

M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04c as extended by M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18 Project Abstract
For the Period Ending June 30, 2022

PROJECT TITLE: Reduce Chlorides in Minnesota Waters by Evaluating Road-Salt Alternatives and Pavement Innovations

PROJECT MANAGER: John S. Gulliver

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FUNDING SOURCE: Environment and Natural Resources Trust Fund

LEGAL CITATION: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04c as extended by M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18

APPROPRIATION AMOUNT: \$400,000

AMOUNT SPENT: \$400,000

AMOUNT REMAINING: \$0

Sound bite of Project Outcomes and Results

This project produced background information, guidance and recommendations on the benefits and consequences of chloride-based road salt and non-chloride alternatives for de-icing and anti-icing Minnesota's roadways, which will assist road maintenance decision makers in reducing pollution from winter road management.

Overall Project Outcome and Results

Over 100,000 tons of road salt are applied to Minnesota's roads each year to prevent or reduce snow and ice cover during the winter season. Sodium chloride is typically used because it is inexpensive and effective, but it can corrode vehicles, pavement, and metal structures (e.g., bridges), and it increases chloride concentration in surface and ground waters throughout the state. This results in additional costs for replacing roadway infrastructure and reduces water quality, habitat, and biodiversity in our natural resources. This project investigated alternatives to sodium chloride-based road salt that reduce snow and ice on roadways with less environmental impact. The project team reviewed scientific research papers, performed laboratory experiments, and used computer models to predict the potential environmental impacts of these chemicals on Minnesota's natural resources.

This project found several outcomes, including: 1) chloride-based road salt concentration can exceed the chronic and acute water quality standards during a typical year; 2) acetate-based alternatives only exceeded water quality standards for low flow rates (low dilution); 3) potassium-based chemicals can be toxic at low concentration, and toxicity thresholds are exceeded when potassium is applied over all roadways for all winter storms; 4) other alternatives such as formate, glycol, glycerol, and succinate have varying performance, application rate, and toxicity thresholds; 5) water-heated sand improves friction compared to bare ice or dry sand on bare ice and can be removed from the environment with simple grit collection chambers; and 6) non-chloride alternatives can reduce the bonding strength of ice to a solid surface. Thus, water-heated sand as an abrasive and organic or hydrophobic non-chloride alternatives can be used to reduce the use of chloride-based road salt and provide more winter benefit on Minnesota's roadways, but modeling predicts that some of these chemicals could exceed toxicity thresholds if applied for all conditions.

Project Results Use and Dissemination

The results from this project have been shared via presentations, interviews, reports, academic journals, and with stakeholders and decision makers during conferences and networking events. Some examples include a web article, two invited annual Minnesota Salt Symposium presentations (2019 & 2021), WCCO's 10 o'clock news "Good Question: How Does Salt Melt Ice?" with Jeff Wagner, the Transportation Research Board Annual meeting (2022), and several conference presentations and professional meetings. We believe sharing this information has enlightened decisions makers about the dangers of chloride road salts and non-chloride alternatives and how best to use each.



Environment and Natural Resources Trust Fund (ENRTF)

M.L. 2018 ENRTF Work Plan Final Report

Today's Date: August 15, 2022

Final Report

Date of Work Plan Approval: June 5, 2018

Project Completion Date: June 30, 2022

PROJECT TITLE: Reduce Chlorides in Minnesota Waters by Evaluating Road-Salt Alternatives and Pavement Innovations

Project Manager: John S. Gulliver

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Location: Statewide

Total Project Budget: \$400,000

Amount Spent: \$400,000

Balance: \$0

Legal Citation: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04c as extended by M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18

Appropriation Language: \$400,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to investigate road-salt alternatives and pavement innovations to reduce lake, stream, and groundwater degradation caused by road-salt chlorides. This appropriation is available until June 30, 2021, by which time the project must be completed and final products delivered.

M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18. ENVIRONMENT AND NATURAL RESOURCES TRUST FUND; EXTENSIONS. [to June 30, 2022]

I. PROJECT STATEMENT:

This project will investigate road salt alternatives and pavement innovations that will reduce or eliminate the high flux of chloride from road salt into our environment and thus improve the water quality of our lakes, streams and groundwater.

Road salt impacts water quality, and will be a primary 21st century pollutant of concern in northern regions. Minnesota annually uses ~90 lbs per person of road salt (sodium chloride) to de-ice our roads and parking lots. Most of the sodium is trapped by the soil, but chloride is washed off of the streets or will move through the soil to receiving water bodies. We know from previous research that salt is accumulating to toxic levels in many lakes, streams and shallow groundwater. In the Twin Cities metropolitan area, for example, there are already 26 impaired lakes, 23 impaired streams and 1 impaired wetland for chloride. There is a strong possibility that lakes in urban Minnesota will become unable to support some of their fresh water organisms. Road salt alternatives and pavement innