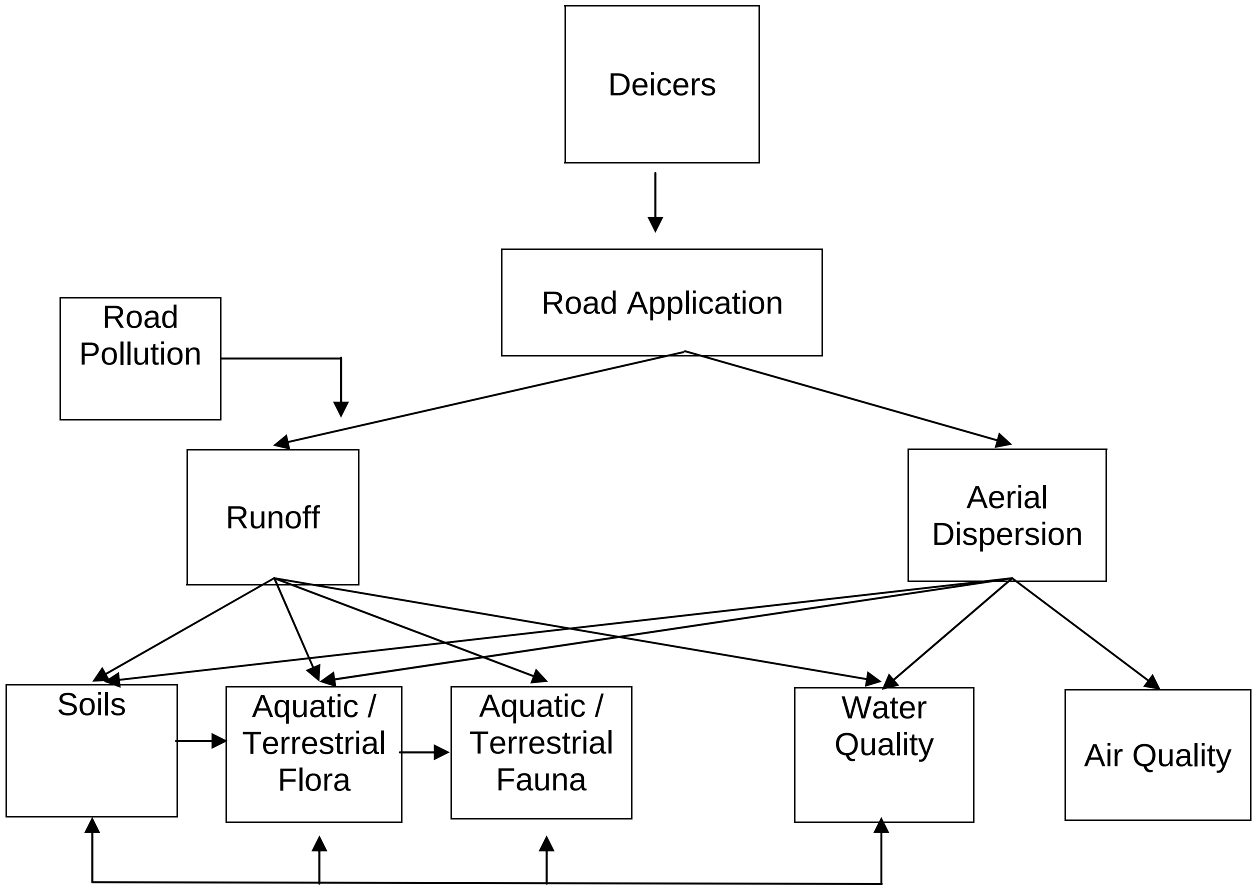

Figure 1: Pathways of deicers into the environment (adapted from Cheng and Guthrie 1998; Fischel 2001).

Road salts that have entered into the adjacent environment and migrated to waterways have been shown, through models and field observations, to cause chloride concentrations to accumulate over time (Demers and Sage 1990; Shaw et al. 2012). Urban ponds and lakes showed higher chloride concentrations in the winter and spring months from November to May (Mayer et al. 1999). Small natural lakes and ponds in urban areas are highly susceptible to changes in chloride concentrations if they receive chloride laden runoff from roads; and those with long residence times are most sensitive and exhibit adverse impacts to aquatic organisms (Mayer et al. 1999; Environment Canada 2001). Aquatic impacts of deicing salts were measured in the Central Sierra Nevada Mountains of California from May 1974 to June 1975, and chloride levels in streams below major freeways and adjacent small lakes were found to have elevated chloride concentrations, as a direct result of road salt applications (Hoffman et al. 1981).

Surface water with high chloride concentrations (exceeding 1000 mg/L) can be diluted by groundwater recharge if there is sufficient flow (Bowden and Hinton 1998). Baseflow of waterways can be used as a measure of groundwater discharge, such that summer baseflow chloride concentrations reflect groundwater chloride concentrations, and input from other surface water sources, or impoundments. The same research found that low chloride baseflow concentrations are generally associated with unpolluted streams, stable stream channels, and healthy fish populations (Bowen and Hinton 1998). Generally streams that still have adjacent riparian forest are healthier.

Other issues related to chloride transport from road runoff include density stratification or late vertical mixing of water bodies (ponds, lakes, etc.) due to salt loading (Bubeck et al. 1971; Bridgeman et al. 2000). Once road salt is in solution and reaches a waterway, the salty water will migrate downward due to its higher density (US EPA 1971; Diment et al. 1973; Fritzsche 1992; Ruth 2003).

Road salts that run off the road can also enter adjacent soils. The degree of percolation of salt-laden runoff into the soil depends on the soil permeability and the season of the year. Less permeable soils favor runoff and, therefore, will have greater horizontal flow or sheet flow over the soil. Greater horizontal movement can also occur in winter due to the presence of frost, or if the ground is frozen in the case of less permeable soils. Elevated salt concentrations in soils cause an osmotic imbalance in plants, which can inhibit plant water absorption, interfere with nutrient uptake; inhibit flowering and seed germination, and retard root growth and long-term plant growth (TRB 1991; Fay and Shi 2012). Damage to vegetation usually occurs within 60 ft of the road, with the most damage occurring to plants closest to the pavement; yet impacts have been observed up to 200 m (~ 650 ft) from treated roads (Wegner and Yaggi 2001; Karraker et al. 2008).

Concentrations Seen in the Field

Typical freshwater chloride concentrations range from 1 to 100 mg/L (Environment Canada 2001; Wetzel 2001). In the Greater Toronto area, the background surface water chloride concentrations were 10 to 25 mg/L, but in more urbanized rivers chloride concentrations were about 100 mg/L, exceeding 1000 mg/L at times. Long-term monitoring at multiple locations found a gradual increase in chloride concentrations over time, 150 to 250 mg/L and from 10 to 20 and from 30 to 40 mg/L over a 23-year period (Bowen and Hinton 1998). Over 300 maintenance patrol yard wells were monitored by the Ontario Ministry of Transportation (MTO) over a 20 to 30 year period, chloride concentrations ranged from below 200 mg/L to greater than 1000 mg/L, with most (74%) less than 200 mg/L (MTO 1997). About a decade later, MTO tested 36 potable water wells and chloride concentrations ranged from 1.5 to 5050 mg/L and 64% of the wells had chloride concentrations greater than 100 mg/L. Monitoring of shallow groundwater (~1 to 20 ft, 0.26 and 5.25 m) at maintenance patrol yards found chloride concentrations ranging from 1 to 24,000 mg/L, with the mean chloride concentration 2600 mg/L for the 102 samples (MTO 1997). Similar testing in Alberta maintenance patrol yards found groundwater chloride concentration between 26 and 26,400 mg/L (Alberta Infrastructure 2000). In Nova Scotia DOT and Public Works patrol yards, groundwater chloride concentrations ranged from 254 to 38,600 mg/L (Environment Canada 2001). A summary of this information in presented in Table 1.

Table 1: Summary table of measured chloride concentrations for background and impacted waters.

Water Body	Background [Cl^- mg/L]	Impacted [Cl^- mg/L]	Reference
Freshwater	2-3, 1-100		Environment Canada 2001; Wetzel 2001
Stream (modeled)	40		Shaw et al. 2012
Surface water, river	10-25	100-1000	Bowen and Hinton 1998
Maintenance yard wells		200-1000	MTO 1997
Potable water wells Shallow groundwater	1.5-5050 1-24,000		
Groundwater	26-26,400		Alberta Infrastructure 2000
Groundwater		254-38,600	Environment Canada 2001; Rushton 1999
Urban pond, lake		100-6000	Watson 2000
Wetlands	18-2700		Benbow and Merritt 2004
Lake	19	260	Bridgeman et al. 2000

Urban pond and lake chloride concentrations have been found to range from 100 to 6000 mg/L. In general, the more traffic lanes treated with road salts, the greater the chloride concentrations found in the adjacent water body (Watson 2000). An assessment of 43 impacted wetlands in the state of Michigan found chloride concentrations ranging from 18 to 2700 mg/L, with 75% of those measured having concentrations less than 334 mg/L (Benbow and Merritt 2004). Chloride concentrations measured in the Third Sister Lake in southeastern Michigan increased from 19 to 260 mg/L from 1981 to 1999 (Bridgeman et al. 2000). Based on a review of available literature by Environment Canada (2001), very high chloride concentrations (e.g., 18,000 mg/L and 82,000 mg/L) had been observed in runoff from roadways and from uncovered abrasive/salt piles, respectively; whereas high chloride concentrations (e.g., averaged 3000 mg/L and 5000 mg/L) had been observed in snow cleared from secondary and primary streets, respectively. According to Environment Canada (2001), "waters from roadways, patrol yards or snow dumps can be diluted to various degrees when entering the environment. In the environment, resulting chloride concentrations have been measured as high as 2800 mg/L in groundwater in areas adjacent to storage yards, 4000 mg/L in ponds and wetlands, 4300 mg/L in watercourses, 2000-5000 mg/L in urban impoundment lakes and 150-300 mg/L in rural lakes." Environment Canada (2001) assessed the potential for impacts to regional groundwater systems using field measurements and mass balance modeling and found that regional-scale groundwater concentrations greater than 250 mg/L could occur from high density road networks that have annual applications of over 20 tons of NaCl per two-lane-kilometer.

A detailed hydrologic analysis was performed on a watershed in Ontario near a major highway, to analyze critical fate and transport characteristics of road salt (Meriano et al. 2009). A complete mass balance of road salt was completed using data from local winter maintenance agencies and some general assumptions, which were used to determine the quantity of road salt introduced into the watershed during two consecutive winter seasons. Multiple monitoring wells were installed in various locations within the watershed and water quality analysis was performed. Researchers determined that 50% of the road salt applied to road surfaces was transported through surface runoff and approximately 50% entered groundwater (Meriano et al. 2009). The groundwater transported high chloride concentrations out of the watershed. Groundwater chloride concentrations were in excess of 1600 mg/L. Significant decreases in chloride concentrations were observed following heavy precipitation due to dilution, while the highest concentrations occurred during brief thaw events in the winter months. Similar results were observed by Corsi et al. (2010), in which minimum concentrations occurred during the month of October. Land use, soil characteristics and subsurface geology influence groundwater chloride concentrations, as well as precipitation and deicer application rates.

During construction of Interstate 93 in the White Mountains of New Hampshire, a large diversion berm was installed to prevent salt laden stormwater from entering Mirror Lake. Despite this effort, road salt travelled through the berm, causing a significant increase in Na^+ concentration of two times the original level and more than tripling the Cl^- concentration over a 25-year period (Rosenberry et al. 1997). The stream branch that drained the highway provided only 3% of the total stream flow to the lake but 53% of the chloride load. This study highlighted the mobility of sodium and chloride ions, which move easily and conservatively through soils, surface waters, and groundwater. The I-93 widening project in New Hampshire has resulted in stricter guidelines and a need to reduce salt usage. Monitoring in 2007 found that while the average chloride concentration was 163 mg/L, well below the 230 mg/L standard, 24% of the samples collected that year were over this standard with most of these elevated concentrations occurring during times of low stream flow (US EPA 2013a).

A case study in North Carolina looking at the impacts of deicing salts to amphibians found that the amount of snow, or water equivalent, is important since for many DOTs the application rate is relatively constant (250 lbs/l-m) per snow or ice event (Winston et al. 2012). Therefore, smaller snow and runoff events can have a greater impact on amphibian populations than larger snowfalls. "Assuming a 250 pound per lane mile application rate, a 10:1.3 snow depth to rainfall depth ratio (*a wet snow*) and that all road salt dissolves as the snow is melting, chloride concentration can be plotted against snow depth (accumulated)" as shown in Figure 2 (Winston et al. 2012). For drier snow packs, with lower water equivalents, this method can over-predict dilution effects.

$$\text{Eq. 1 } [Cl^-] = 11080*(\text{snow depth})^{-1.399}$$

Using equation 1, for a snow depth less than 1.5 in, chloride concentrations were calculated to be greater than 15,000 mg/L. Less than 7 in of snow produced an estimated chloride runoff concentration greater than 1200 mg/L (Collins and Russell 2009). These concentrations are well above the US EPA 230 mg/L chronic limit, and at these concentrations salamanders would be impacted (US EPA 1988). Note that this calculation does not consider any additional dilution that may occur, which greatly contributes to overall chloride concentrations in the environment. Additionally, this calculation assumes a constant application rate independent of the snow event. For most winter maintenance operations the snow event will dictate the application rate, which may be less or more than the value used for these calculations.

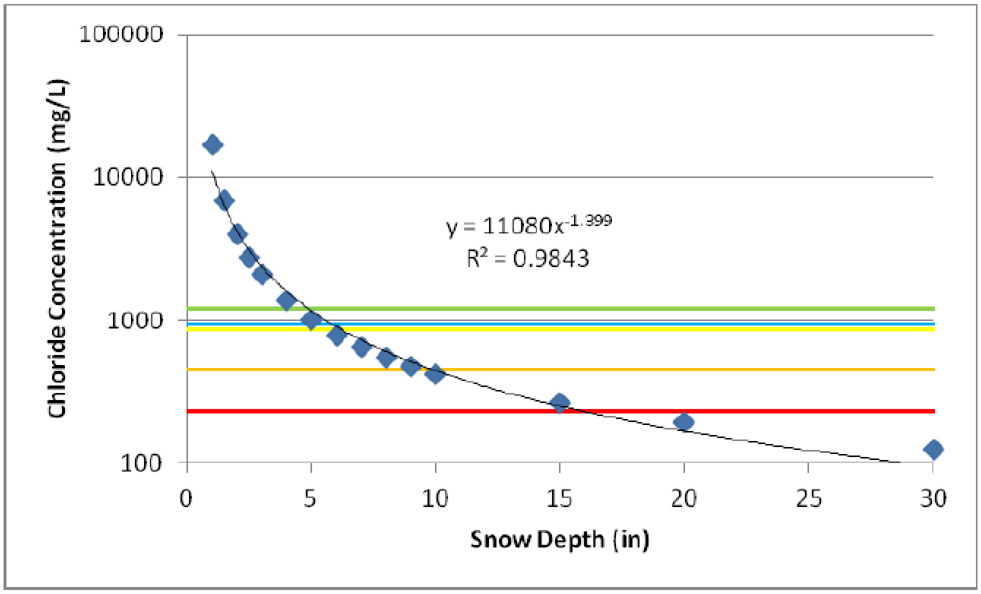

Figure 2: Chloride concentrations as a function of snow depth. Runoff calculated using curve number method. Chloride concentration only valid for 250 lb/l-m application rate (from Winston et al. 2012). Line colors are as follows: Green (1200 mg/L, Collins and Russell 2009), Blue (945 mg/L, Karraker and Ruthig 2009), Yellow (860 mg/L, MN Pollution Control Agency), Orange (450 mg/L, Karraker and Ruthig 2009), and Red (230 mg/L, US EPA 1988).

Figure 2 shows the relationship of chloride concentrations following application at 250 lb/l-m, and depth of snow. A chloride concentration of 1200 mg/L is represented by the green line, which corresponds to a snow of depth of approximately 5 inches. The blue line represents a chloride concentration of 945 mg/L, the yellow line represents a chloride concentration of 860 mg/L, the orange represents a chloride concentration of 450 mg/L, and the red line shows a chloride concentration of 230 mg/L that is attained from a snow depth of approximately 15 inches. In this research it was assumed that the mass of salt used per two-lane-kilometer of provincially maintained road was dissolved and diluted by the volume of average annual runoff that would accumulate on the road surface (based on the width of a two-lane road) (Environment Canada 2001). Estimated runoff concentrations ranged from 30-31,000 mg/L, with 85% of concentrations falling between 1000-10,000 mg/L. Measured road runoff concentrations from a four lane bridge, two lane highway and two lane road were found to fall within the estimated range of chloride concentrations calculated from Environment Canada (2001), with the highest chloride concentration of 19,135 mg/L measured from the bridge (Mayer et al. 1999). Note that the estimated and measured chloride concentrations represent chloride concentrations before dilution by a receiving water body (e.g., highest possible chloride concentration), with samples collected at discharge points, representing roadside ditches or small wetlands adjacent to major roadways.

Work by Lewis (1999) estimated that 50,000 L of anti-icers were applied per mile of interstate highway (4 lanes) per year at that time, or about 12,000 L per lane mile per year, based on past work and application records from Colorado DOT. Annual runoff varies greatly over time and within Colorado, but a value of 300 mm per year was used. A mile of 4-lane highway including the shoulder and embankments was estimated at 90,000 m^2. The amount of moisture passing from the roadway was estimated at 25,000 m^3 per year. Based on these rough estimates, if 50,000 L of anti-icer is applied to one mile of 4-lane highway and diluted by 25,000 m^3 of runoff, then the dilution rate is 500:1 before it enters the environment.

Environmental Impacts by Chloride Deicers and Additives

Many studies have reported damage to soil structure and negative effects on vegetation near roads or negative impacts of deicing salt on terrestrial organisms in laboratory and field tests (Crowther and Hynes 1977; Dickman and Gochnauer 1978; Barrick and Davidson 1980; Demers and Sage 1990; Lewis 1999; Butler and Addison 2000; Robidoux and Delisle 2001; Bryson and Barker 2002; Czerniawska-Kusza et al. 2004; Mineau and Brownlee 2005; Sanzo and Hecnar 2006; William and Little 2011). NaCl from road runoff is responsible for increased salinity or osmolality of surface and ground waters several months after the last road treatment (Thunqvist 2004). Ramakrishna and Viraraghavatan (2005) reported that this could reduce water circulation and re-aeration in lower depths, resulting in changes in population or community structure of aquatic biota. In soils, salt transport, infiltration, and impacts are dependent on a variety of factors and local conditions such as the slope of the roadside, soil type, proportion of silt and clay, and vegetation cover (Ramakrishna and Viraraghavatan 2005). Increasing concentrations of Na^+ and Cl^- affects soil structure, dispersion, permeability and osmotic potential and can cause loss of soil stability and osmotic stress for vegetation and soil macro- and microorganisms. NaCl and CMA may mobilize heavy metals in roadside soils (Backstrom et al. 2004). Sodium can affect soil fertility by exchanging with available nutrients in the soil complex that could eventually lead to cation leaching and subsequently to nutrient deficiencies (Bouzille et al. 2001).

Impacts of Chloride-based Deicers on Soil and Water

Excess soil salinity leads to deterioration of soil structure due to soil crusting and clogging of soil pores by entrapment of dispersed soil clay and silt particles (Morin 2000). Soil crusting reduces shoot emergence of subsurface seeds and root penetration of both surface and subsurface seeds, resulting in reduced plant establishment. Clogging of soil pores reduces a) soil space available for air and water retention and b) air and water penetration and permeation. Reduced soil aeration reduces oxygen supply to plant roots and can affect root growth.

Concentrations of sodium and chloride in soil near the edges of roads in Canada and in patrol yards are high enough to have adverse effects on sensitive soil organisms (Butler and Addison 2000). How seriously these effects impact soil ecosystem function have been difficult to gauge. Soil microorganisms have the ability to adapt to increased salinity to a certain extent, and can reestablish from unaffected areas. The dispersal capabilities of soil fauna such as earthworms are low, as most species are adapted to the relatively high humidity of the soil environment. Where affected areas are small enough - for example, strips of soil adjacent to roads - populations of impacted soil organisms may be able to be reestablished quite quickly if the unfavorable salt conditions are abated (Butler and Addison 2000).

Karraker et al. (2008) investigated the effects of road salt on water quality, by measuring water quality variables at 28 roadside pools and 14 forest pools. Water temperature, pH, dissolved oxygen (DO), and conductivity in each pool were measured monthly May through August. The results showed that the conductivity, pH, DO, and water temperature differed between forest and roadside pools. Mean conductivity was nearly 20 times higher in roadside (357.8 μS; range 11.6 – 2904.8 μS) than forest pools (18.6 μS; range 5.7 – 41.4 μS). Conductivity was strongly correlated with both sodium and chloride. Sixty-one percent of roadside pools had higher average conductivity than all forest pools. Conductivity in roadside pools declined exponentially with increasing distance from the road as shown in Figure 3 (Karraker et al. 2008).

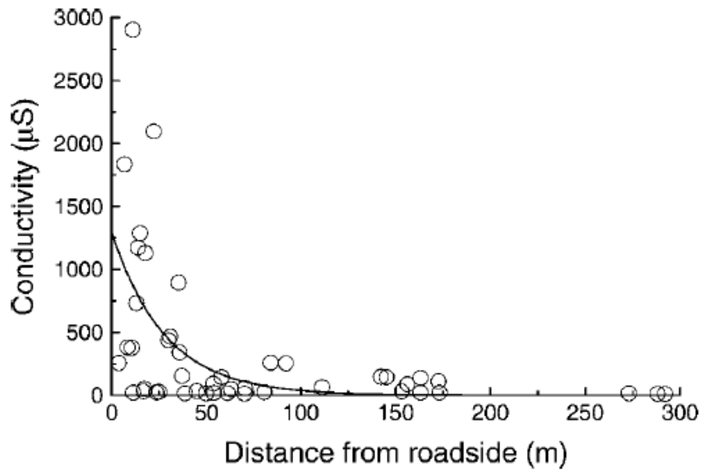

Figure 3: The relationship between conductivity and distance from the roadside (Karraker et al. 2008).

The results also showed that other water quality variables varied among roadside and forest pools and over time (Karraker et al. 2008). Mean water temperature was lower in roadside (48.9°F, 9.38°C) than forest (55.6°F, 13.1°C) pools. Mean pH was higher in roadside (5.3) than forest (4.7) pools. Dissolved oxygen (mg/L) was nearly one-third higher in roadside pools (3.6 mg/L) than in forest pools (2.0 mg/L). Conductivity, pH, and water temperature increased between May and August in both roadside and forest pools. Conductivity and DO in pools were similar in May among years. However, pH decreased and temperature decreased. Forest ponds were larger in perimeter than roadside ponds, but similar in maximum pond depth and canopy cover (Karraker et al. 2008).

It is important to note that deicer impacts on surface and ground waters depend on the site specific properties of the receiving water body. The quantity of rain and snowfall affect the dilution rate of the applied deicers and the flushing rate of the system (TRB 1991). Factors unique to each site can also influence potential impacts, such as temperature, topography, sunlight, and wind. Additionally surface waters have a wide array of physical, biological, and chemical cycles and interacting processes (Mayer et al. 1999). Field testing of chlorides has produced widely variable results from no observed effects (Jones et al. 1992; Baroga 2005), to highly elevated chloride concentrations (TRB 1991; Godwin et al. 2005; Environment Canada 2010).

Soil microorganisms are important for maintaining the structure, quality and fertility of soils. Microbial biomass, its activity and other parameters of soil microbial community are generally accepted as important indicators of soil quality and health. They can serve as early warning signs in the soil environment (Schloter et al. 2003). Černohlávková et al. (2008) investigated the effects of road salting on the quality of forest soils near the road in the Krkonoše Mountains in the Czech Republic. Physical and chemical properties, and microbial parameters of soils were determined and the toxic potentials of soil water extracts were evaluated using the bacterial tests (Microtox and *Pseudomonas putida* growth inhibition test). Increased concentrations of Na^+ ions (up to 100 mg/kg) and pH values up to 8 were found closer to the road. Microbial biomass and respiration activity were significantly reduced at the roadside, and the metabolic quotients showed signs of stress in the microbial community. Stimulated growth of *Pseudomonas putida* occurred in salinized samples closest to the road. In contrast, results showed the unsuitability of bacteria toxicity tests in such cases of pollution. Assessment of intrinsic soil microbial communities appears to be more ecologically relevant, showing effects that cannot be detected by bacterial toxicity tests.

Heavy Metal Leaching by Deicers

Research conducted in Sweden found that concentrations of cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) in soil adjacent to roadways were related to the use of deicing salts (Backstrom et al. 2004). The methods of mobilization of the heavy metals included ion exchange, lowered pH, chloride complex formation, and possible colloid dispersion. The researchers expressed concern about mobilization of heavy metals due to the use of NaCl as a deicing product and potential contamination to shallow ground water.

Soil columns leached with NaCl mobilized organic materials and iron oxides. The potential to carry adsorbed heavy metals along with them increases as electrolyte concentrations decrease (Amrhein et al. 1992; Norrstrom and Jacks 1998). Zinc and cadmium are far more susceptible to changes in pH and become more mobile with increasing acidity (Backstrom et al. 2004; Amrhien et al. 1992). Doner (1978) also performed soil column experiments with both chloride and perchlorate salts to test the theory of complexation as a mechanism of metal transport. Perchlorate has an ionic strength equal to chloride but is known to form very weak metal complexes. The results showed 1.1 to 4 times as much movement of cadmium, nickel and copper for chloride salt leachate as compared to the perchlorate leachate. Cadmium tends to be associated with readily leached compounds and is more mobile than other heavy metals when in soils (Norrstrom and Jacks 1998). The addition of chloride from deicer salts increases the mobility of cadmium via complexation with the chloride. The resulting negatively charged ligand complexes further compete with clay for cadmium ions (Lumsdon et al. 1995). This is also true, to a lesser extent, when CMAs are used by complexation with acetate (Amrheim et al. 1992). Cadmium has also been demonstrated to be more mobile in high salt concentrations by cation exchange with sodium, magnesium and calcium (Amrheim et al. 1992; Backstrom et al. 2004). Chromium is more closely associated with the transport of organic materials and occurs at higher levels when CMAs are used as deicers. This was also true for lead, copper and nickel (Amrhein et al. 1992).

In the Netherlands, a remediation facility consisting of a detention basin and a constructed wetland were tested for retention of heavy metals and Poly-Aromatic Hydrocarbons (PAHs) from road runoff (Tromp et al. 2012). This study found the system was very effective at removing PAHs, 90-95% removal; however, during application of deicers, concentrations of copper, zinc, cadmium, and nickel (Ni) were found to be much higher at the wetland effluent. The researchers recommended modifying the hydraulic management of the system, to bypass the road water runoff, during times when deicers are being used so as to maintain the integrity of the remediation facility.

Impacts of Chloride-based Deicers on Vegetation

Injury of woody plants along roadsides due to salt spray is the result of tissue drought or desiccation and is related to the penetration of phytotoxic ions of sodium and chloride through the stem, bud and leaf tissues (Barrick and Davidson 1980; Chong and Lumis 1990; Bryson and Barker 2002). With woody species, plant injury is often most extensive in the spring, though some plants are able to recover later in the growing season. Repeated injury, year after year, can reduce the vigor and growth of the plants. If the sodium and or chloride concentration are high enough in soil or plant tissue, a plant may be killed outright or may have extensive dieback, which results in plant weakening and death over a number of years (Sucoff 1975; Lumis et al. 1973). In addition, woody plants that are weakened by the repeated stress of road salt are more sensitive to disease, insects or abiotic stresses, such as winter injury or drought (Sucoff and Hong 1976).

According to Butler and Addison (2000), elevated concentrations of sodium and chloride in the substrate or soil can:

- inhibit water and nutrient absorption due to osmotic imbalances, reducing plant growth;

- cause nutritional imbalances for some species;
- cause long-term growth inhibition, or toxicity to plant cells, causing leaf burn or tissue death;
- cause deterioration of soil structure.

An additional impact of elevated chloride in roadside soils is the increased potential of heavy metal contamination (Butler and Addison 2000). Chloride forms complexes with heavy metals, rendering many of them more water soluble and therefore more available for uptake by plant roots. This would increase plant uptake of such metals, possibly resulting in plant toxicity, depending on the type and amount of metals present in the soil. Chloride-related mobilization of cadmium was found to occur through the soil, causing increased plant uptake of cadmium, with concentrations in plant shoots increased from 6.5 to 17.3 mg kg^{-1} and in roots from 47 to 106 mg/kg (Smolders and McLaughlin 1996).

Laboratory and experimental field studies have demonstrated that soil and spray applications of sodium and calcium chloride severely injure plants (Hall et al. 1972; Headley and Bassuk 1991; Dkhili and Anderson 1992). The seedlings of *Acer platanoides*, *A. rubrum*, *Quercus palustris*, and *Q. rubra* were subjected to soil-applied sodium chloride solutions at varying concentrations once every month beginning in October and ending in April, and were harvested in May. Growth measurements and shoot Na^+ and Cl^- content were analyzed. For all four species, plants in the November through February/March salt treatments sustained little plant damage and reduction in growth. The October application of NaCl resulted in heavy plant damage and reduced growth in each species, while April NaCl applications produced similar results in *A. rubrum* and *Q. palustris*. Shoot Na^+ and Cl^- concentrations were greater in plants in the October, March, and April salt treatments. In a second experiment, actively-growing, greenhouse-grown plants of the four species were subjected to either a fertilizer solution plus NaCl at every irrigation or a single application of NaCl followed by normal irrigation thereafter. *A. platanoides* lost its resistance to soil-applied NaCl by mid-summer, while *A. rubrum* and *Q. palustris* were sensitive to a high dosage of NaCl applied at this time. *Q. rubra* was resistant. In both experiments, there were significant interactions between the time of NaCl application and the periodicity of plant growth, with other parameters like soil temperature, precipitation, and leaching of the salt from the soil as well as genetic factors, which affected the amount of salt injury sustained. These findings present a strong case for altering deicing practices in an effort to reduce salt injury to plants near roads. In the critical times, like the dormant season, alternatives such as sand or cinders may be used, but potential impacts of alternative techniques should also be considered.

Death of stems, leaf, and flower buds, usually on first-year shoots, are the commonly observed impacts to deciduous woody plants from deicers. The damage observed in Massachusetts on most plant species was manifested as burning or browning of the leaves or needles, when applications of 240 lbs/l-m of sand and 12 lbs/l-m of salt were used to treat roads (Bryson and Barker 2002). Coniferous species, especially pines (*Pinus spp.*), were sensitive to NaCl injury. In coniferous species, the damage appeared as browning on the ends of the needles, but new growth was not affected. Most of the damage occurred on the needles on the side of the tree that faced the road and where salt spray from cars or plows could have been a factor in the degree of damage. Widespread damage was also seen on spruce (*Picea spp.*), sumac (*Rhus typhina*), and mountain laurel (*Kalmia latifolia*) along roadsides. Species in the same areas showing little to no damage were oaks (*Quercus spp.*), maples (*Acer spp.*), grasses (mixed species), ferns (mixed species), and yarrow (*Achillea millefolium*) (Bryson and Barker 2002). The Na concentrations in the leaves of pines, sumacs, grasses, and oaks decreased as the distance from the road increased. The Na concentrations in pine needles were 3356 mg/kg at 10 ft, 1978 mg/kg at 15 ft, and 1513 mg/kg at 20 ft. The Na concentrations in maple leaves also decreased with distance from the road (e.g., 249 mg/kg at 10 ft and falling to 150 mg/kg at 30 ft). The concentrations of Na in roadside soil ranged from 101 mg/kg at 5 ft to 16 mg/kg at 30 ft from the roadside, with a marked decrease in the Na concentration in the soil after 15 ft. The pH decreased as the distance from the road increased ranging from 7.60 at 5 ft to 5.78 at 30 ft. The electrical conductivity values decreased as the distance from the road increased and ranged from 0.16 dS/m at 5 ft to 0.12 dS/m at 30 ft.

Dirr (1978) pointed out that the pattern of plant injury and elevated soil or tissue chloride levels should be used to confirm that the cause of the damage is de-icing salts. The following injury patterns are associated with road salt injury to plants: a linear pattern along roads or in areas where runoff from roads collects; injury is more severe on the side of the plant facing the road; injury decreases with distance from the road; injury is worse on the downwind side of the road; parts of woody plants that are covered by snow or were sheltered from spray lack injury symptoms; parts of trees that are above the salt spray zone are not injured or are injured less; salt spray injury extends only a short distance into dense plants; injury in coniferous trees becomes evident in late winter and continues into the growing season; and injury in deciduous trees becomes evident in spring when growth resumes and continues into the growing season (Lumis et al. 1973; Dirr 1978).

Research found that cranberry bogs with chloride concentrations of 250 ppm or greater, from deicing salts, would be cause for concern and may require remediation (DeMoranville 2005). The author proposes setting a low water quality standard of 100 ppm for Cl (165 ppm NaCl) for the water supplies. The author cautions that at 100 ppm chloride chronic effects on cranberry bogs can be observed if present for the 2 month irrigation season.

Impacts of Chloride-based Deicers on Wildlife and Aquatic Species

Salt has negative effects on aquatic organisms by altering the osmotic balance between the organism and its surrounding environment. Salt concentrations less than those of the organism's protoplasm or other fluids are common in freshwater and most terrestrial soils, and so the organisms must expend energy to prevent simple diffusion of salts out of their bodies (Findlay and Kelly 2011). If concentrations rise to surpass the isotonic point of the organism, it faces the converse problem of an inwardly directed diffusion gradient and must either exclude ions or actively excrete those that may cross their integument/membrane. Threshold levels for salt effects vary widely across organisms and/or life stages (Findlay and Kelly 2011).

Many studies have addressed the effects of chloride-based deicers on wildlife species, and research has revealed that road salt exposure negatively affects mammals, birds, invertebrates, and amphibians that utilize roadside habitats (Vitt et al. 1990; Mineau and Brownlee 2005; Ramakcrishna and Viraraghavan 2005; Harless et al. 2011; Karraker and Gibbs 2011). However, most field data are correlative, where investigators survey a range of water bodies that may vary in salt loads but undoubtedly also vary in other contaminants (Peters 2009). In a survey of macroinvertebrates in urban streams, Cuffney et al. (2010) found that the chloride ion was frequently and strongly associated with indicators of poor macroinvertebrate communities, but it was acknowledged that other measured (and probably unmeasured) solutes co-varied with chloride, which may have included stream geomorphology, habitat availability, or any of the metals or organic compounds associated with urban runoff or wastewaters.

The deposition of chemical pollutants into roadside wetlands from runoff is a current environmental concern. In northern latitudes, a major pollutant in runoff water is NaCl from deicers. Collins and Russell (2009) conducted a survey from 26 roadside ponds for amphibian species richness and chloride concentration and concluded that chloride concentrations in ponds due to application of de-icing salts, influenced community structure by excluding salt intolerant species.

Wildlife mortality along roadsides where salt has been applied has been documented (Trainer and Karstad 1960; Clark 1981). Such mortality often goes unreported or is attributed to vehicle strikes, with salt acting as a ‘‘fatal attractant’’ (Clark 1981). Mortality among songbirds is reported most commonly in cardueline finches (crossbills, grosbeaks, and siskins) (Tozer 1994).

Many studies have found that as salinity increases, survivorship and mobility decrease (Sanzo and Hecnar 2006; Karraker and Ruthig 2009; Denoel et al. 2010). Amphibians are likely to be the most affected by chemical and deicer runoff. Amphibians possess highly permeable skin and have aquatic larval stages, and many use roadside wetlands for breeding (Harless et al. 2011). Amphibians are considered good indicators of ecosystem health, and inhabit a wide range of habitats (wetlands, ephemeral water bodies, road side ditches, etc.) and for these reasons extensive toxicity testing has been conducted using amphibians (Vitt et al. 1990). Of the amphibian species tested, salamanders may be the most intolerant amphibians to varying salt concentrations (Collins and Russell 2009). Road salts and heavy metals have been shown to have the greatest impacts on amphibians (Birdsall et al. 1986; Sanzo and Hecnar 2006). Studies have found that chloride concentration spikes that occur during spring runoff and from direct runoff from the road threaten embryonic and larval stages of amphibians (Collins and Russell 2009). The effects of hyposalinity on the wood frog (*Rana sylvatica*) included a significant decrease in body weight, not undergoing metamorphosis, decreased activity and increased developmental abnormalities, and death (Sanzo and Hecnar 2006). The extended time to metamorphose has been found to further reduce amphibian survival due to predaceous aquatic beetles and fish (Herreid and Kinney 1966; Breven 1990).

Even between amphibian species, toxicity is highly variable. For example road salts were found to significantly affect embryonic survival of the spotted salamander (*Ambystoma maculatum*), while having little effect on the green frog (*Rana clamitans*) (Karraker and Ruthig 2009). It was found that for salamander eggs, salt concentrations must be less than 450 mg/L for half the eggs to be viable. Another study with field surveys found that spotted salamander and wood frogs (*Rana sylvatica*) did not occupy high chloride ponds, and acute toxicity tests (LC_{50}) found them to be more sensitive than the American toad (*Bufo americanus*) to chloride (Collins and Russell 2009). Spring peepers (*Pseudacris crucifer*) and green frogs (*Rana clamitans*) showed intermediate sensitivities (Collins and Russell 2009).

Karraker et al. (2008) evaluated the effects of road salt on two common vernal-pond-breeding amphibian species, the spotted salamander (*Ambystoma maculatum*) and the wood frog (*Rana sylvatica*). It was found that in the Adirondack Mountain Region of New York, road salt traveled up to 172 m from the highway into wetlands. Surveys showed that egg mass densities of spotted salamanders (*A. maculatum*) and wood frogs (*R. sylvatica*) were two times higher in forest pools than roadside pools, but this pattern was better explained by road proximity than by increased salinity. Experiments demonstrated that embryonic and larval survival were reduced at moderate (500 µS) and high conductivities (3000 µS) in *A. maculatum* and at high conductivities in *R. sylvatica*. Demographic models suggest that the observed egg and larval stage impacts from salt may have important impacts on populations near roads, particularly in the case of *A. maculatum*, for which salt exposure may lead to localized extinction. For both species, the effect of road salt declined rapidly with distance from the roadside, with the greatest impacts observed within 165 ft (50 m). Based on this evidence, it can be argued that efforts to protect local populations of *A. maculatum* and *R. sylvatica* in roadside wetlands should, in part, be aimed at reducing application of road salt near wetlands with high conductivity levels.

A study looked at six commonly used deicers (urea, NaCl, $CaCl_2$, $MgCl_2$, KAc, and CMA) and their toxicity to larval wood frogs (*Rana sylvatica*). Survival was inversely related to higher concentrations for all deicers tested (Harless et al. 2011). Tadpole survival had significantly lower threshold concentrations for all deicers. Acetate based deicers had lethal effects on tadpoles at the lowest concentrations. $CaCl_2$ and $MgCl_2$ were found to be more toxic to frog tadpoles than NaCl, most likely because they have two chloride ions per molecule (Dougherty and Smith 2006; Harless et al. 2011). Interestingly, LC_{50} values decreased with time, suggesting that organisms were either less capable of tolerating deicers over time, or that there was a lag in the lethal effect (Harless et al. 2011). The relative toxicity scale for larval and tadpole frogs was: *NaCl<$MgCl_2$=$CaCl_2$<Acetate based* (Harless et al. 2011).

In a recent study by Pilgrim (2013) toxicity testing was conducted on fathead minnow, *Ceriodaphnia dubia*, *Selenastrum capricornutum* using eight unique chloride, acetate, glycerol, and agriculturally derived deicing products. They were able to rank product toxicity and found (least toxic to most toxic): NaCl<CaCl2<MgCl2<KAc. The test results also indicated that added corrosion inhibitors contribute to toxicity, but this was not further investigated in this study. They also found that certain species were more sensitive to exposure period, such that *Ceriodaphnia dubia* was more sensitive to chronic exposure periods, than acute exposure periods. The authors cautioned that factors such as application rates, length of road that contributes runoff, and site specific climatic factors need to be considered.

Riva-Murray et al. (2002) found that declines in several indices of macroinvertebrate "health" were correlated with higher chloride concentrations, but the absolute levels were so low (less than 50 mg/L) that it is unlikely that direct toxicity was causing the patterns. Thus, while it is fair to say that chloride is associated with negative effects on benthic insects at low concentrations, other contaminants and stressors are most likely affecting populations as well.

Experiments focused on altering salt levels in surface waters have been rare but do provide more direct links between salt concentrations and response variables. For example, NaCl was added to reach ambient concentrations of 1,000 mg Cl^-/L in a stream, and resulted in changes in benthic algae and protozoans within one to a few weeks after initiation of the experiment (Dickman and Gochnauer 1978; Evans and Frick 2002). In another study, Cl^- was added to levels of 2,165 mg/L, and caused an increase in drift of benthic insects out of the experimental sub-channels placed in an Ontario stream within a few hours (Crowther and Hynes 1977).

Research testing the acute toxicity of chloride on four freshwater invertebrate species, including water flea (*Ceriodaphnia dubia*), fingernail clam (*Sphaerium simile*), planorbid snail (*Gyraulus parvus*), and tubificid worm (*Tubifex tubifex*), was completed under different levels of water hardness (all four species) and sulfate concentrations (*C. dubia* only) (Linton and Soucek 2008). Tests with *C. dubia* using different levels of total water hardness and sulfate were performed simultaneously by two different laboratories (Linton et al. 2008). Results were comparable. The 48-h LC_{50} for *C. dubia* acclimated and exposed to acutely lethal chloride concentrations at 25 to 50 mg/L hardness (i.e., 919 mg/L) is approximately half that of *C. dubia* exposed at 600 to 800 mg/L hardness. Conversely, sulfate over the range of 25-600 mg/L exerted only a small (inverse) effect on chloride toxicity to *C. dubia*. The mean 48-h LC_{50} at 25 mg/L sulfate was approximately 1,356 mg/L, while at 600 mg/L sulfate, it was 1,192 mg/L, a reduction of 12%. Again, LC_{50} values between labs were consistent. Ninety-six hour LC_{50} values for three other freshwater invertebrate species ranged from a low of 740 mg/L for *S. simile* exposed to chloride at 50 mg/L hardness, to a high of 6,008 mg/L for *T. tubifex* exposed to chloride at 200 mg/L hardness. For both these species, increasing the acclimation and dilution of water hardness reduced the acute toxicity of chloride by approximately 1.4 to 1.5 times. Water hardness did not appear to influence the acute toxicity of chloride to the planorbid snail, *G. parvus*. Acute LC_{50} values at 50 and 200 mg/L hardness were 3,078 and 3,009 mg/L, respectively. Rank order of sensitivity to acutely lethal chloride at a given water hardness is in the order (most to least): *S. simile*>*C. dubia*>*G. parvus*>*T. tubifex*.

Siegel (2007) tested toxicity thresholds for NaCl and chloride for various species and found freshwater aquatic species react differently to varying exposure concentrations. Based on these findings, invertebrate species appear to be more sensitive to chloride than are vertebrate species, with fathead minnow being the most sensitive species tested (Siegel 2007).

Salt tolerance of aquatic species varies tremendously. Depending on whether fish are fresh or salt water species, fish have been reported to tolerate between 400 and 30,000 mg/L of NaCl (Siegel 2007). Road salting and increased salinity can lead to excess growth of salt tolerant species (Siegel 2007). Interestingly, aquatic species may adapt to increased levels of chloride with time, such that surviving organisms may develop the means by which to handle the osmotic shock imposed by the excess chloride (Mineau and Brownlee 2005). Furthermore, saltwater species are not vulnerable to anthropogenic sources of NaCl, except for fluctuations of greater than 10%.

There is a wide range in salt concentrations known to have negative effects on organisms, and most of these data come from laboratory exposures under controlled conditions with only one stressor (salt) acting at a time. For many organisms, the short-term lethal concentrations are far above levels seen in the environment, except under extreme conditions (Findlay and Kelly 2011). For example, adult freshwater fish species do not show lethal effects until concentrations approach tens of grams of salt per liter (Figure 4). Young fishes show negative effects at much lower levels, but even so, these concentrations are roughly equivalent to those seen in direct road runoff, which are much higher than concentrations occurring after dilution by water sources. Effects near roads are, of course, more evident than for points further from the actual area of salt application with reasonably sharp declines in concentrations within tens of meters of the road (Lax and Peterson 2009; Albright 2005).

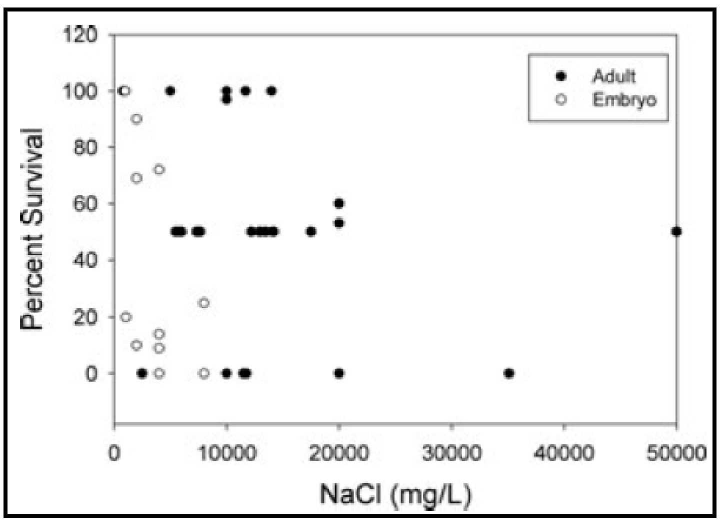

Figure 4: Survival of fish exposed to various concentrations of NaCl in short- and long-term tests (Findlay and Kelly 2011).

Spring rains have been postulated to dilute deicers following input into waterways. One study tested this theory and found spring rains may help when low to moderate chloride concentrations are present, but in situations where water lacks outflow or flushing and chloride concentrations reach 1000 mg/L, permanent damage can occur to egg membranes (Karraker and Gibbs 2011).

Biotoxicity work for Colorado DOT on the boreal toad tadpole, juvenile rainbow trout, *Ceriodaphnia* (aquatic invertebrate), and *Selenastrum* (algae) found that application rates of $MgCl_2$ typically used are highly unlikely to cause or contribute to environmental damage at distances greater than 20 yards from the roadway (Lewis 1999). Work in Chautauqua Lake, New York on sunfish found that NaCl contributed to toxicity but zinc and cadmium were also found to be of concern (Adams-Kszos et al. 1990). A study in Washington observed deicer impacts on

Steelhead (*Oncorhynchus tshawytscha*), Chinook salmon (*Oncorhynchus mykiss*), and bull trout (*Salvelinus confluentus*), threatened and endangered species, and general stream ecology (Yonge and Marco 2001). Elevated chloride concentrations from 5 to 8 mg/L were found, but the authors suggested the deicing activities did not adversely impact the stream ecology.

In Iowa, the US EPA tested acute toxicity of chloride to four freshwater species, water flea (*Ceriodaphnia dubia*), fingernail clam (*Sphaerium simile*), planorbid snail (*Gyraulus parvus*), and tubificid worm (*Tubifex tubifex*) under varying concentration of sulfate and levels of water hardness (Linton and Soucek 2008). The study found that for two species (*S. simile* and *T. tubifex*), increasing the acclimation and dilution of water hardness reduced the acute toxicity of chloride by up to 1.5 times, while sulfate was found to negatively impact chloride toxicity by up to 12% for *C. dubia*.

Research conducted on aircraft and airfield deicers and dust suppressants has laid the foundation for toxicity testing of roadway deicers. Work by Pillard (1995) investigated the toxicity of ethylene and propylene glycol and the associated aircraft deicer additives on *Ceriodaphnia dubia* and *Pimephales promelas*. Corsi et al. (2006; 2009) reported aquatic toxicity data for airfield pavement deicers, KAc and Sodium Formate (NaFm) using US EPA tests methods (US EPA 2002a,b), and aquatic organisms *Vibrio fischeri*, *Pimephales promelas*, *Ceriodaphnia dubia*, and *Selenastrum capricornutum*. The Airport Cooperative Research Program (ACRP) published an extensive document on developing new formulations for aircraft deicers that have lower toxicity and BOD (ACRP 2008). Aircraft deicers tested were acetate and formate based products and ethylene and propylene glycols. Toxicity testing was conducted using US EPA methods on fathead minnow, *daphnia magna*, and rainbow trout. Chauhan et al. (2009) reported that airport runway deicers (e.g., acetates) feature a typical *Daphnia magna* 48-hr LC_{50} value of 1,000 mg/L and a typical *Pimephales promelas* (fathead minnow) 96-hr LC_{50} value of 1,000 mg/L, whereas the more eco-friendly proprietary alternatives featured LC_{50} values up to 4,875 mg/L. For chronic toxicity, common airport runway deicers had *C. dubia* IC_{25} values typically in the range of 400-820 mg/L, and *P. promelas* LC_{25} values typically in the range of 180-280 mg/L, whereas the more eco-friendly proprietary alternatives featured IC_{25} values in the range of 1,100 to 2,600 mg/L.

Aquatic vegetation is similarly vulnerable to the changes in salt concentrations. One algal species has demonstrated extreme sensitivity to exposures to chloride; with concentrations of 71 mg/L inhibiting growth and chlorophyll production, while others can tolerate chloride concentrations between 886 mg/L and 36,400 mg/L (US EPA 1988). An increase in chloride may also allow for non-native species to become more predominant. Other aquatic plants exhibit various sensitivities, with growth inhibition observed in desmids at 200 mg/L, mean effective concentration (EC_{50}) equal to 1482 mg/L in diatoms, and reduced growth and reproduction at 1820 mg/L in angiosperm (US EPA 1988). Although noteworthy, the sensitivities exhibited by the algae and desmids do not weigh into the final threshold determination because the toxicity tests were not conducted with measured concentrations of chloride, a biologically significant endpoint, and an aquatic plant of consequence in U.S. waters.

Bollinger et al. (2005) completed a study of the toxicity of NaCl to house sparrows. In this study, the up-and-down method was used in a pilot study to estimate the lethal oral dose of granular NaCl in wild caught house sparrows. The toxicity of highly concentrated NaCl solution was also investigated. This was followed by an acute dose response study in which house sparrows were dosed orally with granular NaCl at 0, 500, 1,500, 2,500, or 3,500 mg/kg. Sparrows were deprived of water for 6 hr post-exposure in an attempt to mimic specific winter conditions. Groups of three birds at each dose were euthanized at 1, 3, 6, and 12 hr intervals post-exposure, and samples were collected for histopathology and brain and plasma electrolyte analyses. Results indicated an approximate mean lethal dose (LD_{50}) of 3,000 to 3,500 mg/kg in water-deprived birds, which is similar to mammalian values (Figure 5). House sparrows dosed with a concentrated solution of NaCl generally died at doses of 8,000 mg/kg. Clinical signs observed at > 1,500 mg/kg included rapid onset (< 30 min) of depression (indicated by reduced activity and reduced response to visual and auditory stimuli), ataxia, inability to fly or perch, and death in as little as 45 min. Birds that survived for 6 hours usually recovered. Plasma Na^+ concentrations > 200 mmol/L were consistently associated with clinical signs. Pathologic lesions consisted of edema and distension of the caudoventral thin muscled region of the gizzard and were observed 1 hr post-exposure in most birds dosed with >500 mg/kg. Brain Na^+ concentrations in clinically ill sparrows and those that died of NaCl toxicity ranged from 1,297 to 1,615 ppm wet weight or 5,603 to 6,958 ppm dry weight, which differed significantly from control birds. No histologic lesions were observed in brain sections of exposed birds, likely reflecting the acute nature of the exposure. However, fluid accumulation beneath the koilin layer of the gizzard was observed in the majority of birds at high dosage levels. These results indicate that ingesting relatively small numbers of road salt granules or small quantities of highly concentrated NaCl solutions can cause sodium poisoning in house sparrows.

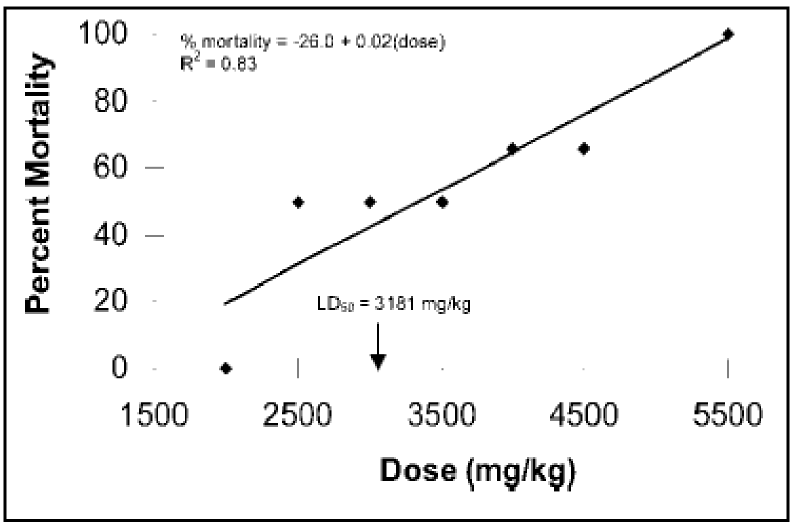

Figure 5: Effects of oral dose of NaCl on mortality of house sparrows (Bollinger et al. 2005).

Models have shown that cyanide has potential to impact some species in areas of high road salt use (Environment Canada 2001). Sodium ferrocyanide and ferric ferrocyanide are used to prevent clumping of solid chloride-based deicers while in storage and during deicing operations (Letts 2000). In Canada, sodium ferrocyanide was added to rock salt at a range of 30 to 240 mg/kg of salt. Potassium ferro- and ferricyanide solutions were originally believed to be much less toxic (no effect at 2000 to 8732 ppm), but due to a fish kill in a stream caused by ferro- and ferricyanides from industrial effluent, it was found that photo-decomposition can release the cyanide ion (Burdick and Lipschuetz 1950). Experimental results found ferro- and ferricyanides to be toxic at 1 to 2 ppm when photodecomposition was considered (Burdick and Lipschuetz 1950).

Photoenhancement, or increased aquatic toxicity due to a chemical transformation of a substance due to UV exposure, was also observed by Little and Calfee (2000), when testing the toxicity of sodium ferrocyanide (from yellow prussiate of soda (YPS) used in fire retardant). Rainbow trout (*Onchorhyncus mykiss*) and Southern leopard frog (*Rana sphenocephala*) were exposed to various fire retardants and UV light treatments. Rainbow trout were always more sensitive to fire retardants than the Southern leopard frog, and both species were equally affected by low concentration of YPS alone when exposed to UV. Cyanide agents can interfere with fish gills impeding breathing causing death (MPCA 2000). In Minnesota, run-off from salt piles was reported to contain between 5 and 40 times the amount of free cyanide than is toxic to half of the fish exposed, caused by concentrated runoff from salt piles that were improperly managed at that time (MPCA 2000).

After reviewing available research, Environment Canada came to the following conclusions about the environmental impacts of road salts: “Based on the available data, it is considered that road salts that contain inorganic chloride salts with or without ferrocyanide salts are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity or that constitute or may constitute a danger to the environment on which life depends. Therefore, it is concluded that road salts that contain inorganic chloride salts with or without ferrocyanide salts are ‘toxic’ as defined in Section 64 of the Canadian Environmental Protection Act, 1999 (CEPA 1999).” (Environment Canada 2001)

Assessing Chloride-based Deicer Toxicity

The most commonly used tools to assess toxicity are the laboratory acute and chronic tests, which apply varying concentrations of a contaminant to a selected species. The information gained from these tests is specific to the species tested and can be used to assess damage at the cellular and subcellular level of organisms. For this reason hundreds if not thousands of species have been tested in this fashion to gather as much information as possible.

Laboratory Testing

The purpose of toxicity testing is to determine the highest concentration of a substance that is safe or has no effect on a population. For toxicity testing, this is usually measured as hatchability, morphological abnormalities, growth, and reproduction, and is reported as the highest concentration with no effect as compared to the control samples (US EPA 2002b).

Test methods

Commonly used test methods include:

Short-term Chronic Toxicity (fresh water organisms)

- ❖ Fathead minnow, *Pimpephales promelas*
  - Larval Survival and Growth Test Method 1000.0 (US EPA 2002b, pg. 53)
  - Embryo-larval Survival and Teratogenicity Test Method 1001.0 (US EPA 2002b, pg.112)
- ❖ Daphnid, *Ceriodaphnia dubia*
  - Survival and Reproduction Test Method 1002.0 (US EPA, 2002b, pg. 141)
- ❖ Green alga, *Selenastrum capricornutum*
  - Growth Test Method 1003.0 (US EPA 2002b, pg. 197)

Acute toxicity (fresh water organism)

- ❖ Daphnia, *Ceriodaphnia dubia* (US EPA Test Method 2002.0)
- ❖ Daphnids, *Daphnia pulex* and *D. magna* (US EPA Test Method 2021.0)
- ❖ Fathead minnow, *Pimephales promelas* (US EPA Test Method 2000.0)
- ❖ Rainbow trout (*Onchorhynchus myskiss*) and Brook trout (*Salvelinus fontinalis*) (US EPA Test Method 2019.0)

Acute toxicity tests are designed to provide dose-response information, expressed as the LC_{50} within a prescribed period of time (24-96 h), or the highest effluent concentration in which survival is not statically significantly different from the control (US EPA 2002a). Sub-chronic and chronic toxicity testing measures the adverse effects to an organism when exposed continuously or repeatedly for multiple days to weeks (US EPA 2002b). The frequency of testing is determined by the regulatory agency. Static non-renewal, static-renewal, and flow-through tests can be used, but the flow-through method using continuous sampling is recommended for on-site tests (US EPA 2002b).

- Static non-renewal: test organisms are exposed to the same test solution for the duration of the test.
- Static-renewal: test organisms are exposed to fresh solution of the same concentration of sample every 24 hours or other time interval.
- Flow-through: sample is pumped continuously from the sample point directly into the dilutor, or grab or composite samples are collected and placed in a holding tank and pumped continuously from the holding tank into the test chamber.

The identified advantages of using the static-renewal tests are significant enough to be the recommend testing option, if flow-through testing is not feasible. The disadvantages are limited to requiring a greater volume of effluent for testing and a potential loss of temporal variation caused by test organism waste.

The water used for testing should be collected, handled, and stored based on practices discussed in US EPA (2002a). The water used for culturing and test dilution should be analyzed for toxic metals, organics, PCBs, and pesticides (US EPA 2002a).

Variability of test results can be caused by "the experience and skill of the laboratory analyst; test organism age, condition, and sensitivity; dilution water quality; temperature control; and the quality and quantity of food provided" (US EPA 2002a). For this reason, toxicity testing should be completed in laboratories with the appropriate facilities and experience.

Species

Laboratory test species approved for short-term chronic toxicity include: fathead minnow (*Pimephales promelas*), the daphnid (*Ceriodaphnia dubia*), and green alga (*Selenastrum capricornutum*) (US EPA 2002b). Laboratory test species approved for freshwater acute toxicity testing include: daphnid (*Ceridaphnia dubia*), daphnids (*Daphnia pulex* and *D. magna*), fathead minnow (*Pimephales promelas*), rainbow trout (*Oncorhynchus mykiss*) and brook trout (*Salvelinus fontinalis*) (US EPA 2002a). Additional test organisms are approved and can be found in Appendix B US EPA (2002a).

Purchased, laboratory grown, or naturally occurring (wild caught) organisms should be observed for viability prior to testing (US EPA 2002b). Methods for culturing organisms in the lab can be found in US EPA (2002a), and methods for collecting organisms from the field can be found in US EPA (1993). Manufacturers of purchased organisms should provide evidence of quality control measures (US EPA 2002b). The life stage of the organism should be considered and consistent among tests (US EPA 2002b). The size of the testing chamber can vary, and is based on the size of the test organism. Quality food should be provided to the testing organisms (US EPA 2002a; b).

The life stage of the test organism is important to consider, given that young organisms are often more sensitive to toxicants than are adults (US EPA 2002a). "For this reason, the use of early life stages, such as first instars of daphnids and juvenile mysids and fish, is required for all tests. In a given test, all organisms should be approximately the same age and should be taken from the same source. Since age may affect the results of the tests, it would enhance the value and comparability of the data if the same species in the same life stages were used throughout a monitoring program at a given facility (US EPA 2002a)."

Calculations

For test results to be acceptable, control survival must equal or exceed 90% (US EPA 2002a). For a short-term chronic toxicity test to be valid, the amount of organisms surviving and final dry weight (fathead minnow) or the quantity of young produced (daphnid), or number of cells/mL (green alga) must be met (US EPA 2002b). The precision and accuracy of the data should be compared with previous results or work by others. Additional information on this topic can be found in the Technical Support Document for Water Quality-Based Toxics Control (US EPA 1991b, pg. 2-4, 11-15).

The most common methods of calculating and reporting toxicity data are presented below:

NOEC – No-Observed-Effect-Concentration (acute & chronic)

The no-observed-effect-concentration (NOEC) is the highest concentration of toxicant to which organisms are exposed in a full life-cycle or partial life-cycle (short-term) test that causes no observable adverse effect on the test organisms (i.e., the highest concentration of toxicant to which the values for the observed responses are not statistically significant from the controls) (US EPA 2002b).

NOAEC - No-Observed-Adverse-Effect Concentration (acute)

The no-observed-adverse-effect concentration (NOAEC) is defined in terms of mortality and is recommended for use when testing toxicity of multi-concentration effluent (US EPA 2002a).

LOEC – Lowest-Observed-Effect-Concentration

The lowest-observed-effect-concentration (LOEC) is the lowest concentration of toxicant to which organisms are exposed in a life-cycle or partial life-cycle (short-term) test, which causes adverse effects on the test organisms (i.e., where the values for the observed responses are statically significantly different from the controls) (US EPA 2002b).

EC - Effective Concentration

The effective concentration (EC) is a point estimate of the toxicant concentration that would cause an observable adverse effect, an all-or-nothing response (such as death, immobilization, or serious incapacitation) in a given percent of the organisms, calculated by point estimation techniques (US EPA 2002b). If the observable effect is death or immobility, the term, **Lethal Concentration (LC)**, should be used. Certain EC or LC values might be judged from a biologic standpoint to represent a threshold concentration, or lowest concentration that would cause an adverse effect on the observed response.

LC_{50} (acute- and chronic-survival)

The LC_{50} is concentration of toxicant that would cause death of 50% of the test population (US EPA 2002b). The higher the LC_{50} value the lower the toxicity.

IC – Inhibition Concentration (IC_{25}&IC_{50})

The inhibition concentration is the toxicant concentration that would cause a given percent reduction in a non-quantal biological measurement for the test population (US EPA 2002b). For example, the IC_{25} is the concentration of toxicant that would cause a 25% reduction in mean young per female or in growth for the test population, and the IC_{50} is the concentration of toxicant that would cause a 50% reduction.

NOECs and LOECs are determined by hypothesis testing. Common test methods include: Dunnett's Test, a T test with the Bonferroni adjustment, Steel's Many-one Rank Test, or the Wilcoxon Rank Sum Test with the Bonferroni adjustment (US EPA 2002b). NOECs and LOECs assume either a continuous dose-response relationship or a non-continuous (threshold) model of the dose-relationship. The LCs, ICs, and ECs are determined by point estimation techniques using: Probit Analysis, Spearman-Karber Method, Trimmed Spearman-Karber Method, Graphical Method or Linear Interpolation Method (US EPA 2002b); however, LC, IC, and EC are derived from mathematical models that assume a continuous dose-response relationship. Other statistical analysis methods can be used as well.

The analysis methods to be used for growth and reproduction of fathead minnow and daphnid, and growth response of green alga can be determined using Figure 6 (US EPA 2002b).

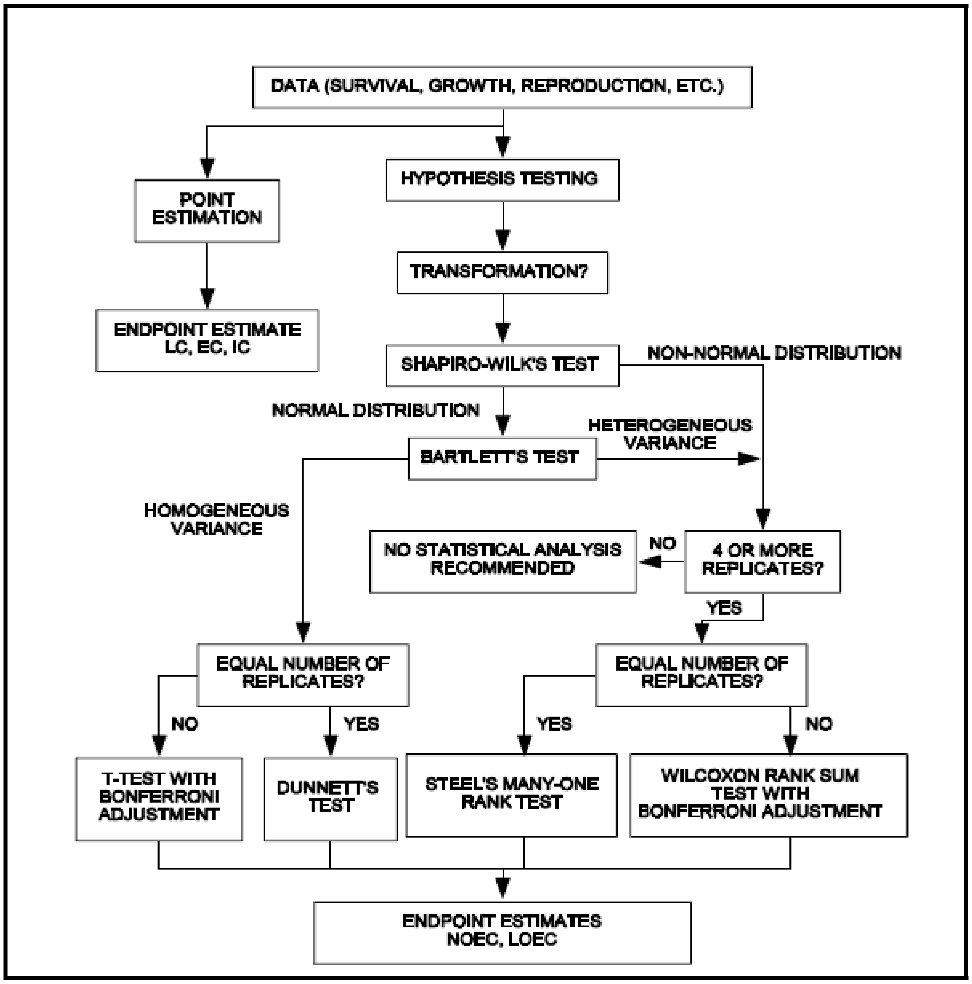

Figure 6: Flow chart of statistical analysis methods of test data (taken from US EPA 2002b).

Analysis of mortality data can be done using various techniques (US EPA 2002b, section 9.5.5, pg. 42). A description of the various hypothesis tests mentioned above can be found in US EPA (2002b, 9.6, pg.44).

Variables to Consider

Temperature of the test chamber(s) should be continuously monitored, and dissolved oxygen and pH should be monitored daily (US EPA 2002a). Monitoring of salinity or conductivity, total residual chlorine, total alkalinity, total hardness, and total ammonia should also be considered (US EPA 2002a). In addition to the type and life stage of aquatic species, the variables discussed below are also typically considered in the laboratory investigation of product toxicity.

Product Concentration & Range Finding Tests

Based on the *Whole Effluent Toxicity: Guidelines for Establishing Test Procedures for the Analysis of Pollutants Supplementary Information Document*, effluent testing for toxicity should include a minimum of five effluent concentrations and a control (US EPA 1995). Example test effluent concentrations provided include: 100% effluent, 75% effluent, 50% effluent, 25%

effluent, and 12.5% effluent (US EPA 2002b). Product concentrations to be used in laboratory testing of deicer toxicity may need to be determined using range finding tests. Range finding tests are not required by the US EPA (2000a) but may be necessary if testing a product or effluent of unknown toxicity. Because limited research on the toxicity of chloride-based deicers has been completed, range finding tests may be necessary for each individual product.[1] A range finding study is an acute toxicity test of groups of five organisms that allows the determination of an appropriate concentration range for the tests to be conducted. Tests are run over an 8 to 24-hr period. An example of a range finding test would be to use concentrations of 1, 10, 100 and 1000 ppm of toxicant and a control. From these results a smaller range of toxicity can be bracketed, such as from 10 to 100 ppm. Then the formal tests can be run at the more focused concentrations of 10, 50, 100 and 200 ppm, for example.

Water Temperature and Flow Rate

The US EPA (2002a; b) test methods specify testing temperature ranges for the chronic and acute test methods. These test methods recommend continuous monitoring of water temperature. For static non-renewal and static-renewal test methods, water flow rate is not relevant. For flow-through testing, water flow rate can be considered and is specified in US EPA (2002a; b).

Water hardness

Water described as "hard" contains high amounts of dissolved magnesium and calcium (Ramakcrishna and Viraraghaven 2005), which may be compounded by the application of $MgCl_2$ and $CaCl_2$ deicers. Hard water is not a health hazard. In fact, the National Research Council states that hard drinking water generally contributes a small amount toward the total calcium and magnesium needed in the human diet (US EPA 2012). The US EPA established standards for drinking water, which are designed to protect health and ensure that the public water supply is of good quality (US EPA 2012). Standards fall into two categories: Primary Standards and Secondary Standards. Public water system operators are required to provide annual water quality reports, referred to as consumer confidence reports (CCRs). The CCR may include information about the hardness level of the water delivered. For private water supplies, water hardness testing can be done at most water testing laboratories. In addition, a variety of water hardness test kits and dip strips are available for purchase, which are generally easy to use, relatively inexpensive, and can provide a good estimate of hardness. Deicers can be a source of calcium and magnesium which can increase water hardness (US EPA 2012). Since $MgCl_2$ and $CaCl_2$ can affect water hardness, there is most likely a relationship between water hardness and deicer toxicity.

A report was published in 2009 on detailed work completed by the Iowa Department of Natural Resources and US EPA, in which additional toxicity testing was completed to assess the toxicity of chlorides on more sensitive aquatic species (compared to rainbow trout (*Onchorhynchus mykiss*) and fathead minnow (*Pimephales promelas*)), and to gather additional long-term chronic exposure data. Findings from this testing includes the following:

- Species were found to be more sensitive to short term, acute exposures of elevated chloride concentrations, and the agencies recommended using a final acute criterion of 682 mg/L (instead of 860 mg/L).
- The Acute to Chronic Ratio (ACR) for the more sensitive species tested, which are lower order organisms than previously tested, resulted in a higher recommended chronic criterion of 406 mg/L (instead of 230 mg/L).
- Increased water hardness and sulfate ions buffer against potential toxic effects of chloride.

[1] The final report from Clear Roads titled *Determining the Toxicity of Deicing Materials* (Pilgrim 2013) provides range finding data for specific NaCl, $MgCl_2$, $CaCl_2$, acetate, glycerol, and agriculturally derived deicing products and additives.

These findings are significant in that they show the need for measuring water hardness and sulfate concentrations during toxicity testing. Water hardness and sulfate concentrations can be measured either prior to selection of the testing location or during field monitoring. Water hardness and sulfate values can be used to re-calculate acute and chronic chloride toxicity values. The calculated acute and chronic chloride toxicity values can then be used in the analysis process. The following equations were developed for calculating acute and chronic criteria based on the influence of site specific water hardness and sulfate concentrations (Iowa DNR, 2009):

Eq. 2 Acute Criteria Value (mg/L) = $(254.3)^{\dagger}\, 287.8^{\ddagger} \times (WH)^{0.205797} \times (S)^{-0.07452}$

Eq. 3 Chronic Criteria Value (mg/L) = $(161.5)^{\dagger} 177.87^{\ddagger} \times (W\,H)^{0.205797} \times (S)^{-0.07452}$

† - Values recommended by Iowa DNR (2009)
‡ - Values used for example equations in MassDOT (2012)
WH – Water Hardness (mg/L)
S – Sulfate (mg/L)

For example, 254.3 x (80 mg/L)^0.205797 x (20 mg/L)^-0.07452 =
= 254.3 x 2.46 x 0.7999
= 500 mg/L adjusted Acute Criteria Value based on WH=80 mg/L and S=20 mg/L

The results of the Iowa DNR and US EPA study can be used by other states to set site specific acute and chronic chloride criteria based on measured water hardness and sulfate levels. This criterion has been adopted by Iowa and US EPA Region 7. The new chloride criteria does not change regulatory requirements for drinking water, but does provide site-specific criteria for aquatic life protection that is based on local water hardness and sulfate levels. This may impact effluent permits and will allow permittees to request modifications to the current permits based on the US EPA approval of the new chloride criteria.

Sulfates

Sulfates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$), and gypsum ($CaSO_4 \cdot 2H_2O$) (Greenwood and Earnshaw 1984). These dissolved minerals contribute to the mineral content of drinking water. Sulfate standards are set at 250 mg/L for drinking water (as a secondary maximum contaminant level (SMCL)) because sulfates can cause a cathartic reaction (especially in children) in the presence of sodium and magnesium, and causes unwanted taste to the water (WHO 2004; US EPA 2012). Sulfates in aqueous solutions may be determined by a gravimetric method in which sulfate is precipitated as barium sulfate (WHO 2004); this method is suitable for sulfate concentrations above 10 mg/L (ISO 1990).

Sulfate is a constituent of TDS and may form salts with sodium, magnesium, potassium, and other cations (Iowa DNR 2009). Sulfate is widely distributed naturally and may be present in natural waters at concentrations ranging from a few to several hundred mg/L.

PROPOSED SULFATE CRITERIA FOR IOWA WATERS			
Chloride / Hardness mg/L as $CaCO_3$	Cl- < 5 mg/L	5 ≤ Cl- < 25	25 ≤ Cl- ≤ 500
H < 100 mg/L	500	500	500
100 ≤ H ≤ 500	500	[-57.478 + 5.79 (hardness) + 54.163 (chloride)] * 0.65	[1276.7 + 5.508 (hardness) – 1.457 (chloride)] * 0.65
H > 500	500	2,000	2,000

Figure 7: Proposed Sulfate Criteria for Iowa Waters (taken from Iowa DNR 2009).

Sulfate ions were found to buffer against chloride toxicity in work by the Iowa DNR and US EPA (Iowa DNR 2009). Figure 7 shows the proposed methods to calculate sulfate concentration based on water hardness and chloride concentration. The calculated sulfate value, in conjunction with water hardness, can then be plugged into Equations 2 and 3 to recalculate acute and chronic chloride toxicity criteria.

Biological Oxygen Demand

The amount of oxygen consumed by aquatic organisms in breaking down nutrients is known as the biological oxygen demand or BOD. Sources of oxygen-consuming nutrients include waste water from sewage treatment plants, stormwater runoff from farmland or streets, feedlots, and failing septic systems. Oxygen is measured in its dissolved form as dissolved oxygen by a DO meter. If more oxygen is consumed than is produced, dissolved oxygen levels will decline and may cause some aquatic organisms to migrate away from the site, weaken, or die (ACRP 2008; US EPA 2012).

Currently available aircraft deicing and anti-icing fluids are made of either propylene glycol or ethylene glycol. The breakdown of glycol can cause elevated BOD (ACRP 2008). The commonly used products in the U.S. with the lowest BODs are formulated from potassium acetate and sodium formate. Common environmental concerns resulting from BOD in snow and ice control products include low dissolved oxygen in receiving waters, bacterial growth in receiving waters, and odor associated with the runoff. BOD is determined by incubating a sealed sample of water for five days and measuring the loss of oxygen from the beginning to the end of the test.

Alkalinity

Alkalinity is a measure of the capacity of water to neutralize acids (see pH description). Alkaline compounds in the water such as bicarbonates (e.g., baking soda), carbonates, and hydroxides remove hydrogen (H^+) ions and lower the acidity of the water. Without this acid-neutralizing capacity, any acid added to a stream would cause an immediate change in the pH. Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall, runoff, or wastewater. Alkalinity is one of the best measures of the sensitivity of a waterway to acid inputs. For total alkalinity, a double endpoint titration using a pH meter (or pH "pocket pal") and a digital titrator or buret is recommended. This can be done in the field or in the lab. If analyzing alkalinity in the field, a digital titrator is recommended over a burette (Godfrey 1988; APHA 1992; US EPA 2012).

pH

pH is a term used to indicate the alkalinity or acidity of an aqueous substance. Acidity increases as the pH gets lower, or gets closer to 1.0; thus, pH affects many chemical and biological processes in the water. For example, different organisms flourish within different pH ranges. Most unimpaired aquatic systems have a pH range of 6.5 to 8.0, and most aquatic organisms prefer this pH range. Outside this range, the diversity of aquatic organisms is reduced due to stress on physiological systems of most organisms and reduced reproduction. Low pH can also allow toxic elements and compounds to become mobile and "available" for uptake by aquatic organisms. pH can be analyzed in the field or in the lab. If it is analyzed in the lab, the pH must be measured within 2 hours of the sample collection due to the effect of carbon dioxide on the sample. If a high degree of accuracy and precision is required, pH should be measured with a laboratory quality pH meter and electrode (APHA 1992; US EPA 2012).

Toxicity Standards that Apply to Chloride-based Deicers

US EPA has recommended standards for chloride concentration in drinking water at 250 mg/L (US EPA 2010). At this concentration, water may have a salty taste. The 1988 US EPA Chloride Guidance set the Final Acute Value for chloride as 1720 mg/L. US EPA has set an acute criterion of 860 mg/L by applying a safety factor of 2 to this value. Based on the mean acute values, this criterion does not protect certain organisms, such as some Daphnia (US EPA 1988). The final chronic value of 230 mg/L was derived by dividing the Final Acute Value by the acute to chronic ratio of 7.593. The acute and chronic criteria are the maximum one-hour average and the maximum four-day average, respectively. These standards were determined based on acceptable toxicity test data acquired in a laboratory setting. These chloride criteria only apply when the chloride is associated with sodium. Chloride toxicity increases when it is associated with other cations, such as potassium or magnesium, which may occur once the ions of road salt have dissolved and migrated at potentially different rates (MPCA 2000).

Limitations in how chloride criteria has been determined using the current US EPA guidelines include not accounting for the effects of hardness, sulfate, or temperature, which have been shown to have significant effects on chloride toxicity (Iowa DNR 2009). Additional toxicity data collected on plants and algae were also not included in the current chloride criteria, which are common to roadway environments (Eldridge et al. 2010). Currently the US EPA is reviewing the chloride criteria generated in 1988 because it has recognized that it is critical to incorporate environmental variables such as hardness and sulfate into toxicity data. In addition, a weight of evidence approach is being analyzed to change the rules in which studies are selected for use in the criteria and how this information is used.

Iowa implemented new chloride criteria in 2009 based on work completed with the US EPA (Iowa DNR 2009). Toxicity data on the water flea (*Ceriodaphnia dubia*), planorbid snail (*Gyraulus parvus*), tubificid worm (*Tubifex tubifex*), and fingernail clam (*Sphaerium simile*), revealed a relationship between chloride toxicity, water hardness, and sulfate concentrations. The Iowa DNR then developed a set of criterion equations rather than values for chloride that consider water hardness and sulfate concentration (Eq. 2 and 3). Additionally, the method of calculating criterion chronic concentration (CCC) was significantly modified, which included using a higher Acute Chronic Ratio, 417 mg/L instead of the 1988 US EPA value of 230 mg/L (Iowa DNR 2009). It was also observed that vertebrates have a higher ACR than invertebrates. This approach to assessing chloride toxicity is better able to provide accurate toxicity results for site specific locations (Iowa DNR 2009).

Additionally, Evans and Frick (2001) published a review of chloride toxicity data in 2001, which presented a new approach to derive chloride criteria for aquatic life. The method consists of a three tier approach in which the first and second tiers determine if the substance reaches levels of concern in the environment with possible adverse effects. The third tier evaluates the potential for the substance to have harmful impacts on the environment. Evans and Frick (2001) investigated the available chloride toxicity data and utilized data involving two to four day exposure periods for the acute data and followed the approach from US EPA (1988) to calculate chronic toxicity values. Regression analysis using a sigmoidal function was then used to determine percent of taxa affected for given concentrations. Limited 96-hr exposure data was available thus reducing the accuracy of the analysis. However, Evan and Frick (2001) were successfully able to determine confidence intervals for chronic toxicity in which 10% of species were shown to be affected at chloride concentrations of a lower and upper bound of 194 mg/L and 295 mg/L, respectively.

The ambient water quality guidelines for chloride were adopted by the British Columbia Ministry of Environment in 2003. They state that the average concentration of 5 weekly measurements over a 30-day period for freshwater and aquatic life are not to exceed 150 mg/L with a maximum not to exceed 600 mg/L (Nagpal et al. 2003). The background chloride concentrations in British Columbia of 1 to 100 mg/L Cl^- have been attributed to storage and application of road salts. The development of these guidelines included conservative safety factors comparable to the US EPA (1988) guidelines. As such, a safety factor of two was applied to determine the maximum chloride concentration of 1204 mg/L from acute toxicity studies of the tubificid worm and a safety factor of five was used to determine the chronic toxicity concentration of 150 mg/L (Nagpal et al. 2003).

Field Test Methods for Deicer Toxicity and Monitoring of Relevant Parameters

Summary of Field Toxicity Testing by Corsi et al. (2010a; b)

This section presents laboratory and field research completed by Corsi et al. (2010a; b) that tested the toxicity of chloride-based deicers. This research project is highlighted because it is the most comprehensive and focused investigation into chloride based deicers impacts on aquatic species in field environment.

Chloride was measured as specific conductance, to determine aquatic toxicity through direct impacts on aquatic organisms (bioassays using *Pimephales promelas* and *Ceriodaphnia dubia*) on the local scale. Streams monitored continuously for specific conductance were selected for inclusion and were regionally representative. Real-time specific conductance data was used as an indicator of road salt in streams and was then used to initiate the sample collection. Water quality samples were collected manually for a two week sampling period. Samples were collected by either submerging sample bottles directly into the center of the channel for wadeable streams or by using a weighted-bottle sampler to collect cross-section integrated samples from a bridge for non-wadeable streams. Flow-weighted composite samples were collected based on procedures presented in Corsi et al. (2001).

Continuous measurements for specific conductance were recorded at least every hour, and as frequently as every 5 minutes. This varied based on site hydrologic conditions. Instantaneous specific conductance was also measured at other sites. All specific conductance monitors were maintained in accordance with the US Geologic Survey (USGS) standard method (Gibs et al. 2007). US EPA (1979) method 325.2 was used for water analysis and US EPA (2002a; b) toxicity tests of *Pimephales promelas* and *Ceriodaphnia dubia* bioassays were used to assess acute and chronic toxicity testing, as well as the modified US EPA method to determine acute (lethal endpoints) and chronic effects (sublethal endpoints) (Geis et al. 2003).

Static renewal acute tests were conducted at 68°F (20°C) and chronic tests at 77°F (25°C). Both were conducted with a 16:8-hr light:dark cycle. *P. promelas* acute tests were initiated with 4 to 14 day old juveniles, replications of 5 and then 10 fish were used. The fish were placed in 250 ml plastic cups with 200 ml of sample, and each treatment consisted of four replicate samples. Treatment solutions were renewed daily and fish were fed live brine shrimp two hours prior to the 48-hr test renewal. The bioassay ended at 96-hr and survival was recorded as the acute endpoint.

C. dubia acute test were initiated with young less than 24-hr old. Treatments consisted of four replicates per sample containing five *C. dubia* per replicate. Test chambers were 30 ml plastic cups containing 15 ml sample volume each. The test solution was renewed at 24-hr (US EPA static-renewal test method; US EPA 2002b). The *C. dubia* acute test was terminated at 48-hr when survival was recorded. *P. promelas* chronic growth tests were initiated with less than 24-hr-old larval fish. Live brine shrimp were fed to the fish three times daily. The tests were terminated on day 7 and growth by weight as the chronic endpoint was determined.

In 2000, methods were modified to address mortality due to bacterial pathogens that are commonly found in the study site streams. Prior to 2000, test treatments consisted of four 250 ml plastic cups, each containing 200 ml of sample and 10 larval fish. Tests were revised, and now use 30 ml plastic cups, each containing 25 ml of test solution. Replicates were increased with the method modification from four to ten replicates, with only two fish per test chamber.

In the *C. dubia* chronic reproduction test, organisms were fed with each water renewal. Production of young was recorded daily, and the tests were terminated after 80% of controls released their third brood (6 to 7 days). Test chambers consisted of 30 ml plastic cups, each containing 20 ml of test solution. Each treatment consisted of 10 replicates with one organism per test chamber. The number of young produced was used as the chronic endpoint (Corsi et al. 2010b).

Historical data using the USGS National Water Information System (NWIS) database for stream chloride concentrations from 1969 to 2008 were analyzed, and compared to the US EPA water-quality criteria and analyzed for seasonal differences. Specific conductance was used to characterize the chloride concentration of water samples (Corsi et al. 2010a). Linear regression analysis was conducted from concurrent chloride and specific conductance measurements from stream samples. It should be cautioned that despite good correlation between chloride concentration and specific conductance of water samples, ions other than sodium cations or chloride anions can contribute to the specific conductance and disrupt this correlation. Low specific conductance values (less than 1400 μS/cm) can be prone to the influence of other ions, so these lower values were not included in the analysis (see (Corsi et al. 2010b) for additional information). Data was reported as NOED, LC_{50} and IC.

Corsi et al. (2010a) recommends that to better understand the relation between urban land use and stream biology, focused monitoring would be needed to characterize the range of chloride concentrations and duration of road-salt influence in streams during deicing periods. Corsi et al. (2010a) also recommends using continuous- and event-based monitoring focused around deicing periods, and cautions that a period of fixed-interval sampling will not fully characterize road salt influence except by happenstance.

Field Sample Collection Options

Water sample collection from the field can be done in two ways using 1) discrete samples and 2) composite samples (US EPA 2002a). Discrete samples are easy to collect with a minimal amount of equipment and time, and provide a measure of instantaneous toxicity, but they only reflect a short period of time and are often collected on an infrequent basis. The chances of detecting a spike in contaminant concentration would depend on sampling frequency. Composite samples are collected over a longer time period (24-hr period or designated time period), and better capture concentrations occurring over that time period and are more like to detect spikes in concentration, but collecting these samples is harder, more expensive, and time intensive. Composite samples can be collected as flow-weighted (recommended for assessment of overall storm/runoff average) or time-weighted. With composite samples, spikes in concentration may not be detected because they are masked by dilution from the less concentrated waters sampled. US EPA offers collection methods by sampling type in US EPA (2002b).

Trowbridge et al. (2010) found that collecting discrete samples monthly is a sufficient method for measuring annual average chloride concentration. "This finding is significant in that it would allow for monthly samples to be used rather than more costly labor-intensive use of data loggers to determine if US EPA's recommended water quality standards are exceeded within a particular stream" (MassDOT 2012). This would not be a good sampling method in areas where runoff, or melt water, is an issue. This sampling method would be appropriate where groundwater with high chloride concentrations recharges waters during times of low flow, or where groundwater flow dominates.

The 230 mg/L chronic exposure and 860 mg/L acute exposure criterion, based on four-day and one-hour average concentration which should not be exceeded more than once in three years, would require routine sampling at frequent intervals during peak runoff periods in order to accurately capture the one-hour and four-day average chloride concentrations (MassDOT 2012). Additionally samples should be collected over a sufficiently long time period so that the frequency of peak runoff concentrations within a three-year period can be captured.

For rivers and streams, samples should be collected mid-stream at mid-depth, and for lakes at mid-depth (US EPA 2002b). Once collected, effluent and receiving water samples should be handled, preserved, and shipped according to US EPA guidelines (US EPA 2002b).

Toxicity testing of deicers using fresh water organisms can be completed in two ways; 1) using water samples collected in the field, and 2) in-situ monitoring of chloride concentrations and then creating synthetic testing solution with chloride concentration based on those observed in the field measurements.

Selection of a sampling location can be based on the water body's location, what the water body contributes too, the land-use within proximity to the waterway, identified problem areas, or ecologically sensitive areas. Selection of sampling sites that have had historic monitoring or that have a USGS gauging station will aid in long term analysis.

Sampling periods can target runoff events during road-salt application periods. For work completed by Corsi et al. (2010a), new testing was completed during winter months, and historic data was used to look at year round, summer and winter, and specific conductance data, to determine historic chloride concentrations.

Timing of Sampling

Field sample timing may vary depending on the goals of the research. When designing a sampling plan, consider the sampling environment, species of interest, and the life stage of those species. For example, amphibians reproduce in early spring, March through May, in North Carolina, therefore it is important to analyze snowfall and the associated salt load (determined from salt usage data) during this time frame to fully assess impacts to their larval growth stages (Winston et al. 2012).

Road salts are generally applied during winter months, when temperatures are low and most organisms are inactive, or dormant. Flushing events can occur much later in the season (in the spring) at which time organisms have become active and begin reproducing (Silver et al. 2009). The importance of sampling following a major flushing event is well documented and generally captures the highest potential concentration of contaminants seen in the environment (Nason et al. 2011). During winter, direct runoff has been found to reach waters as point source runoff, overspray from vehicles, and snow removal as pulse events (Rosenberry et al. 1997; Silver et al. 2009). The residence time of road salts, or how long they remain in a waterway, has been measured at up to 6 months (Rodrigues et al. 2010).

Times of low flow, or base flow, can serve as a preliminary indicator of baseline concentration for a monitoring program (Bowen and Hinton 1998). This could be done using simple and inexpensive base flow surveys, measuring chloride concentrations or conductivity, to then determine stream degradation. Base flow can also capture groundwater chloride concentrations. Chloride contaminated groundwater can be an additional source of chloride to waters (Kelly et al. 2008). The unsaturated zone can act as a reservoir for chloride, where it can then migrate vertically downward to the groundwater (Lax and Peterson 2009). A study in Denmark found that 10 to 20% of applied road salt ends up in groundwater (Kristiansen et al. 2011).

A conventional method of determining chloride concentrations in a water source is to collect specific conductance profiles and create a relationship based on ionic concentrations (Novotny et al. 2008). The depth of sampling within a water body should be considered for all samples collected. For example, hyposaline layers have formed in lakes near or at the bottom impacting aquatic organisms in those areas, reducing oxygenation of benthic sediments, and preventing aquatic turnover or mixing (Novotny et al. 2008). Another method to detect chloride in solution is the use of chloride ion-selective electrodes (ISE).

Variables to Consider for Testing

At a minimum the US EPA recommends testing effluent or receiving water for pH, conductivity, total residual chlorine, and dilution water for pH and conductivity, and recommends testing total alkalinity and total hardness (US EPA 2002b). Based on work by the Iowa DNR and US EPA, additional testing of sulfate concentrations is recommended, in conjunction with water hardness testing (Iowa DNR 2009). In the initial sampling, testing for heavy metals and poly aromatic hydrocarbons (PAH) should be considered. Additional information on these and other variables to be tested can be found in Variables to Consider for Laboratory Testing.

Weather data collected from NOAA, RWIS, SNOWTEL, NWS, airports, and related sources will aid in the final analysis. Weather data collection should include:

- Air temperature – maximum and mean
- Precipitation type and amount
- Water equivalent of snow calculations

Information on winter maintenance operations performed throughout the year that may impact the field site should be recorded. Consider collecting information on - sanding, salting, deicing, anti-icing, pre-wetting, and plowing operations for all road segments in the watershed.

Bioassessment as Tool to Measure Toxicological Effects

Understanding the basic toxicity of a deicer is a starting point for determining the impacts a product can have on an ecosystem. This can be done in the laboratory and by chemical monitoring in the field, but to complement this, biomonitoring can be used to assess the ecological condition of a waterway using biological indicators, or biocriteria (Yoder and Rankin 1998; Gerhardt 1999; Adams 2002). Biocriteria are a set of preselected attributes used to assess, in this case, the toxicity of a product on a functioning ecosystem. Biocriteria can take into consideration physical, chemical and biological stressors and the effects on organisms, spatially and temporally. Biological variables that can be tested include (Gerhardt 1999):

- Toxicity – organisms' response to chemicals at various organizational levels using bioassays or early warning detection systems,
- Ecosystem response – assessment of ecological integrity.

Essentially, biocriteria allow for a more complete assessment of toxicity of a product to an ecosystem, including impacts to the food web and lifecycle. Two general methods used in biomonitoring include: 1) testing *autoecological* parameters using ecotoxicological biomonitoring in the lab, in-situ, or using online biomonitoring, or 2) *synecological* parameters, looking at long-term trends using biomonitoring in the field (Gerhardt 1999). Gerhardt (1999) developed a flowchart outlining a proposal for integrated environmental monitoring (Figure 8). The proposed integrated environmental monitoring utilizes traditional descriptive biomonitoring, but also uses predictive approaches (mathematical and statistical models).

Another method that can be used to assess chloride toxicity is the Chloride Contamination Index (CCI) developed by Williams et al. (2000) to assess the response of macroinvertebrates to rising salt concentrations in springs from deicing products. A community analysis of macroinvertibrates in each spring was completed, and a correlation was developed between the identified invertebrates and mean chloride concentration in each spring. Organisms found were classified based on their tolerance to chloride, and labeled either tolerant or non-tolerant. One of the major findings from this research was the identification of a sensitive species that could be used as an indicator for moderate to high chloride contamination in springs. Williams et al. (2000) concluded that springs serve as good access points to study aquifer contamination.

Another method to assess the health of a water body is using an Index of Biotic Integrity (IBI), which describes health of the ecological structure and function of the waterway (US EPA 2013b). The IBI requires a biological assessment of the waterway over time. The state of Maine has utilized IBIs to measure impacts to waters to aid in implementing a water quality management policy (Courtemanch et al. 1989). The Maine Department of Environmental Protection (DEP) began a statewide biomonitoring program in 1986 looking at the condition of aquatic communities, DO, and numbers of bacteria. Waters were then classified by level of use (AA-highest to C-lowest quality): therefore, what is required to maintain water quality is flexible and based on site-specific factors and water condition.

Findlay and Kelly (2011) have pointed out that field studies of salt effects on aquatic organisms are more realistic, since the whole suite of other environmental controls (stresses) is present; however, it also becomes more tenuous to assign a direct cause/effect linkage.

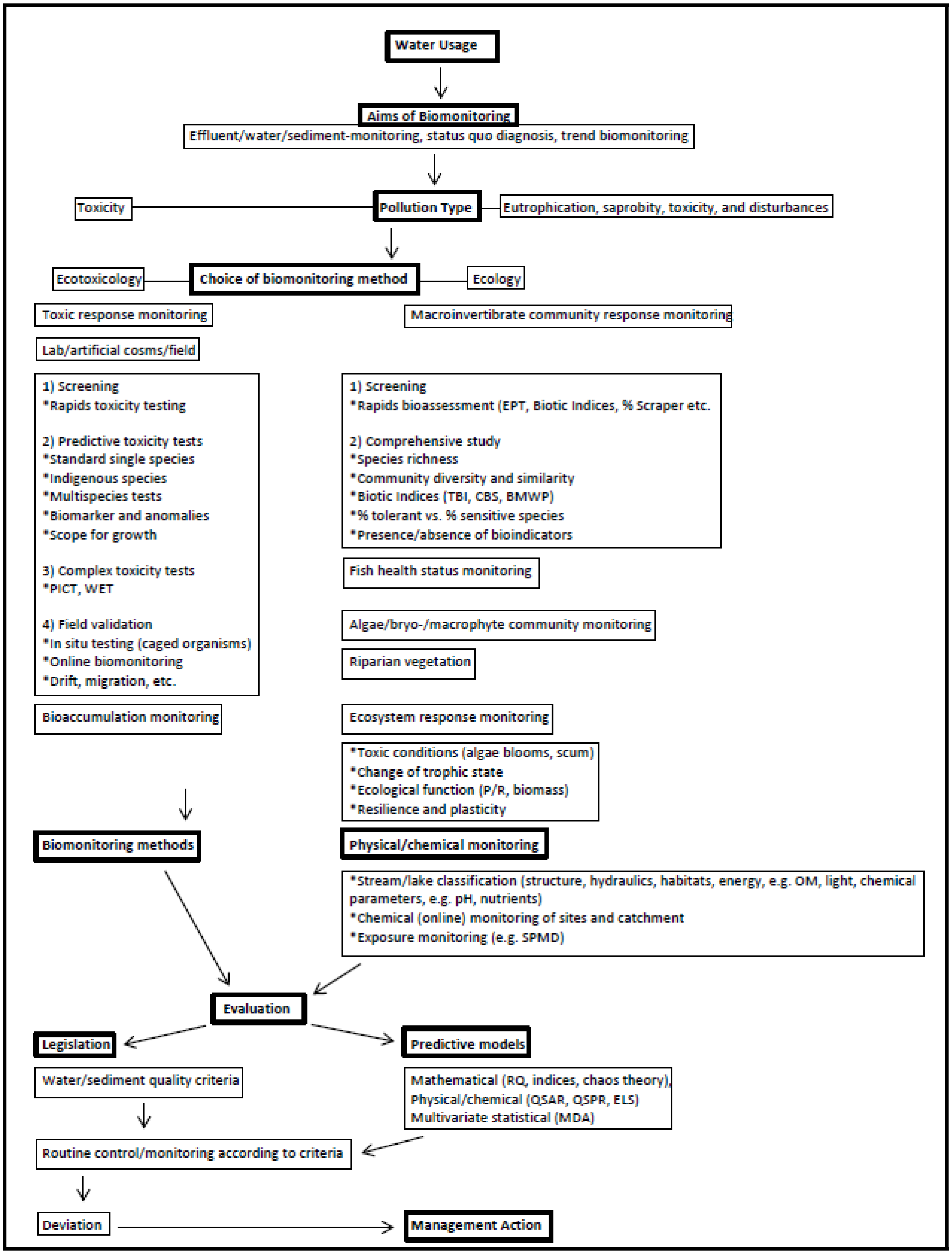

Figure 8: Proposed integrated environmental monitoring plan by Gerhardt (1999).

Ongoing Research

The following research projects could provide further guidance on this topic once completed.

ACRP 02-39 Applying Whole Effluent Toxicity (WET) Testing to Airport Deicing Runoff
This ongoing research project, funded through the Airport Cooperative Research Board is slated to be completed in early 2014. It is exploring the viability of using WET testing at airports to monitor storm water deicing discharges, identifying strengths and weaknesses of the test method by evaluating testing protocols, assessing if lab WET results can translate to in-situ water quality impacts, and providing guidance on the feasibility of WET testing at airports.

Effects of Deicing Salts in a Detention Pond Treating Road Water
This ongoing research project in France is measuring deicer salt storage in a detention pond originally installed to treat road water runoff and act as flow control (Suaire et al. 2013). Researchers are measuring salt and heavy metal concentration of the influent (inlet) and effluent (outlet) of the detention pond. The goal is to evaluate the amount of road salt applied to roads, versus the amounts entering and leaving the detention pond, as well as monitoring mobilization of heavy metals caused by the presence of deicing salts. This information will be correlated with winter maintenance practices associated with measured meteorological conditions.

All water bodies have some natural background chloride concentration. Anthropogenic sources of chloride to surface waters include industrial and municipal wastewaters, effluent wastewater from water softeners, road salt, agricultural runoff, and production water from oil and gas wells (Missouri DNR 2013; Whipps 2013).

The most commonly used deicers containing chlorides are sodium chloride, magnesium chloride, or calcium chloride, or a combination (e.g., salt brine with $CaCl_2$ added as a cold temperature modified product). Chloride-based deicers can be applied as liquids, generally for anti-icing with application before the storm, or as solids for deicing with application during the storm. They are also used to prevent stored road sanding materials from freezing. For this purpose, salt is added to sand at 5 to 10% by weight (for 1 ton or 2000 lbs of sand, 100 to 200 lbs of salt would be added). Departments of Transportations mostly use chloride-based deicers during winter maintenance operations because they are the least expensive, and can be used relatively easily to maintain safety and mobility for the traveling public while minimizing their application to necessary levels. General information relevant to winter maintenance practices for each chloride-based deicer is discussed in Table 2. Typical use temperature ranges for $MgCl_2$ and $CaCl_2$ begin at 5 °F because it is less expensive to use NaCl above this temperature. For this reason, $MgCl_2$ and $CaCl_2$ are added to salt brine at low concentrations to make cold temperature modified products that work well at temperature below 15 °F.

Table 2: General information on chloride-based deicers relevant to winter maintenance practices.

Chloride Based Deicers	Typical Application Rates in Liquid Form (gal/l-m)		Typical Application Rates in Solid Form (lbs/l-m)			Typical Use Temp. Range (°F)[d]	Relative Cost (per ton, varies based on delivery costs)[e]
	Anti-icing [a]	Pre-wetting[b]	Deicing[c]	Anti-icing equivalent	Pre-wetting equivalent		
NaCl	20 to 80	8 to 10	200 to 800	50 to 200	20 to 25	32 to 15	$42
$MgCl_2$	30 to 45	6 to 12	100 to 400	107 to 160	21 to 43	15 to 5	$111
$CaCl_2$	30 to 45	6 to 12	100 to 400	107 to 160	21 to 43	2 to -20	$140

Notes:

a. Fischel (2001) and Peterson et al. (2010)

b. Blackburn et al. (2004) and Salt Institute (2012)

c. Fischel (2001) and Salt Institute (2007)

d. Fischel (2001)

e. Kelting and Laxson (2010)

Basis for anti-icing and pre-wetting equivalent calculations:

NaCl brine of 23% has 2.49 lbs of salt per 1 gallon water.

$MgCl_2$ brine of 30% has 3.57 lbs per 1 gallon water.

$CaCl_2$ brine of 30% has 3.57 lbs per 1 gallon water.

Chloride-based deicers have been used for decades and have been the primary snow and ice control products used by roadway agencies. Chloride laden runoff from roads can splash or spray onto soil and plants, and flow off the road into soil and into surface and ground waters. Elevated chloride concentrations may affect the taste of drinking water and are known to be toxic to aquatic life. Elevated chloride concentrations in waters associated with chloride laden runoff from roadways and maintenance yards have ranged from 10s of mg/L to 10,000s mg/L (MTO 1997; Bowen and Hinton 1998; Alberta Infrastructure 2000; Shaw et al. 2012). Long-term studies have shown chloride concentrations in groundwater are increasing, particularly in the North Eastern United States (NAS 2005), but also in western areas where reclaimed water is used for irrigation. Current standards used by the Environmental Protection Agency for chloride in surface waters are:

- Chronic - four-day average concentration of dissolved chloride, associated with sodium, should not exceed 230 mg/L, and
- Acute - one-hour average concentration should not exceed 860 mg/L, more than once every three years on the average [US EPA 440/5-88-001)] (US EPA 1988).

The US EPA standard should apply to most locations except where more conservative values may be necessary, where locally important and sensitive species are present. For chloride associated with magnesium, calcium, or potassium, more conservative acute and chronic concentrations may need to be designated. For groundwater and other water supply situations, the drinking water standards would apply.

How are aquatic pollutants regulated?

The federal water quality guidelines are just that, guidelines, and do not have regulatory impact until adopted as a state water quality standard (US EPA 1988). *A state can adopt the federal standard or develop a site-specific or pollutant specific standard if it is adequately justified*. The Clean Water Act (CWA, 1972) states that every state must adopt water quality standards to protect, maintain, and improve the quality of the nation's surface waters (U.S. Code Title 33, Chapter 26 SubChapter III (U.S. Code 2009)). The CWA establishes the basic structure for regulating discharges of pollutants into water of the U.S. and regulates quality standards for surface waters (US EPA 2013a). The CWA makes it unlawful to discharge any pollutant from a point source into navigable water unless a permit was obtained. Components of the CWA include defining the designated uses of the waterway, water quality criteria, and anti-degredation - a federal "policy that states a particular water resource cannot get worse unless justified by economic and social development considerations." For chloride, the designated uses are protection of aquatic species and drinking water quality.

The National Pollution Discharge Elimination System (NPDES) permit program controls water pollution by regulating point sources that discharge pollutants into waters of the United States (US EPA 2009). Point sources are discrete conveyances such as pipes or man-made ditches. Industrial, municipal and other facilities are required to obtain permits if their discharges go directly to surface waters. In most cases, NPDES permit programs are run by states.

Acute toxicity tests used in the NPDES permit program to identify effluents and receiving waters containing toxic materials in acutely toxic concentrations can found in the EPA document, *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms* (US EPA 2002a). Chronic toxicity tests can be found in the *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms* (US EPA 2002b). Tests recommended for permit compliance in the NPDES program include IC_{25}, IC_{50} or LC_{50}, or NOEC (US EPA 2002b).

Use Attainability Analyses

The designated use of a water body can be changed if it is shown that it is not attainable. A use attainability analysis (UAA) is a structured scientific assessment of the beneficial uses a water body could support, given application of required effluent limits and implementation of cost-effective and reasonable best management practices (Idaho DEQ 2013). Waters must be protected for the most sensitive of their uses. UAAs identify 1) existing uses, 2) reasons attainment may not be feasible based on physical, chemical, biological, and economic factors, 4) the highest attainable use, and 5) downstream uses of the water (US EPA 2012c). Any individual or entity can conduct a UAA. UAAs are intended to be revised over time as designated uses of waters change, and may provide more or less protective criteria based on the findings.

Recent Changes

A report published in 2009 detailed work completed by the Iowa DNR and US EPA in which additional toxicity testing was completed to assess the toxicity of chloride on more sensitive aquatic species and to gather more long-term chronic exposure data. *The results of the Iowa DNR and US EPA study can be used by other states to set site specific acute and chronic chloride criteria based on measured water hardness and sulfate levels.* This criterion has been adopted by Iowa and US EPA Region 7. The new chloride criteria does not change regulatory requirements for drinking water, but does provide site-specific criteria for aquatic life protection that is based on local water hardness and sulfate levels. This may impact effluent permits and will allow permittees to request modifications to the current permits based on the US EPA approval of the new chloride criteria. The new chloride criteria "appear to provide a more accurate representation of the potential toxic effects of elevated chloride levels in freshwater streams and rivers." (MassDOT 2012)

A 2010 petition from the Missouri Agribusiness Association to the Missouri Clean Water Commission and the Department of Natural Resources was submitted seeking an amendment of the state's water quality criteria for sulfates and chlorides. The request was based on chloride criteria for aquatic life protection *based on new research and toxicity data indicating that chloride toxicity is dependent on water hardness and chloride toxicity is dependent on sulfate concentration*.

Missouri State Sulfate and Chloride Limit for Aquatic Life Protection [10 CSR 20-7.031(4)(L)] reads as follows:

- Low-flow streams – concentration of chloride plus sulfate shall not exceed 1000 mg/L.
- Other waters – total chloride plus sulfate concentration shall not exceed the estimated natural background concentration by more than 20%.

Missouri plans to reassess impaired waters using the new criteria and has proposed delisting what would be considered unimpaired waters when applying the new criteria. States that are considering or have adopted the Iowa DNR and US EPA chloride criteria include: Illinois, Iowa, Missouri, Ohio, and Pennsylvania, and the Canadian Province of British Columbia.

Impaired or threatened waters (rivers segments, streams, lakes) identified by states, where the required pollution controls are not enough to maintain or reach applicable water quality standards are added to the 303(d) list maintained by the US EPA, and will have TMDLs established based on the severity of the pollution and the sensitivity of the waters (US EPA 2012b). Nationwide there are 977 303(d) listings for salinity, chlorides, and TDS. In 2004, New Hampshire added five chloride impaired waters along I-93, with a total of nine streams violating the states standard for chloride after elevated groundwater chloride levels were detected, associated with years of heavy road salt use (Fredrick and Goo 2006). Parameters that are of interest to chloride toxicity and are covered by the 303(d) listing include chlorides, TDS, TSS, and BOD. These will be discussed in further detail. Chloride toxicity has been shown to be dependent on water hardness, and to a lesser degree sulfate levels in the water (Iowa DNR 2009); based on this information these parameters will also be discussed.

Total Dissolved Solids

Total dissolved solids (TDS) are closely related to streamflow and velocity and should be correlated with these factors (US EPA 2012). In arid regions where water is scarce and evaporation rates are high, TDS values tend to be higher. Rises in TDS are often associated with rainfall in developed or developing areas, especially in arid areas where infiltrating rainfall travels through soils before discharging to streams.

Total dissolved solids values associated with the palatability of drinking water range from 300 mg/L for good), and 900 to 1200 mg/L for poor (WHO 1996). Rising TDS concentration have been associated with deicer use. Information on TDS test methods and sample collection methods can found in US EPA (2012a).

For those who adopt the new chloride criteria, US EPA WET testing may be replaced by the ion criteria for chloride and sulfate, as they appear to be better indicators than TDS, conductivity, and salinity for water quality protection (Iowa DNR 2009).

Total Maximum Daily Load, or TMDL, is a calculation of the maximum amount of a pollutant that waters can receive and still safely meet water quality standards (US EPA 2013a). TMDLs are developed for impaired waters that are identified by states, territories and tribes under the Clean Water Act. Total maximum daily load values set previously may be impacted by new chloride criteria developed based on the Iowa DNR (2009) report. As of June 2013, salinity, total dissolved solids, chlorides and sulfates were listed as the cause of impairment of 1,981 waterways (US EPA 2013b).

Biological Oxygen Demand

The amount of oxygen consumed by aquatic organisms in breaking down organic materials, including nutrients, is known as the biochemical oxygen demand or BOD. Sources of oxygen-consuming nutrients include waste water from sewage treatment plants, stormwater runoff from farmland or streets, feedlots, and failing septic systems. Oxygen is measured in its dissolved form as dissolved oxygen by a DO meter. If more oxygen is consumed than is produced, dissolved oxygen levels will decline and may cause some aquatic organisms to migrate away from the site, weaken, or die (ACRP 2008; US EPA 2012).

Currently available aircraft deicing and anti-icing fluids are made of either propylene glycol or ethylene glycol. The breakdown of glycol can cause elevated BOD (ACRP 2008). The commonly used products in the United States with the lowest BODs are formulated from potassium acetate and sodium formate. Common environmental concerns resulting from BOD in snow and ice control products include low DO in receiving waters, bacterial growth in receiving waters, and odor associated with the runoff. Biological oxygen demand is determined by incubating a sealed sample of water for five days and measuring the loss of oxygen from the beginning to the end of the test. Note that glycols (or urea, which is used at times on runways) are not commonly used for highway anti-icing/deicing control.

Water Hardness

Water described as "hard" contains high amounts of dissolved magnesium and calcium (Ramakcrishna and Viraraghaven 2005), which may be compounded by the application of $MgCl_2$ and $CaCl_2$ deicers. Hard water is not a health hazard. In fact, the National Research Council states that hard drinking water generally contributes a small amount toward the total calcium and magnesium needed in the human diet (US EPA 2012). The US EPA established standards for drinking water which are designed to protect health and ensure that public water supply is of good quality (US EPA 2012). Standards fall into two categories: Primary Standards and Secondary Standards. Public water system operators are required to provide annual water quality reports, referred to as consumer confidence reports. The CCR may include information about the hardness level of the water delivered. For private water supplies, water hardness testing can be done at most water testing laboratories. In addition, a variety of water hardness test kits and dip strips are available for purchase, which are generally easy to use, relatively inexpensive, and can provide a good estimate of hardness.

Water hardness was found to buffer against chloride toxicity in work by the Iowa DNR and US EPA (Iowa DNR 2009). Water hardness values, in conjunction with sulfate values, can be used to recalculate acute and chronic chloride toxicity values. In the case of Iowa, by taking into consideration local water hardness and sulfate values, they were able to use a much higher chronic toxicity standard for chloride of 406 mg/L, instead of 230 mg/L, but the acute toxicity standard was lower at 680 mg/L, instead of 860 mg/L (Iowa NDR 2009).

Reducing the Impacts of Chloride-based Deicers

To reduce the impacts of chloride-based deicers, there are four potential management strategies, including reducing the amount of chloride deicers applied (either through minimization and/or use of other control substances), treatment of runoff that includes deicers, mixing runoff to reduce concentration peaks, and/or routing of deicing runoff away from sensitive receiving systems, either surface and/or groundwater systems.

In the evaluation of potential control methods, it is important to consider the treatability of chloride. Chloride is a conservative substance that is very difficult to treat other than through evaporation. Potential treatment options include reverse osmosis or membrane filters (with a remaining brine stream) or routing to an evaporation pond. The use of evaporation ponds will only be cost effective in limited conditions of lower humidity and in locations with the availability of significant storage areas. As most deicing needs occur during cold periods of the year, significant storage would be required to allow for long-term evaporation. Use of reverse osmosis or membrane filters for stormwater runoff would be cost-prohibitive and would still require the routing of the remaining brine stream to either an evaporation pond or treatment plant that could accept it.

Therefore, for managing the impacts of chloride deicing materials, the three most successful strategies are to 1) minimize its use, 2) mix runoff volumes to reduce peak concentrations, 3) route deicing containing runoff to less sensitive receiving waters. Source control via either minimization of the amount needed to meet deicing requirements and/or product substitution is likely the best option whenever possible. The other options are to use stormwater BMPs to mix larger volumes of stormwater to reduce within storm peak chloride concentrations and/or route the runoff away from sensitive receiving waters. This can be accomplished either via routing around a sensitive receiving system or infiltrating to groundwater when groundwater chloride or TDS is of less concern. The sections below present these options.

Methods to Reduce the Amount of Chloride-based Deicers Used or Lost

The following section discusses strategies that can be used to reduce deicer application rates and the amount of deicers applied through proactive approaches to winter maintenance operations. Using less chloride-based deicer means less is going into the environment and that related toxic impacts are reduced, avoided, or further delayed. Departments of transportation have demonstrated that proactive approaches such as anti-icing and salt management techniques can reduce the amount of chloride deicers applied. In recent years, winter maintenance practitioners have implemented new technologies, tools, and methods to reduce the amount of snow and ice control chemicals used. While cost saving has been the primary driver, these practices also reduce the amount of chlorides applied and therefore reduce impacts to the environment (Fay and Shi 2012; Fay et al. 2013). The most successful approaches consist of use of alternative products, snow removal, anti-icing, pre-wetting, precision application and use of AVL and GPS technology, frequent and consistent staff training and equipment calibration, appropriate material storage, utilizing real time weather and pavement condition data, including programs like MDSS, and creating detailed maintenance records, all of which will be presented in this section.

Salt Management Plans

Salt management plans (SMP) provide maintenance agencies with a strategic tool to effectively implement salt management practices while providing safe, efficient, and cost-effective road management. The SMPs apply to all winter maintenance staff and personnel (TAC 2003). Pioneered by Canadian transportation agencies, an SMP is generally agency-based and aims to follow the principles of safety, environmental protection, continual improvement, fiscal responsibility, efficient transportation systems, accountability, measurable progress, communication, and a knowledgeable and skilled workforce (TAC 2003; Venner 2004). Fundamental components of an SMP may consist of a statement of policy and objectives, situational analysis, documentation, and proposed approaches to achieve goals or protect identified sensitive areas. The Transportation Association of Canada (TAC) recommends using general and broad guidelines developed at the federal level to act as a framework for further development of local guidelines, considering the amount of salts used, roadway systems, funding constraints, local weather conditions and variability in conditions across a country, state, province, county or municipality (TAC 2003; Venner 2004). SMPs assess specific progress and identify areas for further improvement. Important components of an SMP may include:

- A statement of policy and objectives based on policy with guiding principles from a high-level organization.
- Situational analysis – on road use, salt vulnerable areas, sand and salt storage sites, snow disposal sites, training, and related issues.
- Documentation, in which activities are recorded, monitored, audited and reported periodically to assess the progress and identify areas for further improvement.
- Proposed approaches.
- Training and management review.

In order to implement a successful SMP, it is recommended that agencies provide detailed records and annual reports for each storm event and winter season. These records may contain valuable information such as salt usage and performance records, which can be analyzed to determine general trends or develop improved management strategies (MSHA 2012). In addition, annual audits and inspections can identify specific areas of or for improvement. Procedure improvements and shifts in snow and ice management policy are sometimes documented in ice and snow policies or formal DOT levels of service (Venner 2012).

Specific modifications to basic SMP guidelines can be implemented to address specific budgets, and climatic and road conditions. For instance, the City of Toronto, Canada utilizes electronic salt dispensers to control the salt flow and mixes sand into the salt when conditions permit (to reduce salt use). DOTs in the US are increasingly turning to these technologies as well. Maryland, Michigan, Ohio, and many other DOTs use AVL tracking systems to monitor past and present locations of winter roadway maintenance equipment and to improve efficiencies (Welsh 2005; Venner 2011; Venner 2012; MSHA 2012).

Additional Resources for Salt Management Plans

City of Toronto. 2004. *Salt Management Plan Summary*. City of Toronto, Works & Emergency Services, Transportation Services Division. http://www.toronto.ca/transportation/snow/pdf/02smp.pdf

County of Northumberland. "Salt Management Plan." Updated June 2011. http://www.northumberlandcounty.ca/en/departments_publicworks/resources/Salt_Management_Plan_2011.pdf

Environment Canada. 2004. "Code of Practice for the Environmental Management of Road Salts." EPS 1/CC/5. http://www.ec.gc.ca/nopp/roadsalt/cop/pdf/1774_EngBook_00.pdf

Ostendorf, D.W., Hinlein, E.S., Rotaru, C., and DeGroot, D.J. 2006. "Contamination of Groundwater by Outdoor Highway Deicing Agent Storage." *Journal of Hydrology*, Vol. 326, pp. 109-121.

Transportation Association of Canada (TAC). 2003. *Synthesis of Best Practices, Road Salt Management*. Transportation Association of Canada http://www.tac-atc.ca/english/resourcecentre/readingroom/pdf/roadsalt-1.pdf

Transportation Association of Canada (TAC). http://www.tac-atc.ca/

Maryland State Highway Administration. 2013. *Statewide Salt Management Plan* http://sha.md.gov/OOM/Statewide_Salt_Management_Plan.pdf

Venner, M. 2004. Sections 8.3: Strategic Planning for Reduced Salt Usage, and 8.4: Stewardship Practices for Reducing Salt and Other Chemicals, 8.5: Winter Operations Facility Management, in AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures.

Product Substitution

Many western DOTs have reduced the use of chloride deicing materials via deployment of sand/gravel for traction improvement during freezing conditions. For example, in the Lake Tahoe basin, the use of chloride deicing materials is to be minimized and traction is managed via use of salt as well as sand/gravels by both CalTrans and Nevada DOT (Caltrans 2013). The agencies have to test sand and gravel for phosphorus content as well as strength to limit both nutrients and fine particulates that could be released due to crushing of the applied materials. They also sweep after snowmelt events to remove the sanding materials to minimize fine particulates. Many other western states deploy sand/gravel for traction control during wet weather (e.g., Oregon and Washington DOTs).

Other products that can be substituted for chloride-based deicers include acetate, formate, and bio- or ag-derived products. These products work most effectively at varying temperatures (often working at colder temperatures), can be more expensive than chloride products, can reduce or prevent corrosion to vehicles and infrastructure, and exert higher biological oxygen demand than most chloride-based products. Many of these products contain proprietary ingredients, and the environmental impacts of these should be investigated.

Additional References for Product Substitution

Caltrans. 2013. *Deicer Report for California Department of Transportation, Fiscal Year 2013/2013*. Order No. 99-06-DWQ, NPDES No. CAS000003. California Department of Transportation, Marysville, California.
http://www.dot.ca.gov/hq/env/stormwater/annual_report/ar_oct_2013/ar_DeicerReport.pdf

Levelton Consultants Ltd. 2007. *NCHRP Report 577: Guidelines for the Selection of Snow and Ice Control Materials to Mitigate Environmental Impacts.* Transportation Research Board of the National Academies, Washington, D.C.

Shi, X., et al. 2009. *Evaluation of Alternate Anti-icing and Deicing Compounds Using Sodium Chloride and Magnesium Chloride as Baseline Deicers*. Report No. CDOT-2009-01. Colorado Department of Transportation, Denver, Colorado.

Snow Removal

The most efficient way to dispose of snow is to let it melt near where it accumulates; however, where space is limited, snow can be transported to a designated melting site (TAC 2003). In the Lake Tahoe basin, snow/ice is removed (hauled) from urban areas and transported to designated storage and melting areas, therefore allowing the management of melt runoff. Although this strategy could be expensive, it may be warranted to remove the snow/ice that contains potentially harmful levels of chlorides and other pollutants in small or urbanized areas that drain to a sensitive receiving water. Many factors needs to be considered when establishing a snow melt site, see Fay et al. (2013) for a comprehensive list of factors to consider.

Additional References for Snow Removal

Caltrans. 2013. *Deicer Report for California Department of Transportation, Fiscal Year 2013/2013*. Order No. 99-06-DWQ, NPDES No. CAS000003. California Department of Transportation, Marysville, California.
http://www.dot.ca.gov/hq/env/stormwater/annual_report/ar_oct_2013/ar_DeicerReport.pdf

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http://maintenance.transportation.org/Documents/nchrp%2020-7_Task%2013Revised%20Chapter%208%20with%20Summary%20of%20Research.pdf

Transportation Association of Canada (TAC). 2003. *Synthesis of Best Practices, Road Salt Management*. Transportation Association of Canada http://www.tac-atc.ca/english/resourcecentre/readingroom/pdf/roadsalt-1.pdf

Venner, M. 2004. Sections 8.3: Strategic Planning for Reduced Salt Usage, and 8.4: Stewardship Practices for Reducing Salt and Other Chemicals, 8.5: Winter Operations Facility Management, in AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures.

Anti-icing, Deicing and Pre-wetting Practices to Optimize Salt Use

Starting over a decade ago, transportation agencies transitioned from reliance on deicing to utilizing anti-icing wherever possible (O'Keefe and Shi 2005). Anti-icing is the application of material (generally liquid) prior to a storm system to prevent the bonding of ice to the pavement (Figure 9). Deicing is the application of material (generally solid) after a storm system to break the ice-pavement bond. Anti-icing can lead to improved level of service, reduced need for chemicals, abrasives or plowing, and associated cost savings and increased safety and mobility (Hossain et al. 1997; Kroeger and Sinhaa 2004; Conger 2005; O'Keefe and Shi 2005). Caltrans has seen about a 50 percent material savings by shifting from application of solid rock salt to salt brine (liquid application) (personal communication, Dave Frame, Caltrans, April 5, 2012). Other DOTs have reported smaller, but nevertheless consistent reductions in salt applications (Venner 2012).

Figure 9: Anti-icing (left) and deicing operations (photos courtesy of Wisconsin and Kansas DOTs), respectively.

A recent study from Clear Roads synthesized the current practice of during-storm direct liquid applications (DLA) and identified the following benefits: reduced application rates, reduced loss of materials, faster time to reach bare lane, fast action/safer conditions, further prevention of ice-pavement bonding, accurate low application rates, and reduced corrosion effects (Peterson et al. 2010).

Pre-wetting, which is the use of chemicals to wet abrasives or solid deicers before application to quickly activate material for immediate ice melting performance, and reduce scatter and bounce, is becoming more common (Venner 2004). Pre-wetting has been shown to increase the performance of solid chemicals or abrasives and increase their longevity on the roadway surface, thus reducing the amount of material required (Hossain et al. 1997). Additionally, pre-wetting is preferable to the application of dry salt to roadways, which may blow away or bounce off the road prior to actively melting snow and ice. In a recent case study, the use of brine to pre-wet salt resulted in a 15% reduction in product usage, as the pre-wet salt exhibited equivalent ice melting performance, better adherence to the road surface, and less loss to bounce and scatter (personal communication, Peter Noehammer, City of Toronto, March 28, 2012). A Michigan DOT study has reported significant material loss of up to 30% occurs when using dry salt applications on dry pavement, which is represented in Figure 10Figure 11 (Michigan DOT 2012). Another pre-wetting method known as slurry is the application of up to 30% liquid to solid product and has shown promising results (Fay et al. 2013).

Figure 10: Pre-wet salt application (http://www.snowexproducts.com/)

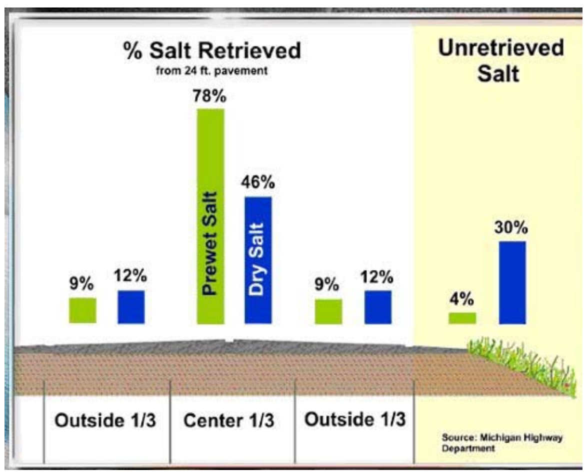

Figure 11: Graphical display of the amount of salt retrieved from the pavement when pre-wetted and not pre-wet and the location of salt placement by equipment (Michigan DOT 2012).

In sum, the benefits of pre-wetting are as follows:

- Reduced application rates
- Reduced loss of materials from roadway surface prior to snow/ice event (Keeps material where it will do the most good)
- Faster post-storm cleanup (snow/ice removal from roadways)
- Fast acting and further prevention of ice-pavement bonding
- Reduced corrosion effects

Additional Resources for Anti-icing, Deicing and Pre-wetting to Reduce Salt Use

Burtwell, M. 2004. "Deicing Trails on UK Roads: Performance of Prewetted Salt Spreading and Dry Salt Spreading." Transportation Research Circular Number E-C063. In the *Sixth International Symposium on Snow Removal and Ice Control Technology*. Spokane, Washington. pp. 564.

CTC & Associates, LLC. 2009. *Anti-icing in Winter Maintenance Operations: Examination of Research and Survey of State Practice*. Transportation Research Synthesis 0902. http://www.lrrb.org/pdf/trs0902.pdf

Federal Highway Administration (FHWA). 1996. *Manual of Practice for an Effective Anti-icing Program: A Guide for Highway Winter Maintenance Personnel*. FHWA-RD_95-202. http://www.fhwa.dot.gov/reports/mopeap/eapcov.htm

Mass DOT. 2012. *Environmental Status and Planning Report* EOEA#11202. MassDOT Snow & Ice Control Program.

Michigan Department of Transportation (MDOT). 2012. *Salt Bounce and Scatter Study*. Project Summary Report, Final Report. MDOT Operations Field Services Division. http://www.michigan.gov/mdot/0,1607,7-151-9623_26663_27353---,00.html

Thompson, G.E. 2004. "Anti-Icing and Material Distribution Performance Measures for Achieving Level of Service Through Mobile Data Collection." Transportation Research Circular Number E-C063. In the *Sixth International Symposium on Snow Removal and Ice Control Technology*. Spokane, Washington, pp. 503. http://onlinepubs.trb.org/onlinepubs/circulars/ec063.pdf

Venner, M. 2004. Section 8.4: Stewardship Practices for Reducing Salt and Other Chemicals, (see Anti-Icing and Pre-Wetting sub-sections), in AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures, Vol. 8.

Precision Application and AVL/GPS Technology

Washington State (WS) DOT estimated that the use of precision controllers prevents over-application and saves up to 10% of material applications resulting in an approximate savings of $1.2 million annually (Venner 2012). Nova Scotia DOT and Public Facilities reported that calibrated application was saving $500,000 annually (Venner 2012). Michigan DOT estimates savings of $3 million annually, or 10% of agency costs. Increasingly, these systems are also combined with Geographic Positioning System and AVL systems (Venner 2011). Half of WSDOT's fleet is outfitted with AVL and automated data collection, eliminating the need for maintenance technicians to fill out paperwork on their activities for the day. This results in about 10,000 hours per year that maintenance employees are out plowing instead of filling out paperwork, equating to $350,000 per year in labor savings (Venner 2012). In a national survey of DOTs in 2011, Delaware, Idaho, Kentucky, Minnesota, Missouri, and North Carolina DOTs all reported using GPS/AVL to manage resources/materials usage and to optimize operations.

A new and emerging technology known as geo-fencing is currently being evaluated as a possible best management practices technique. Geo-fencing uses GPS software to set boundaries in specific locations along spreader routes. Within the boundaries, spreader applications are stopped or adjusted automatically to reduce or prevent the potential for overlap applications as several salt application vehicles travel through the common routes multiple times. In addition, geo-fencing can be utilized to inform or alert operators when they enter environmentally sensitive areas or areas of concern so critical adjustments can be made (Mass DOT 2012). Such areas may include:

- Groundwater recharge areas
- Areas with exposed or shallow water tables with medium to high permeability soils
- Sources of drinking water
- Salt-sensitive vegetative communities
- Salt-sensitive wetlands
- Small ponds and lakes

- Creeks and Rivers with low flows as compared to roadway runoff
- Salt-sensitive agricultural areas
- Salt-sensitive habitats for species at risk

Additional Resources for Precision Application and AVL/GPS Technology

Burtwell, M. 2004. "Deicing Trails on UK Roads: Performance of Prewetted Salt Spreading and Dry Salt Spreading." Transportation Research Circular Number E-C063. In the *Sixth International Symposium on Snow Removal and Ice Control Technology*. Spokane, Washington. pp. 564.

Fay, L., Akin, M., Shi, X., and D. Veneziano. 2013. *Revised Chapter 8, Winter Operations and Salt, Sand and Chemical Management, of the Final Report on NCHRP 25-25(04)*. American Association of State Highway and Transportation Officials. http://maintenance.transportation.org/Documents/nchrp%2020-7_Task%2013Revised%20Chapter%208%20with%20Summary%20of%20Research.pdf

Mass DOT. 2012. *Environmental Status and Planning Report* EOEA#11202. MassDOT Snow & Ice Control Program.

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Venner, M. 2004. Section 8.4: Stewardship Practices for Reducing Salt and Other Chemicals, (see Anti-Icing and Pre-Wetting sub-sections), in AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures, Vol. 8.

Equipment Calibration

Calibration of equipment ensures that equipment is operating optimally, and in the case of material spreaders, that the appropriate amount of material is being applied. Not calibrating equipment can result in over or under application, potentially leading to wasted product or hazardous driving conditions, respectively. A calibration policy is recommended as part of the facility management plan and should be reinforced in staff training (TAC 2003; Fay et al. 2013). Times to calibrate are:

- When a piece of equipment is acquired or installed;
- Prior to and at points throughout a winter season; or
- When material calculations indicate a significant discrepancy (Fay et al. 2013).

Calibration for all application methods (solid and liquid), and for each product type (sand, salt, salt brine, etc.) should be completed routinely. Records of calibration results and who conducted the calibration should be kept. Proper calibration will allow for the most efficient use of equipment, and prevent waste or loss of product to the environment, potentially reducing impacts.

Additional Resources for Equipment Calibration

Fay, L., Akin, M., Shi, X., and D. Veneziano. 2013. *Revised Chapter 8, Winter Operations and Salt, Sand and Chemical Management, of the Final Report on NCHRP 25-25(04)*. American Association of State Highway and Transportation Officials. http://maintenance.transportation.org/Documents/nchrp%2020-7_Task%2013Revised%20Chapter%208%20with%20Summary%20of%20Research.pdf

Transportation Association of Canada (TAC). 2003. *Synthesis of Best Practices, Road Salt Management*. Transportation Association of Canada http://www.tac-atc.ca/english/resourcecentre/readingroom/pdf/roadsalt-1.pdf

Venner, M. 2004. Sections 8.3: Strategic Planning for Reduced Salt Usage, and 8.4: Stewardship Practices for Reducing Salt and Other Chemicals, 8.5: Winter Operations Facility Management, in AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures.

Weather Information, Forecasting - RWIS & MDSS

Weather forecasts and real-time environmental monitoring, e.g., RWIS (Road Weather Information System) aid maintenance managers in developing effective and efficient treatment strategies, and allow for optimization of equipment and materials used (Figure 12). Accurate weather forecasts can be utilized to reduce application rates while providing the same, or better, level of service. Weather information may be gathered from a variety of sources such as free and public weather services, private-sector weather forecast services, RWIS, and decision support systems (e.g., MDSS), each providing distinct levels of detail. Near-real-time weather and road condition information and customized weather services are valuable to the success of proactive maintenance strategies (Shi et al. 2007; Ye et al. 2009). Real-time data for air temperature, wind, type and amount of precipitation, as well as forecast weather conditions, pavement temperature, bridge temperature, and pavement conditions play a vital role in winter maintenance decision making. It has been reported that accurate weather and road conditions forecasts and information have enabled a reduction in chloride deicer usage (Fay et al. 2013).

Figure 12: RWIS (photo courtesy of Kansas DOT).

In addition to RWIS, MDSS (Materials Decision Support System) is becoming a popular tool to provide accurate and reliable weather information to state agencies (Venner 2004). MDSS is a powerful software application system, which processes RWIS data in order to develop forecast information and assist maintenance personnel in the decision making processes of determining roadway maintenance activities. MDSS systems provide real-time and post storm analysis to evaluate materials used, rate of application, and timing of application.

The utilization of RWIS and MDSS can provide valuable information, which can assist roadway maintenance agencies in determining the most effective strategies aimed to reduce impacts and increase level of service (Mass DOT 2012). A pavement condition and treatment data flow chart for MDSS is shown in Figure 13. The MDSS software uses collected weather, pavement, traffic, and environmental data to develop road weather forecasts and make suggestions on products, applications rates and frequency of repeat applications or snow removal based on defined rules of practices. After each treatment occurs, and the information is input into the system, updated treatment options are provided.

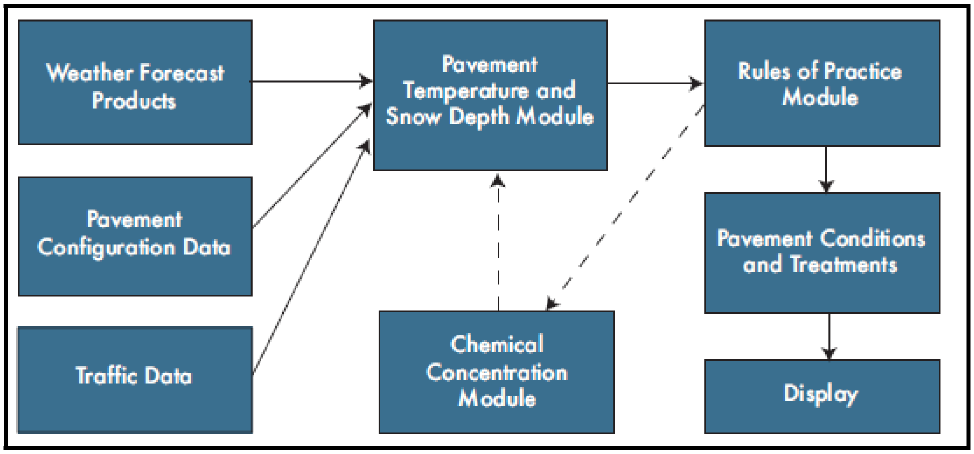

Figure 13: Typical MDSS pavement condition and treatment data flow (NCAR)

Using MDSS, Indiana realized salt savings in one winter (2008-2009) of 228,470 tons ($12,108,910) and when normalized for winter conditions based on storm severity, total salt savings were 188,274 tons ($9,978,536) based on salt prices of $53/ton (McClellan et al. 2009). MDSS proved to be a strong management tool for planning ahead of the storm. A cost-benefit analysis of MDSS implemented in New Hampshire, Minnesota, and Colorado identified benefits as reduced material use, improved safety and mobility, and significant cost savings (Ye et al. 2009). The benefits were found to outweigh the costs associated with the technology in all three states, with benefit-cost ratios ranging from 1.33 to 8.67 due to varying conditions and uses of resources. Identified benefits and needs were:

- MDSS provides a quantitative evaluation of performance measures.
- MDSS can be used as training tool.
- Outcomes associated with changes in rules of practice can be evaluated through MDSS.
- Use of MDSS requires a quality weather forecast.
- The quality of the recommendations from MDSS is dependent on properly sited, maintained and reliable ESS.
- Less use of maintenance vehicles.
- Consistent/seamless treatment of roads among maintenance sheds.
- Savings in material, labor, fuel, and reduced equipment wear and tear.

Benefits and costs studies associated with the use of weather information for winter highway maintenance found that winter maintenance costs decreased as the use of weather information increased or as accuracy improves (Ye et al. 2009). Table 3 summarizes the benefits and costs associated with the use of weather information for winter maintenance. Focusing forecasts on the road environment and investing in equipment with high accuracy ultimately provide more focused information about the road environment, and allow for the development of better winter maintenance strategies (Ye et al. 2009).

Table 3: Case Studies of Use of Weather Information to Guide Winter Highway Maintenance (Ye et al. 2009).

Case Study State	Winter Season	Winter Maintenance	Benefits ($)	Weather Information	Benefit–Cost	Benefits / Maintenance

		Cost ($)		Costs ($)	Ratio	Costs (%)
Iowa	2006–07	14,634,000	814,000	448,000	1.8	5.6
Nevada	2006–07	8,924,000	576,000	181,000	3.2	6.5
Michigan	2006–07	31,530,000	272,000	74,000	36.7	0.9

Additional Resources on Weather Forecasting and RWIS

Ballard, L. 2004. "Analysis of Road Weather Information System Use in California and Montana." Transportation Research Circular Number E-C063. In the *Sixth International Symposium on Snow Removal and Ice Control Technology*. Spokane, Washington,pp. 190.

Ericksson, D. 2004. "Reducing Salt Consumption by Using Road Weather Information System and Mesan Data." Transportation Research Circular Number E-C063. In the *Sixth International Symposium on Snow Removal and Ice Control Technology*. Spokane, Washington, pp. 278.

Ketcham, S. A., Minsk, L.D., and L.S. Danyluk. 1998. *Test and Evaluation Project 28: Anti-icing Technology, Field Evaluation Report*., FHWA Report RD-97-132. http://ntl.bts.gov/lib/5000/5700/5786/132.pdf

Mitchell, G.F., Richardson, W., and A. Russ. 2006. *Evaluation of ODOT Roadway/Weather Sensor Systems for Snow & Ice Removal Operations/RWIS Part IV: Optimization of Pretreatment or Anti-icing Protocols*. Final Report Prepared for Ohio Department of Transportation and FHWA.

National Cooperative Highway Research Program (NCHRP). 2005. *Synthesis 344: Winter Highway Operations A Synthesis of Highway Operations*. Transportation Research Board. http://onlinepubs.trb.org/onlinepubs/nchrp/nchrp_syn_344.pdf

Strategic Highway Research Program (SHRP). 2000. *1999-2000 Technology and Usage Survey Results: Anti-icing Techniques and Road Weather Information System Technology*. Strategic Highway Research Program, Anti-icing/RWIS Lead States Team.

Strong, C., and L. Fay. 2007. *RWIS Usage Report*. A Final Report prepared for the Alaska Department of Transportation and Public Facilities Division of Program Development, Juneau, AK. http://www.westerntransportationinstitute.org/documents/reports/4W1526_Final_Report.pdf

Venner, M. "Innovative, Cost-Effective DOT Maintenance & Operations: Practices with Multiple Benefits," AASHTO Summer Maintenance Meeting, 2011 and 2012.

Venner, M. 2004. Section 8.4: Stewardship Practices for Reducing Salt and Other Chemicals, (see RWIS sub-section), in AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures, Vol. 8, Winter Maintenance.

Zwahlen, H.T., Russ, A., and S. Vatan. 2003. *Evaluation of ODOT roadway/weather sensor systems for snow and ice removal operations Part I: RWIS*. Russ College of Engineering and Technology Final Report.

Staff Training

Training of winter maintenance staff and personnel is of particular importance for the effective and efficient use of chloride roadway deicers. A comprehensive training program is recommended to demonstrate the purpose and value of new procedures, to address staff concerns and potential resistance to change, and to ensure needed competencies. Training can focus on techniques to use less deicer without compromising public safety or mobility of the traveling public, while still maintaining or exceeding the state's defined level of service. Successful training programs are designed to identify the learning goals and have a logical progression to the lesson plan. Successful training programs have been shown to reduce deicer usage and improve winter maintenance operator practices (Eckman and Nuckles 2011).

Learning goals such as LOS guidelines, principles of ice formation, chemistry of road salts, and environmental impacts of road salts need to be identified and addressed during training. To be most effective and easily remembered, it is recommended to hold annual training shortly before the onset of the snow and ice season. This helps ensure current learning goals are taught, reinforced, and tested. In addition, many DOTs utilize statistical data to provide regular feedback to managers and operators, such as posting annual material or cost savings to reinforce the importance of training efforts. Operators should be encouraged to share information, experiment with new concepts, and challenge old ideas (TAC 2003; Venner 2004). AASHTO's Compendium of Environmental Stewardship Practices, Policies, and Procedures' volume on winter maintenance and salt management includes a section on DOT training programs as well as other salt reduction and management practices at DOTs.

A comprehensive training program is recommended to demonstrate the purpose and value of new procedures, to address resistance to change, and to ensure competency of personnel carrying out their duties. Components of training may include (also see Table 4):

- Assessing the needs of the staff.
- Considering who to be trained and how best to convey the information to an audience and maximize the learning (verbal and visual aids, group discussion, practical application, etc.).
- Designing the training program to identify the learning goals, components and a logical progression, and developing a lesson plan.
- Determining the training methods (in class, in field, post-storm debriefing, etc.)
- Having a current staff member conduct the training, in order to add credibility and provide opportunity for follow-up questions and feedback.
- Evaluating the training program (including implementation of the training material).
- Assessing how much transfer of knowledge occurred and the need for refresher courses.

Table 4: Staff training recommendations (Northumberland 2011)

Job Class	Training	Frequency
Operations Manager	Association Road Supervisors Association	Quarterly
	RWIS - Weather Forecasting	Once
	Snow and Ice Colloquium	Annually
	Intermunicipal Public Works committee	Monthly
	Proper use of infra-red thermometers	Once
	Interpretation of weather and pavement conditions	Once
	Ontario Good Roads Association	Continuous
Roads Foreman	Road Supervisors Association meetings	Quarterly
	Salt Smart – T.A.C. Train-the-Trainer	Once

	RWIS - Weather Forecasting	Once
	Proper use of infra-red thermometers	Once
	Interpretation of weather and pavement conditions	Once
	Combination Plow Training	Once
Operator	Annual driver training updating	Annually
	Bi-annual staff meeting – fall session	Bi-annually
	Annual updating of winter maintenance routes	Annually
	Winter road patrol sheets - Proper record keeping	Annually
	Proper use of infra-red thermometers	Once
	Combination Plow Training	Once

The important role of technology in staff training has been validated by agencies. Computer-based training (CBT) has been proven to be a powerful tool for staff training. A CBT has been developed under the leadership of AASHTO and for the winter maintenance staff in state and local governments. The course consists of several lessons containing a total of about forty units, covering a host of topics about winter roadway management. A general overview can be seen using the link below http://sicop.transportation.org/Documents/CBT_Flyer_v2b%5B1%5D.pdf.

Additional Resources for Staff Training

Smithson, L.D. 2006. "Achieving Technology Transfer with Interactive Computer-Based Training." Presented at *SIRWEC 2006 XIII International Road Weather Conference*. Turin, Italy. In the proceedings *SIRWEC 2006, Applied Research Lectures,* pp. 164-169.

Transportation Association of Canada (TAC). 2003. *Synthesis of Best Practices, Training*. http://www.tac-atc.ca/english/resourcecentre/readingroom/pdf/roadsalt-2.pdf

Transportation Association of Canada (TAC). http://www.tac-atc.ca/

Venner, M. 2004. Section 8.6: Training for Salt Management and Winter Operations, AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures.

Monitoring and Record Keeping

Monitoring environmental parameters and practicing effective record management of snow and ice control products and related procedures can aid in material saving, create a more effective working environment, increase efficiency, reduce person and equipment hours, and enable cost savings. Collected data help DOTs report on point source and non-point source runoff from roadways or stockpiles. Monitoring chloride concentrations on and along roadways and in adjacent water bodies can provide an indication of potential impacts to stream biota. Furthermore, information from monitoring chloride concentrations in salt-vulnerable areas can inform selection of appropriate winter maintenance and mitigation strategies. A municipality in Canada implemented a monitoring approach that included maintenance agencies working with their local conservation authority to add chloride sensors to their stream monitoring network.

A quality assurance (QA) plan should be developed prior to sampling and analysis. The sampling design plan should discuss what types of samples are being collected, where they are being collected, the timing of sampling, and how the samples should be handled. The analysis protocol should discuss the test methods being used, the analysis methods for the data, and any relevant reporting parameters. The QA plans should be available, on site, reviewed prior to the initiation of sampling or analysis, and followed by trained staff. Additional information on the development of QA plans can be found at: http://www.epa.gov/QUALITY/qs-docs/g5-final.pdf (US EPA 2002d).

For toxicity testing, QA plans should be developed for laboratory toxicity testing and should consider sample replicates and controls, food sustainability, reference toxicants, and performance evaluations of samples (ELAP 2008).

The following issues should be considered before initiating a water monitoring program (TAC 2003):

- At what frequency and where will samples be collected?
- Will sampling be continuous (in-situ) or periodic (grab samples or grouped samples)?
- Will there be health and safety issues with data collected during/post storm events or will maintenance of sensors be needed during storm conditions?
- Will the data be communicated back to a central location automatically?
- Will sampling location need power and telephone capability for data communication (or could it use solar with cell phone and avoid issue).
- Will there be any confounding data such as chlorides entering the environment from other sources (such as private use or private contractors, water softeners, landfills, or wastewaters)

Detailed Maintenance Records

Consider maintaining the following records, at a minimum: winter severity ratings, total number of events requiring road salt application during the winter season, and materials usage. Table 5 shows a list of recommended records and reports.

Table 5: Example list of records and reports maintained during the winter season (Northumberland 2011)

Title	Description
Salt/Sand/Grit Inventory	Inventory record of salt materials delivered to works yard including date, supplier, quantity, etc.
Road Patrol	Daily record of road conditions
GPS Vehicle Report	Report generated by GPS unit installed on maintenance vehicles detailing date, time, speed, trip length, etc.
Dickey-John Spreader Controls	Continuous reporting of application of materials on roadways
Daily Activity Reports	Daily record of Operator’s activities performed through the shift

Transportation agencies should consider keeping detailed records of the following items and issues:

- Confirm that all salt materials are stored under cover
- Confirm that all storage sites include collection and treatment of wash water and drainage
- Inspection and repair records for salt application vehicles
- Purchase and stockpiling records for salting materials
- Brine production quality control (e.g., concentrations)
- Pavement temperature trends in daily logs, along with pavement conditions, weather conditions and winter treatment strategy (TAC 2003)
- Temperatures, snow depths and durations during snow/ice storms with applied salt
- Traffic levels during snow/ice storms with applied salts
- Total length of road (lane miles) on which salt is applied
- Storm and overall winter severity ratings
- Total number of events requiring road salt application during the winter season
- Materials usage (e.g., total quantity of road salts used)
- Description of non-chloride materials used for winter road maintenance
- State of calibration equipment
- Average chloride concentration and frequency of sampling at each sampling location, if available (Highway Deicing Task Force Report 2007)

Storm severity is a combination of storm impacts and the relative difficulty of mitigating the impacts (Strong et al. 2005; Farr and Sturges 2012). A winter (or weather) severity index (WSI) turns weather impacts relative to storm severity into a numerical value. A WSI can be applied to each storm event, for a whole year, or winter season. A winter severity index is an important parameter to consider when relating winter maintenance practices to impacts to the environment. For example, if chloride concentrations are being monitored during a winter season that is experiencing unusually cold weather with a lot of precipitation, andhas required more or higher deicer applications, chloride values may be higher than in typical years. In this case applying a WSI to the calculation would normalize the data so that big snow, average, and drought years can be treated equally.

Additional Resources for Monitoring and Detailed Maintenance Records

Anderson, B. 2004. "Measuring Winter Maintenance – what's behind the numbers?" Prepared for the *2004 Annual Conference of the Transportation Association of Canada*, Quebec City, Quebec. http://transportationassociation.ca/english/resourcecentre/readingroom/conference/conf2004/docs/s17/anderson.pdf

Environment Canada. 2004. "Code of Practice for the Environmental Management of Road Salts." EPS 1/CC/5. http://www.ec.gc.ca/nopp/roadsalt/cop/pdf/1774_EngBook_00.pdf

Perera, N., B. Gharabaghi, and P. Noehammer. 2009. "Stream chloride monitoring program of City of Toronto: implications of road salt applications." *Water Quality Research Journal of Canada*, Vol. 44, No. 2, pp. 132-140.

Transportation Association of Canada (TAC), 2003. *Synthesis of Best Practices, Drainage and Stormwater Management*. Transportation Association of Canada. http://www.tac-atc.ca/english/resourcecentre/readingroom/pdf/roadsalt-4.pdf

Transportation Association of Canada (TAC). 2003. *Synthesis of Best Practices, Pavement and Salt Management*." Transportation Association of Canada. http://www.tac-atc.ca/english/resourcecentre/readingroom/pdf/roadsalt-5.pdf

Venner, M. 2004. Sections 8.3: Strategic Planning for Reduced Salt Usage, and 8.4: Stewardship Practices for Reducing Salt and Other Chemicals, (See sub-section on Monitoring, Recordkeeping, and Decision Support in Maintenance Management Systems, including sub-sections on Evaluating Treatment Effectiveness and also Performance Measures) in AASHTO Compendium of Environmental Stewardship Practices, Policies, and Procedures.

Program Evaluation and Continuous Improvement

The importance of monitoring, data collection, and data analysis cannot be stressed enough. Many DOTs have realized significant cost and material savings and identified effective practices through monitoring and data collection. An example is the development of a model by the Iowa DOT that allocates salt to garages based on weather conditions and policy usage requirements (personal communication, A. Dunn, October 23, 2012). To establish the model, Iowa DOT needed to have historic weather data, information on salt use at the garage level, the number of lane-miles and prescribed LOS for each road type for each garage, environmental parameters measured by RWIS, and actual working hours. The collected data was used to create a salt budget for each garage, providing a program evaluation tool for Iowa DOT to manage their salt use.

Maintenance decision support systems provide pavement weather forecasts and suggestions on product use and route timing, but can also be used to evaluate programs during and post storm. See the section on MDSS for more information and additional references. Salt Management plans can also be used as a tool to evaluate programs (see the section on Salt Management Plans for more information).

Another example of using collected data to identify best practices is the use of Life-cycle assessment (LCA). An LCA is a framework for evaluating the environmental impacts of products or processes over the entire life cycle. In the context of winter road treatment, an LCA would enable the comparison of all steps in the delivery and use of a product, from mining raw materials, manufacturing or processing the chemical, storage and application to eventual fate in the environment. Much like full-cost accounting quantifies all of the infrastructure and environmental costs of chloride-based treatments and their alternatives; an LCA provides quantitative measurements of the environmental consequences of different decisions that would be useful for DOTs, chemical suppliers and environmental scientists seeking improvements in winter road treatment processes (White and Shapiro 1993; Fitch et al. 2013).

Fitch et al. (2013) developed an LCA model for winter maintenance chemicals to understand which actions a DOT can take to reduce the negative life-cycle environmental impacts of these activities. Three representative treatments compared: conventional rock salt, CMA, and preemptive treatments of roadways with a brine of salt and/or CMA. The results show that CMA has significantly higher emissions than chloride-based treatments. As expected, CMA does reduce overall chloride emissions relative to salt treatment, but this comes at the cost of significantly higher life-cycle energy, water, BOD, and greenhouse gas emissions. Most of the emissions associated with using CMA occur upstream of the DOT, during the mining and production of the base materials. Consequently, it is unlikely that DOTs can further reduce the effects associated with the use of this chemical by improving their application or management practices. Any significant improvements associated with the environmental burden of this alternative will almost certainly need to come from improvements in the production process. *On the other hand, the use of brine appears to be the best option available to DOTs.* This option requires less total energy, releases fewer greenhouse gases, consumes less water, and emits less BOD than either CMA or dry salt. The benefits of using brine over using dry salt were significant. *This study suggests that modest steps at the DOT level can result in meaningful reductions in life-cycle effects. In particular, a switch to using salt brine as a treatment method,* *rather than rock salt, enhances efficiency and reduces total energy use, water use, and greenhouse gas emissions without requiring a significant financial investment by the DOT.*

What can be done once chlorides have been applied?

Over the past decade, DOTs have been working on reducing salt application to the minimum necessary to maintain public safety and mobility. Their practices are mainly centered around source control; however, salt has been accumulating in the environment and next to roadsides for decades. This section presents potential methods for addressing chlorides that have already accumulated in roadside soils and waterbodies.

Methods to Remove Chlorides

Recently, increased chlorides in the environment associated with road salt have been identified as a major environmental concern, partly due to the nature in which chlorides move through the subsurface and the difficulties inherent in remediation. Traditional methods of removing chlorides from water such as reverse osmosis and membrane filtration are very expensive and require significant maintenance, and are not appropriate for transportation rights-of-way. Although effective chloride removal strategies are still being developed, some innovative approaches involve phytoremediation or capturing chlorides on filter media, like concrete. Research focused on removing road salt related chlorides from the environment is presented below.

Phytoremediation

Phytoremediation is the use of plants to aid in the removal of contaminants within soils, groundwater and surface waters. The main transport processes of phytoremediation consist of sorption and plant uptake, which are dependent upon the properties of the plants and contaminants involved. In order for removal of a conservative substance like chloride to be successful, the plants must be harvested and removed prior to plant die-off. Since phytoremediation is a relatively new strategy with limited data, regulatory agencies have not yet widely accepted this technique. Nevertheless, recognition of phytoremediation as a cost-effective, long term remediation strategy for soils is increasing (Schnoor et al. 1995). Depending upon the selected plant systems, plant growth and continued treatment can be achieved for 25 to 50 years with hybrid poplar trees (Schnoor et al. 1995). In addition, results from a heavy metal contamination site suggest that significant cost savings can be accomplished with phytoremediation, while traditional technologies are up to ten times more expensive (Garbisu and Alkorta 2001). Still, reported planting costs are approximately $10,000 per acre, plus the cost of monitoring (Schnoor et al. 1995).

Phytoremediation has been utilized to remove a wide variety of contaminants from the environment. Successful treatment of a variety of hazardous waste contaminants such as organics, agricultural runoff, metals, landfill leachate, and chlorinated solvents has been achieved using phytoremediation techniques (Schnoor et al. 1995). Phytoremediation has some associated limitations, though. Phytoremediation is most effective at sites with shallow subsurface contamination since treatment mechanisms are dependent on plant root depths, which are limited to 50 cm (~20 in) for herbaceous plants and 3 m (~10 ft) for trees (Pilon-Smits 2005). In addition, phytoremediation may require longer treatment times compared to excavation or pump–and-treat systems due to the nature of biological systems. For this reason, phytoremediation techniques are commonly integrated with other treatment technologies. For example, soil with the highest concentrations of contaminants may be excavated and phytoremediation used as a polishing technique to remove the remaining pollutant (Pilon-Smits 2005). Removal and appropriate disposal of plants used for phytoremediation may be required for long-term performance.

In Quebec, halophytes, plants able to grow in high salinity areas, were selected, harvested and used in ditches to remove salt from runoff water (Morteau et al. 2006), where an estimated 4 to 10.6 tons of salt were added to ditches each year from winter roadway operations. All of the plants accumulated salt throughout the study; Atriplex, also known as Saltbrush, accumulated the most salt by mass. The amount of salt taken up by the plants was dependent on plant morphology, species, and the concentration of salt exposure. Recommendations developed based on this research included the following:

- Base the size of the marsh, ditch and filter bed on annual field data of runoff flow rates and observed salt concentrations.
- Grow plants in a greenhouse instead of transplanting from another field location.
- Study invasion of other marsh plants, and evaluate the ecological and physiological tolerance of each plant species in a saline environment.

Finally, phytoremediation will likely only be successful for treating soils and remaining salt laden pore waters. Typically, the large volumes of runoff and timing of the events as compared to active plant growth and activities is such that use of phytoremediation will not be feasible for runoff control in most cases, unless very large storage is possible.

Using Traditional Stormwater Structural BMPs to Manage Chlorides

Stormwater structural BMPs are practices that include treatment and flow management for runoff. Chlorides cannot be removed from runoff with traditional controls, therefore structural BMPs used in the management of chloride laden runoff can include diversion into different receiving waters (for example from surface waters to groundwaters or less sensitive receiving waters). They can also play a role in mixing chloride laden waters throughout the event to minimize peak concentrations, even though the chloride load overall will remain the same.

This section focuses on BMPs that can redirect runoff or capture for mixing chloride-laden runoff. The basic mechanisms for pollutant removal in traditional BMPs consist of gravity settling, infiltration of soluble nutrients through soil or filters, or biological and chemical processes (Turner-Fairbank Highway Research Center 1999). The chloride anion is conservative; differing from organics in that it does not break down further, and is difficult to remove once in water and soil (Environment Canada 2001).

Only a few structural BMPs have shown promising results at capturing and managing chlorides. The BMPs presented here can be used to effectively manage runoff velocity and improve the quality of highway storm water runoff in general. Structural BMPs should be designed, sited, installed, and maintained properly. They can be used individually; however, it is generally recommended that they be used in combination to enhance overall performance, increase service life, and preserve downstream water bodies.

Vegetation along roadsides can play a role in the general treatment of runoff through chemical and biological processes. Salt-tolerant species, such as perennial rye-grass, show a high resistance to the toxic effects of salt and in areas with high and frequent applications of salts, and can be considered in vegetated BMPs and landscaping strips. A combination with fescue-grass at 70:30 when building new roads or reconstructing existing road is also recommended (Baltrenas and Kazlauskiene 2009; Eppard et al. 1992).

There are many NCHRP and other available guidance documents on highway runoff and urban best management practices and therefore design details and sizing guidelines are not discussed in this document, except as how they apply to chloride management. Useful BMP guidance is provided in:

> National Cooperative Highway Research Program (NCHRP). 2006. *Evaluation of Best Management Practices and Low Impact Development for Highway Runoff Control.*

Washington, DC: NCHRP Report 565, National Cooperative Highway Research Program, Transportation Research Board. National Academies Press, Washington D.C.

National Cooperative Highway Research Program (NCHRP). 2012. *Guidelines for Evaluating and Selecting Modifications to Existing Roadway Drainage Infrastructure to Improve Water Quality in Ultra-Urban Areas*. National Cooperative Highway Research Program Report 728, Transportation Research Board, Washington D.C.

Water Environment Research Foundation (WERF). 2005. *Critical Assessment of Stormwater Treatment Controls and Control Selection Issues.* 02-SW-01. IWA. Water Environment Federation. IWA Publishing, London.

In addition, there are a number of ongoing and soon to be completed NCHRP projects that will result in useful guidance related to BMP selection and design and costing including:

Long Term Performance and Life-Cycle Costs of BMPs National Cooperative Highway Research Program (NCHRP) 25-40. In Progress. http://apps.trb.org/cmsfeed/TRBNetProjectDisplay.asp?ProjectID=3192

Guidance for Achieving Volume Reduction of Highway Runoff in Urban Areas National Cooperative Highway Research Program (NCHRP) 25-41. In Progress. http://apps.trb.org/cmsfeed/TRBNetProjectDisplay.asp?ProjectID=3193

Bridge Stormwater Runoff Analysis and Treatment Options National Cooperative Highway Research Program (NCHRP) 25-42. In Progress. http://apps.trb.org/cmsfeed/TRBNetProjectDisplay.asp?ProjectID=3194

Permeable Shoulders with Stone Reservoirs National Cooperative Highway Research Program (NCHRP) 25-25/Task 82. In Progress. http://apps.trb.org/cmsfeed/TRBNetProjectDisplay.asp?ProjectID=3315

Each of the above efforts is scheduled to have reports available in 2014.

Storage and Release

The first class of potential structural BMPs for improving the management of runoff includes ponds and wetlands. The primary management mechanism for chloride in these BMPs would be the mixing of runoff to reduce the peak concentrations as well as mixing of baseflows and non-chloride laden runoff in stored wet pools to reduce concentrations. The introduction of off-site area runoff from areas that are not being deiced would also reduce concentrations of the discharge. Finally, in limited cases, evaporation ponds may be feasible. These types of BMPs are briefly discussed below with regard to their potential role in chloride management.

Detention, Retention, or Evaporation Ponds

Dry and wet detention ponds are all examples of structures that can be used to remove pollutants through sedimentation or settling. However, none of these will remove chlorides (i.e. sequester chlorides) to a significant extent without some special adaptation of its operation. Some may serve to dilute chlorides if base flows, additional non-deicing tributary areas or preceding storm events were lower in chlorides; others can smooth out chloride concentrations within an event or over multiple events depending on the wet pool volume, limiting spikes in chloride concentrations released. Dry ponds can hold runoff during periods of high flow, and then remain dry in between storm events. Wet ponds generally hold water year round. Salt laden runoff can be captured in these ponds and then potentially be disposed of; for example, the runoff can be reused to make brine. If the water can be evaporated off, the remaining material can be disposed of (removed) or reused for dust mitigation on unpaved roads or in brine making operations (Fitch et al. 2004; Golub et al. 2008; Fay et al. 2013). DOTs have successfully used evaporation ponds to prevent chloride migration offsite (Fay et al. 2013).

An ongoing research project in France is measuring deicing salt storage in a detention pond originally installed to treat road water runoff and act as flow control (Remi et al. 2013). Continuous monitoring of salt and heavy metal concentrations of the influent (inlet) and effluent (outlet) of the detention pond is being conducted. The goal is to evaluate the amount of road salts applied to roads, versus the amounts entering and leaving the detention pond, as well as monitoring mobilization of heavy metals caused by the presence of deicing salts. This information will be correlated with winter maintenance practices associated with measured meteorological conditions and will provide valuable information that winter maintenance agencies will be able to use for their benefit and determine effective chloride remediation strategies, both there and abroad. A likely result of this study may be that the pond will smooth chloride peak concentrations that otherwise would have occurred; it may also dilute them with incoming runoff or baseflows from areas with less or no chloride application or direct baseflow from discharging groundwater. The total chloride load overall would likely remain the same.

Li and Davis (2009) found that bioretention ponds in Massachusetts removed chlorides and many other TDSs from surface runoff. The reduced runoff volume from using the bioretention facility contributed to lower pollutant output and increased water quality. A bioretention structure's ability to improve water quality may increase in proportion to the depth and area of the structure (Li and Davis 2009).

<u>Wetlands and Shallow Marshes</u>

Constructed wetlands utilize both physical and chemical processes such as adsorption, filtration, sedimentation, plant uptake, and decomposition to treat runoff (Staples et al. 2004) (Figure 14)**Error! Reference source not found.**. Again, chloride is a very difficult pollutant to treat and any removal would be due to some plant uptake, which would only be effective over the long-term with harvesting. The wetland would have to have a large enough detention time to allow for significant uptake to occur. For example, a wetland that was designed to hold the average size storm event would in many storm events not have sufficient residence time for uptake to occur during discharge.

Figure 14: A constructed wetland: just after completion (left) and after one season of plant installation (right) (Pitman and Patoprsty 2010).

Recent research has demonstrated the negative effects of road salts on constructed wetlands (Tromp et al. 2012). Also, as previously discussed, road salts can also mobilize hazardous materials causing significant impacts to water sources. In a treatment system consisting of a detention basin and a vertical flow wetland, heavy metals and poly-aromatic hydrocarbons were monitored, and high retention efficiencies above 60% were achieved for poly-aromatic hydrocarbons; however, during periods of high levels of road salt exposure, copper, cadmium, zinc and nickel concentrations increased at the effluent of the wetland, due to mobilization of these metals from contact with sodium chloride (Tromp et al. 2012).

Additional Resources for Ponds, Wetlands and Shallow Marshes

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Infiltration

Infiltration of stormwater is a very effective stormwater management technique under many conditions. However, given chloride's treatment transport characteristics, infiltration of runoff that contains chloride-based deicing materials can cause groundwater concerns. Road salting has been found to significantly affect chloride content and salinity of groundwater in many locations (Pitt et al. 1994, 1996). The potential for long term accumulation of salts in groundwater is a function of the nature of the aquifer and the loading of saline water versus fresh water – aquifers that exist in closed or relatively closed basins are more susceptible to long term increases in salts.

Roadway runoff in cold climates, where salt is used, have a high potential for contaminating groundwater because salts are water soluble, non-filterable, not readily sorbed to solids, and can leach into groundwater as infiltration occurs (Pitt et al. 1994, 1996). Because conventional treatment methods are not effective at removing salts, the potential for salt contamination of groundwater may be an overriding factor in determining the feasibility of stormwater infiltration. In areas where sand and gravels are being applied to enhance snow and ice management and reduce the use of salt, infiltration practices may be challenging. As application of sand and gravel can include fines or with crushing by vehicles can turn into fines, infiltration facilities can become clogged. Therefore, although infiltration of stormwater that includes chlorides based deicers can be beneficial to surface waters, both the impact of chlorides as well as potential clogging issues associated with use of sanding/gravel methods should be considered.

Infiltration Trenches

Infiltration trenches and basins treat runoff and reduce surface runoff water volume by allowing water to infiltrate into the surrounding/underlying soils and underlying groundwater systems (Staples et al. 2004) (Figure 15 & Figure 16). Infiltration technologies require a pre-settling or pre-treatment to remove suspended solids that would otherwise clog the system and reduce the infiltration capacity. Infiltration trenches are excavated trenches filled with stone and lined with filter fabric where runoff is collected and allowed to percolate into the soil (Staples et al. 2004). These trenches reduce runoff volume and have moderate to high ability to remove some soluble pollutants from the runoff; it is important to note that they require regular maintenance to ensure the inlet structure is functioning properly. Infiltration systems have been found to effectively remove fine silts, clays, and phosphorus in the Lake Tahoe region (TIRRS 2001). In Washington State, infiltration technologies including ponds, bio-infiltration ponds, trenches, vaults and drywells are the preferred methods for flow control and runoff treatment, offering the highest levels of pollutant removal (WSDOT 2011). According to Golub et al. (2008), “the depth of ground water and soil type limits the use of this option.” The sensitivity of underlying groundwater to increased chloride loadings is a key factor.

Figure 15: An infiltration trench (left) and an infiltration basin (right). Photos from http://www.lowimpactdevelopment.org/greenstreets/practices.htm.

Infiltration Basins

Infiltration basins function similarly to infiltration trenches, but more closely resemble a dry pond (Staples et al. 2004) (Figure 15). Infiltration basins hold runoff, which allows for longer infiltration times; however, these basins can release runoff from larger storm events depending on the design. Design considerations such as infiltration rates and site selection play an important role in their effectiveness. Infiltration basins are not recommended in areas with compacted soil, high or shallow groundwater levels, areas with contaminated soils or groundwater, and steep slope areas. Where stormwater has high levels of sediment, failure may occur and expensive remediation or re-installation may be required. Use of dense vegetation with deep roots at the bottom of the basin can enhance infiltration capacity and reduce soil erosion.

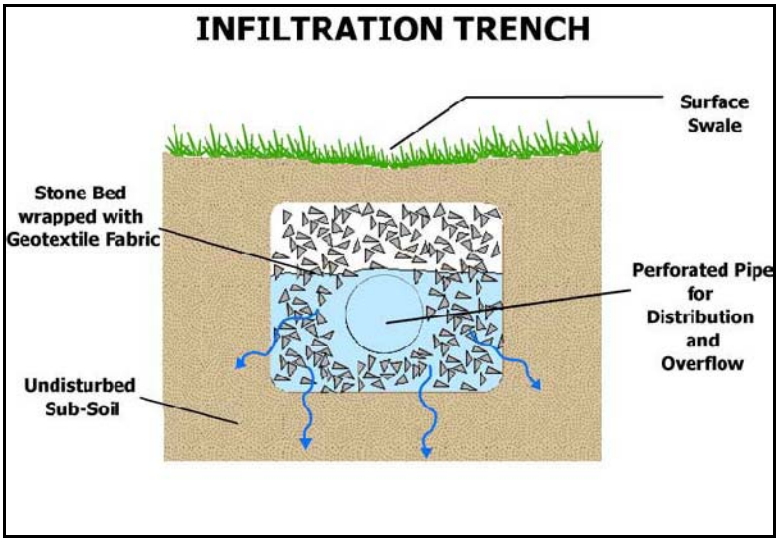

Figure 16: Schematic illustration of an infiltration trench (www.lowerpottsgrove.org/stormwater/pdf/tredyman06.pdf)

Additional Resources for Infiltration Trenches and Basins

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Vegetated Swales and Filter Strips

Biofiltration is the use of closely grown vegetation to filter runoff (Figure 17). This is achieved by allowing water to flow through the vegetation, which decreases the runoff velocity and allows particles to settle (Staples et al. 2004). Biofiltration systems are generally open channels and are sometimes referred to as swales, filter strips or natural and engineered dispersion. These systems provide effective removal of pollutants through mechanisms such as adsorption, decomposition, ion exchange, filtration, and volatilization. Biofiltration is most effective when combined with other treatment options such as ponds, infiltration trenches, or wetlands (Watson 1994). Vegetated swales can be used for snow storage and allow the meltwater to infiltrate. Vegetated swales and filter strips require minimal maintenance (mainly mowing and sediment/debris removal), which helps to keep their life-cycle cost low.

Bioinfiltration swales can be dry, grassy or vegetated channels (Staples et al. 2004; WSDOT 2011). Swales are generally located in naturally low topographic areas of uniform grade such as road ditches (Staples et al. 2004). They are also useful for runoff control on highway medians (Barr Engineering Company 2001). Dry swales may have check dams to temporarily pond runoff to both increase the removal of suspended solids and reduce the runoff velocity. Wet swales vary from dry swales by having very impermeable soils, often located close to the water table (Staples et al. 2004). Wet swales improve water quality through mechanisms such as adsorption, sedimentation, and microbially-assisted decomposition of pollutants (Barr Engineering Company 2001). Bioinfiltration swales would be expected to have the same potential issues with groundwater and the infiltrations systems discussed above.

Figure 17: A vegetated swale along a highway (Caltrans).

Grass swales, with both pre-treatment grass filter strips and vegetated check dams, were used to treat highway runoff and were found to not remove chloride but store it, such that it accumulated during the winter and was then released throughout the year (Stagge et al. 2012). Pretreatment grass filter strips were also found to serve as chloride reservoirs, and when used with bioswales increased chloride effluent concentrations significantly. Any chloride removal was determined to be from infiltration. During rain events of 3 cm (about 1 inch) or less, bioswales in combination with check dams were found to significantly reduce total volume and flow magnitudes (Davis et al. 2012). During larger storms, the bioswales functioned to smooth the fluctuation in flow.

Additional Resources for Vegetated Swales and Filter Strips

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Anchorage (Alaska). 1994. *Guidance for Design of Biofiltration Facilities for Stream Water Quality Control*. Watershed Management Program, Montgomery Watson(Firm).

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Alternative Method to Remove Chlorides

In addition to the more conventional approaches to remove chlorides associated with winter road way operations from the environment such as the use of phytoremediation, new and emerging technologies focus on capturing chloride in filter media such as dolomite, calcium, or concrete. This technology is in the very early stages of research and minimal data is available. The primary treatment mechanism involved in this new method is sorption of chloride to the filter media, which is dependent on the capacity of the filter media. Recycled concrete has been shown to make an effective sorption material for chlorides and is capable of increasing chloride penetration rates and chloride binding capacity, which would help increase chloride removal efficacy if correctly implemented (Villagrán-Zaccardi et al. 2008); however, more research is needed to determine effective application methods and materials. Given the mass of chlorides released during snow melt events, it will likely be very challenging if not cost prohibitive to use media for chloride removal.

Task 3 Scope of Work for Laboratory and Field Testing of Deicer Toxicity

Guide for Assessing the Toxicological Effects of Chloride-based Deicers in Water Bodies Adjacent to Highways

Research Problem Statement

This proposed project will build on the success of NCHRP 25-25/Task 86 (Toxicological Effect of Chloride-based Deicers in the Natural Environment), address the identified knowledge gaps in this increasingly important subject area, and provide the much needed guidance for transportation agencies and other stakeholders to minimize the environmental footprint of their winter roadway operations.

Background

State departments of transportation (DOTs) are continually challenged to provide a high level of service on winter roadways and improve safety and mobility in a cost-effective manner, while at the same time minimizing adverse effects to the environment, vehicles, and transportation infrastructure. Level of service, cost-effectiveness, and corrosion have traditionally been considered more urgent priorities than other less well-characterized impacts, such as impacts to water quality. It is increasingly important to understand the environmental footprint of deicers, including their impacts on aquatic ecosystems.

Since the 1960s, chloride salts have been the primary products used by roadway agencies for deicing and more recently for anti-icing and pre-wetting. Due to their long and widespread use, the environmental impacts of such deicers have been subject to significant research efforts (Hawkins 1971; Roth and Wall 1976; D'Itri 1992; Paschka et al. 1999, Ramakrishna and Viraraghavan 2005; Levelton Consultants Limited 2007; Shi et al. 2009). Nonetheless, as identified by the NCHRP Report 512, "a clear need exists for more monitoring and characterization of snowmelt runoff from highways" to better understand deicer impacts to the environment, including aquatic ecosystems.

Chloride salts are readily soluble in water, difficult to remove from water, and tend to accumulate in water over time (Howard and Haynes 1993). Deicers have been found to negatively impact aquatic community structures. Elevated chloride concentrations have correlated with reduced species richness and food web dynamics (Sanzo and Hecnar 2006; Collins and Russell 2009; Van Meter et al. 2011). Laboratory and field studies in Canada found that in southern Ontario, Quebec and other areas of heavy road salt use, chloride concentrations found in ground and surface water are often sufficient to affect biota (Environment Canada 2001). Such toxicity can be associated with the direct effect of deicers and/or with the indirect effect via their interactions with runoff chemistry. Numerous studies have reported environmental risks of chloride-based deicers, indicating that the actual effects depend on individual site conditions as well as the type and amount of deicers applied (Dagher and Rouleau 1990; Winston et al. 2012; Fay and Shi 2012).

Toxicity testing has not been required of manufacturers or vendors producing chloride-based deicers and the associated additives (e.g., corrosion inhibitors and thickeners). As such, little toxicity data has been collected or published in the field of winter maintenance (Corsi et al. 2010a). Toxicity research has been conducted on similar products used in other fields including aircraft or airfield deicers (Corsi et al. 2006) and dust suppressants (Williams and Little 2011), but available data on toxicological impacts are still very limited.

The most commonly used tools to assess toxicity are the laboratory acute and chronic tests, which apply varying concentrations of a contaminant to a selected species. The information gained from these tests is specific to the species tested and can be used to assess damage at the cellular and subcellular level of organisms. For this reason, hundreds if not thousands of species have been tested in this fashion to gather as much information as possible. The US EPA has utilized aquatic toxicity tests of pure chemicals to establish current water quality criteria. In contrast, stormwater, municipal, and industrial water discharges are regulated by whole effluent testing (US EPA WET program), which assesses the toxicological effects of all effluent pollutants to aquatic organisms (US EPA 2013). Assessing the direct impacts of deicers to the ecosystem or higher levels of biological organization can be accomplished with bioassessements, or biological monitoring. Biological monitoring allows for a direct assessment of the aquatic biota and directly measures the biological health of the waterway.

Objective

The purpose of this research is to develop a guide that (1) establishes procedures and methods for evaluating the aquatic toxicity of chloride-based deicers both in the laboratory and in the field; and (2) provides quantitative information and insights regarding the toxicological effects of common chloride-based deicers used in snow and ice control operations on water bodies adjacent to highways.

Research Proposed

Task 1 Agency Survey

In this task the Literature Review developed as part of Phase 1 (NCHRP 25-25/Task 86) will be employed to provide background information for the development of an agency survey to identify products and species to be tested; field exposure scenarios with varying pathways of deicer transport and fate; potential sites for field testing; and identification of sites with historic, current, and on-going monitoring of relevant parameters. The team will develop a draft survey and provide it to the project panel for feedback. A draft list of survey participants will also be provided. The survey will seek input from state and provincial agencies in North America. Based upon the panel's input, the survey questions and survey participants will be finalized. The research team should target survey responses from at least 25 stakeholders (DOTs, water quality agencies, US EPA, DEQs, etc.). The information gained in this task will be used to shape the experimental design in Task 2.

Task 2 Experimental Design Work Plan

A draft experimental design work plan that includes both laboratory and field testing will be developed under this task. The work plan will clearly identify the questions to be answered by conducting the work plan. The main goal of this task is to establish a framework for testing that can be duplicated or adopted by others if necessary, for instance, to assess the toxicological effects of roadway deicers on sensitive water bodies or those of truck wash water or stormwater runoff from salt storage sites.

Task 2.1 Laboratory Testing Plan

In this task a laboratory testing plan will be developed, in part based on Task 1 findings. The work plan will identify chloride-based deicers and anti-icers (sodium chloride, magnesium chloride, and calcium chloride) of interest for laboratory toxicity testing. Species chosen for testing should be both broadly applicable across geographical locations and good indicators for endangered species. Multiple species should be chosen to reflect this concept. Using information from the Phase 1 Literature Review and the experience of the research team, the work plan will identify acute and chronic test methods to be used, discuss how the tests will be conducted (e.g., static renewal, flow-through), list product testing concentrations, identify parameters that will be monitored (conductivity, temperature, water hardness, sulfate, etc.), and describe the methods by which the data on the response variable will be reported, e.g., LC_{50}, IC_{25}, and NOEC, at a known level of confidence. A statistical design of experiments (DOE) will be utilized to facilitate the exploration of the effect of multiple factors and their synergistic effects on the aquatic toxicity of selected deicer products. A Quality Assurance (QA) Plan should be developed for the laboratory toxicity testing and should consider sample replicates and controls, food sustainability, reference toxicants, and performance evaluation of samples.

Task 2.2 Field Testing Plan

A field testing plan will be developed as part of this task based on information gained from the Phase 1 Literature Review and Task 1 survey results. The field testing plan will identify a host of potential representative field monitoring scenarios considering the diverse possibilities in the fate and transport of deicer contaminants in the natural environment. The testing details will include sampling method, frequency, locations, duration of testing, and related information. Suggested testing may include monthly grab samples; hourly grab samples before, during, and after a storm/runoff event; 24-hr composite samples collected during peak runoff or spring thawing; continuous monitoring via the use of probes; and snowbank samples. Sampling events should consider changes in water flow rates annually and life-stages of organisms, as well as examine runoff from likely sources, and monitor gradients downstream as they pass through the system over time. The research should also consider establishing in-situ water quality monitoring stations to monitor environmental parameters at each sample site. Suggested sample collection sites include areas of known chloride impacts, areas where a major highway crosses or parallels a water body, areas identified as sensitive or impaired, urban and non-urban aquatic locations, and areas with historical data collection of relevant parameters. For each site winter maintenance practices – product type, application method, application rate, frequency of application, and weather and precipitation type and amount data – should be collected. The research should also consider safety and ease of access to the field sampling locations. For each sample site, preliminary water quality testing should be completed (e.g., water hardness, sulfate, pH, DO, and BOD) prior to the initiation of sampling. Test methods used to quantify the environmental parameters and toxicity of the samples collected in the field will be identified.

A sub-set of field sites will have biological assessments of the aquatic ecosystem completed. Bio-assessment sites can be chosen based on initial field toxicity testing and measurement of environmental parameters at each field site. Field sites chosen for bio-assessment should have their preliminary level of impairment identified utilizing US EPA methods (US EPA 2013) to establish a baseline and to identify the possible presence of other stressors. For each bioassessment location, the watershed should be characterized by land use type, percent impervious cover, historical water quality impairments (e.g., 303(d) listing), and related factors. The bio-assessment results should be related back to the toxicity data also collected at the respective sites, and a discussion of impacts to the ecosystem based on the data collected for this project should be completed. The plan will include the recommended analysis procedures for evaluating the relationships between monitored environmental parameters, toxicity data, and bio-assessments.

A QA plan should be developed for the field sampling and site monitoring and should consider sample collection techniques, sample storage methods, replicate and control sample collection, data collection techniques, site safety, and short- and long-term storage of field testing equipment.

Task 3 Prepare a technical memorandum providing the results of Tasks 1 and 2

A draft technical memorandum will be prepared that presents the survey method, responses, and summarized findings from Task 1, and the Task 2 Experimental Design work plan for laboratory and field testing. The memorandum will be submitted to the project panel for review and approval before proceeding to subsequent tasks. As part of the review process, the Task 2 Experimental Design work plan for laboratory and field testing will be peer-reviewed by toxicologists outside of the work team and project panel. The project panel will be responsible for identification of individuals to peer-review the document.

Task 4 Conduct a conference call with NCHRP to discuss the Task 3 technical memorandum

Following project panel review of Task 3, a conference call will be held with the project panel and project team to discuss the work completed. In the call, any issues, concerns, and suggestions should be discussed. Following the call, the team will incorporate any requested revisions into the Task 3 Technical Memorandum.

Task 5 Laboratory Investigation

This task will involve laboratory testing according to the finalized Task 2 Experimental Design Work Plan in a laboratory that is equipped to conduct this type of toxicity testing. The developed QA plan for the laboratory should be followed and reflect actual laboratory practices and procedures, and the plan should be available to those conducting the testing. Acute and chronic toxicity tests will be conducted on the selected deicers and test species. The results will be tested for validity, and a report will be submitted to the project panel for review. An early update on this task's progress will be provided to the project panel in the form of a brief report, and a conference call will be held if deemed necessary. Additional testing, or testing of additional products or species may be requested for additional cost. The results will be reported in a technical memorandum to be incorporated into the Task 6 report. The memorandum will also make recommendations for any adjustments to the field testing based upon results of the laboratory testing.

Task 6 Interim Report

This task will entail the preparation of an interim report that provides the results of Tasks 1 through 5; an updated, detailed outline of the field investigation plan; and an updated work plan reflecting any comments received from the panel.

Task 7 Field Investigation

This task will involve field monitoring and sampling of locations identified in the Task 2 Experimental Design Work Plan. The developed QA plan for the field testing should be followed and reflect actual sample collection practices and procedures, and be available to those conducting the testing. Preliminary samples will be collected from the identified locations and tested for the identified water quality parameters, and for acute and chronic toxicity using the identified test methods and species. Preliminary samples will be collected as necessary to establish a baseline. Samples will then be collected from the identified locations based on the sampling plan identified in the Task 2 Experimental Design Work Plan. Collected samples will be tested for acute and chronic toxicity and identified environmental parameters, and if in-situ monitoring is occurring, data will be processed and a report will be written. Bio-assessments will be conducted at a subset of field locations using methods identified in the Task 2 Experimental Design Work Plan. An early update on this task's progress will be provided to the project panel in the form of a brief report, and a conference call will be held if deemed necessary. Additional field sampling or testing beyond what is presented in the Task 2 Experimental Design Work Plan will require project panel approval, and if approved, additional funds may be requested. The results from the field investigation will be prepared in the form of a report. The report will be submitted as a draft with any comments addressed in the final report.

Task 8 Best Practices Guide

In light of the findings from the previous tasks, this task will entail the preparation of a best practices guide that (1) establishes procedures and methods for evaluating the aquatic toxicity of chloride-based deicers both in the laboratory and in the field; and (2) describes quantitative information on the aquatic toxicity of common deicers used in highway snow and ice control operations. A draft version of the guide will be prepared and any comments will be addressed in the final report.

Task 9 Stakeholders Workshop

The team will conduct a 1.5-day workshop at the National Academies Beckman Center in Irvine, California (including invited attendees and panel members) to demonstrate the applicability of the guide to its primary users. Suggested invitees include practitioners, scientists who have completed studies in this field of research, US EPA representatives, DOT staff, and local agency staff. NCHRP will be responsible for all meeting and hotel logistics, travel expenses for participants, confirmation of attendance, and expenses related to meals and lodging. The contractor will be responsible for covering all other costs, such as the travel expenses of team members, invitations, agenda, electronic presentations, and handout materials.

Task 10 Updated Guide

Based on the written comments received from the panel and results of the workshop, the research team will revise the guide and submit it to project panel for final review as part of the final report.

Task 11 Final Report

The Final Report will clearly present a summary of the survey results, the laboratory and field test results, the findings and conclusions of the research, a discussion relating to winter maintenance practices, weather and precipitation information related to the measured chloride concentrations and observed impacts, the revised best practices guide, recommendations for future testing, and next steps in the development of policy or guidelines to better assist DOTs in the collection and analysis of water quality data relative to chloride toxicity. Outcomes of this research should include:

- a clearly defined field testing method for chloride-based deicers toxicity that can be easily duplicated and translated for use with other product types.
- a discussion of winter severity, level-of-service, actual treatment practices and how these relate to chloride loading from winter maintenance practices, and how this relates to the toxicity data collected from each field site.
- a discussion of: what degree organisms are being harmed by chlorides, other stressors (water temperature, drought, etc.) and their relative importance, and acute and chronic toxicity results compared to the bioassessment results.
- identification of available options and studies needed to enable States to adopt new aquatic life standards for chloride.

The draft final report will be submitted to project panel for review and any necessary changes will be incorporated.

Estimate of the Problem Funding and Research Period

Recommended Funding: $800,000

Research Period: 36 months (including 3 months for review and revision of a draft final report)

Relevant References

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CHAPTER 4 Conclusions and Suggested Research

State DOTs are continually challenged to provide a high level of service on winter roadways and improve safety and mobility in a cost-effective manner, while at the same time minimizing adverse effects to the environment, vehicles, and transportation infrastructure. Level of service, cost-effectiveness, and corrosion have traditionally been considered more urgent priorities than other less well-characterized impacts, such as impacts to water quality. It is increasingly important to understand the environmental footprint of deicers, including their impacts on aquatic ecosystems.

Increasing contamination derived from the continued use of chloride-based deicers has become a significant environmental concern that has detrimental effects on water, soil, vegetation, and wildlife that have been observed in the field and verified in the laboratory. Of particular interest are the toxicological effects of chloride-based deicers in the natural environment. Extensive acute and chronic toxicity testing of chloride impacts to aquatic organisms has been conducted, yet additional research is needed both in the laboratory and in the field to shed more light on the toxicity of chloride-based deicers and their fate and transport in various environments, as well as understanding the ecological impacts, including impacts to food web dynamics.

Chloride-based deicers, including NaCl, $MgCl_2$, and $CaCl_2$, are the most commonly used deicing products because they are inexpensive and allow DOTs to maintain safety and mobility for the driving public. Chloride-based deicers have been used for decades by winter maintenance agencies, but easily run off the road surface into the adjacent environment. Chloride laden runoff can become point source or non-point source pollution and can negatively impact soil, plants, animals, and waters.

Chloride salts are readily soluble in water, difficult to remove from water, and tend to accumulate over time. Deicers have been found to negatively impact aquatic community structures. Elevated chloride concentrations have correlated with reduced species richness and impacted food web dynamics. Laboratory and field studies have found that in areas of heavy road salt use, chloride concentrations found in ground and surface water are elevated, often sufficient to affect biota. Such toxicity can be associated with the direct effect of deicers and/or with the indirect effect via their interactions with runoff chemistry. Numerous studies have reported environmental risks of chloride-based deicers, indicating that the actual effects depend on individual site conditions as well as the type and amount of deicers applied.

Toxicity testing has not been required of manufacturers or vendors producing chloride-based deicers and the associated additives (e.g., corrosion inhibitors and thickeners). As such, little toxicity data has been collected or published in the field of winter maintenance (Piligrim 2013; Corsi et al. 2010a). Toxicity research has been conducted on similar products used in other fields including aircraft or airfield deicers (Corsi et al. 2006) and dust suppressants (Williams and Little 2011), but available data on toxicological impacts are still very limited.

The most commonly used tools to assess toxicity are the laboratory acute and chronic tests, which apply varying concentrations of a contaminant to a selected species. The information gained from these tests are specific to the species tested and can be used to assess damage at the cellular and subcellular level of organisms. For this reason, hundreds if not thousands of species have been tested. The US EPA has utilized aquatic toxicity tests of pure chemicals to establish current water quality criteria. Suggested testing practices include using the static-renewal method or a flow-through system. Continuous real-time in-situ monitoring of temperature, salinity specific conductivity, pH, water hardness, and DO will provide the most complete data set for assessing the presence and impacts of chloride deicers in a water body. Ideally this system would download data directly to a server for real time viewing. The data could then be used to determine if and when sampling should occur and how frequently. Sampling techniques used may vary based on desired outcomes; monthly grab samples may be used to assess average chloride concentration, but to capture chloride concentration spikes associated with application of deicers and runoff events, discrete samples or 24-hr composite/continuous sampling can be used.

Toxicity testing completed to date has identified amphibians, specifically salamanders, as sensitive indicator species for impacts of chlorides on aquatic species. Toxicity testing of any additives to deicers is equally important for assessing the toxicity of chlorides themselves, as was shown with the toxicity of ferrocyanides, used as anti-caking agents in deicers. Currently, the acute and chronic laboratory toxicity test methods determine toxicity for various life-stages of organisms, but research is needed in the area of the impacts of chloride-based deicers on the ecology of the waterbody and impacts to food web dynamics. To gain better insights into the role of roadway deicers on stream ecology, field monitoring of aquatic species and populations, bioassessments or biomonitoring over time, and continuous monitoring of the environmental parameters in waterbodies should be considered in the field toxicity testing. Biological monitoring allows for a direct assessment of the aquatic biota and directly measures the biological health of the waterway.

Federal ambient water quality criteria for chloride are (US EPA 1988):

- 230 mg/L, maximum chronic exposure level, four-day average concentration
- 860 mg/L, maximum acute exposure level, one-hour average concentration

These criteria are not supposed to be exceeded more than once in a three year period. The drinking water standard for chloride is 250 mg/L. The Clean Water Act requires states to adopt water quality standards; these can be the established federal standards or states can develop site specific or pollutant specific standards if adequately justified. When identifying the designated use of a waterway, using a Use Attainability Analysis is one method to potentially justify whether an effluent limit is reasonably attainable or if a more or less stringent effluent limit should apply.

Work by the Iowa DNR and US EPA found that some species were more sensitive to short term, acute exposures of elevated chloride concentrations and recommended a lower acute criterion of 682 mg/L (instead of 860 mg/L), but a higher chronic criterion of 406 mg/L (instead of 230 mg/L), based on the ACR for the more sensitive species tested (Iowa DNR 2009). It was also found that increased water hardness and sulfate ions buffer against potential toxic effects of chloride. The results of the Iowa DNR and US EPA study can be used by other states to set site specific acute and chronic chloride criteria based on measured water hardness and sulfate levels. This criterion has been adopted by Iowa and the US EPA Region 7, as well as many more states. The new chloride criteria does not change regulatory requirements for drinking water, but does provide site-specific criteria for aquatic life protection that is based on local water hardness and sulfate levels. This may impact effluent permits and will allow permittees to request modifications to the current permits based on US EPA approval of the new chloride criteria.

Of particular concern is the accumulative risk the chloride salts may present over the years, as they are difficult to remove, highly mobile, and non-degradable. At this point in time, there is no reasonable method for removal of chloride, sodium, magnesium and calcium from water, soil or vegetation. Methods that can be used to reduce the toxicity of chloride-based deicers include 1) reducing the amount of chloride base deicers applied, 2) treatment of chloride laden runoff, 3) mixing chloride laden runoff to reduce peak chloride concentrations, and 4) routing chloride laden runoff away from sensitive surface and groundwater systems.

One method that can be used to reduce chloride-based deicer toxicity is source control, using the minimum amount of chloride-based deicer needed to achieve the prescribed level of service. The following methods can be used by DOTs to reduce or minimize the amount of chloride-based deicer used or lost in their daily operations.

Salt Management Plans- SMPs are a tool that can be used to create safe, efficient, and cost-effective salt management. SMPs assess progress and identify areas for improvement.

Product substitution – Substitution with another product, or blending with sand/gravel. Each product has a unique effective temperature range and toxicological impacts, and these should be considered prior to use.

Snow removal – Accumulated snow can be moved to another site for melting if space is limited or if it is necessary to move the snow away from sensitive areas to reduce chloride loading. Moving snow can be costly and may only be practical in urban settings or for protection of designated areas.

Deicing, Anti-icing and Pre-wetting Practices that Optimize Salt Use – Deicing is generally the application of solid material during a storm event, anti-icing is generally the application of liquid product before a storm event, and pre-wetting is the addition of liquid product to salt or sand. Great strides have been made in the last 10 years to make deicing, anti-icing and pre-wetting as efficient as possible, so that minimum amount of product is applied to achieve the prescribed LOS.

Precision Application and AVL/GPS Technology – Precision application is the use of special equipment to apply solid, liquid and blended material. AVL and GPS technology have been added to maintenance vehicles and application equipment to increase efficiency in routes and for data collection. Significant cost and material savings have been realized with implementation of these technologies.

Equipment Calibration – Calibration of equipment ensures optimal operation. Calibration should be done frequently and included as a part normal training practices.

Weather Information and Forecasting Services, including RWIS and MDSS – Weather information, weather and pavement forecasts, and data provided by RWIS can be used to develop effective and efficient treatment strategies by DOTs. Maintenance decision support systems provide much of this information directly into the cabs of trucks, as well as suggestions on product application rates and timing of application, and can be used as a management tool. The use of weather information, forecast services, RWIS, and MDSS has individually and in combination been shown to provide significant cost, material, and person-hours savings.

Staff training – Training is important for effective and efficient use of chlorides.

Monitoring and Keeping Records – Collected information on environmental parameters, road weather conditions, and maintenance records can be used in product management and identification of best practices. Consider collecting water quality data in areas identified as important, sensitive, or impacted by DOT practices.

Program Evaluation and Continuous Improvement - The salt budget management tool is an example of an effective method to evaluate a program using collected data. MDSS has also been used as a management tool during and post storm, using data collected by the system on forecasts and recommendations. A Life Cycle Assessment is a tool that can be used to evaluate environmental impacts of products or processes over the entire life cycle. An LCA was performed on winter maintenance products and found that switching to salt brine from solid salt or CMA showed reduction in life-cycle effects, through enhanced efficiency and reduced energy and water use, and lower greenhouse gas emissions.

Each of the technologies, tools, and methods discussed, when implemented correctly, has been shown to reduce the amount of chloride-based deicers needed by transportation agencies to achieve their prescribed level of service, as well as reduced the amount lost to the environment. Future research efforts and management should focus on reducing loss of product at patrol yards, reducing roadway application rates and reducing the frequency of application of deicers, and improving appropriate snow disposal and subsequent waste water treatment (Environment Canada 2001).

Once chloride-based deicers have been applied, the following techniques can be used to minimize the toxicity of chloride in the environment. Phytoremediation has been shown to remove chlorides from runoff, but needs sufficient time for the biological process to work, and the plants that take up the chloride must be disposed of prior to die-off. Phytoremediation is most effective at sites with shallow subsurface contamination and works best as a polishing technique for treating soils and remaining salt laden pore water. Traditional stormwater structural BMPs can be used to manage chloride concentrations in runoff by redirection or capture and mixing to dilute concentrations. This can reduce the potential toxicity of highway stormwater runoff. Only a few structural BMPs have shown promising results at capturing and managing chlorides in runoff. Ponds and wetlands are BMPs that store and release captured runoff. Detention, retention and evaporation ponds allow for mixing of chloride laden runoff with base flow or non-chloride runoff, reducing spike chloride concentrations and overall smoothing chloride concentrations. Wetlands and shallow marshes also reduce spike chloride concentrations, if they have sufficient storage capacity, and in most cases also utilize phytoremediation. In some cases chlorides have been shown to detrimentally impact wetlands. Infiltration of stormwater is an effective stormwater management technique, but with chloride laden runoff contamination of ground water is a concern. Infiltration trenches and basin can be used to reduce surface water volume, but the depth of groundwater and soil type may limit their use. Vegetated swales and filter strips utilize bioinfiltration to filter and reduce runoff velocity, and work best when combined with other treatments. Vegetated swales can be used for snow storage. Grass swales have been found to store chlorides from runoff and later re-release it acting as a chloride reservoir. Other methods to remove chlorides from runoff include reverse osmosis, filtration, and adsorption; these methods were only briefly discussed because they are costly, have functional constraints, or are in the development stage.

A scope of work for a Phase 2 research project was developed based on research needs and gaps identified from the literature review. The objective of the Phase 2 research project is to develop a guide that will establish procedures and methods for evaluating the aquatic toxicity of chloride-based deicers both in the laboratory and in the field; and provide quantitative information and insights regarding the toxicological effects of common chloride-based deicers used in snow and ice control operations on water bodies adjacent to highways.

Suggested Research

The following is list of research needs on this topic based on gaps in the research or areas of little to no research completed to date, as identified in the literature review process and in discussions with leading experts in this field:

1) How does the size (volume of water transported) of the waterbody influence the impacts of chloride contamination on aquatic life?
2) How do cold temperatures or other seasonal factors affect the tolerances or the potential impacts on aquatic life such that seasonal standards or criteria may be appropriate?
3) Conduct a cost/benefit analysis and identify the environmental pros and cons of using non-chloride deicing alternatives for DOTs.
4) Identify where to conduct water quality sampling for determining representative chloride exceedances and how downstream dilution at confluences impacts this.
5) Develop a cost effective method for continuous monitoring of water chloride concentrations and relaying this information real time.
6) Investigate the toxicological impacts of additives to deicing products.

7) Develop a cost-effective method for removing chloride from water.

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ABBREVIATIONS, ACRONYMS, INITIALISMS, AND SYMBOLS

AASHTO – American Association of State Highway and Transportation Officials
ACR – Acute to Chronic Ratio
ACRP – Airport Cooperative Research Program
AVL – automatic vehicle location
BMP – Best Management Practice
BOD – biological oxygen demand
C - Celsius
Ca^{2+} - calcium
$CaCl_2$ – calcium chloride
CCC - criterion chronic concentration
CCI – chloride contamination index
CCR – consumer confidence reports
Cd - cadmium
CEPA – Canadian Environmental Protection Act
Cl^- - chloride
CMA – Calcium Magnesium Acetate
Cu - copper
CWA – Clean Water Act
DEQ – Department of Environmental Quality
DLA – direct liquid application
DNR – Department of Natural Resources
DO – dissolved oxygen
DOE – design of experiment
DOT – Department of Transportation
F – Fahrenheit
GPS – global positioning system
IBI - Index of Biotic Integrity
IC – inhibitory concentration
ISE - ion-selective electrode
KAc – potassium acetate
KFm – potassium formate
LC – lethal concentration
LCA – Lifecycle Cost Assessment
LD – lethal dose
LOEC - lowest-observed-effect-concentration
LOS – Level of Service
MDSS – Maintenance Decision Support System
Mg^{2+} - magnesium
$MgCl_2$ – magnesium chloride
MTO – Ontario Ministry of Transportation
Na^{2+} - sodium
NaAc – sodium acetate
NaCl – sodium chloride
NaFm – sodium formate
NCHRP – National Cooperative Highway Research Program
Ni - nickle
NOAEC - no-observed-adverse-effect concentration

NOEC – no observed effect concentration
NPDES - National Pollution Discharge Elimination System
NWIS – National Water Information System
PAH – poly-aromatic hydrocarbons
Pb - lead
QA – Quality Assurance
RWIS – Road Weather Information System
SCOE – Sub Committee on the Environment
SMCL - secondary maximum contaminant level
SMP – salt management plan
TAC – Transportation Association of Canada
TDS - total dissolved solids
TMDL – total maximum daily load
TSS – total suspended solids
UAA – Use Attainability Analysis
US EPA – United States Environmental Protection Agency
USGS – United States Geologic Survey
UV – ultra violet
WET – Whole Effluent Toxicity
WHO – World Health Organization
WSI – winter or weather severity index
YPS – yellow prussiate of soda
Zn - zinc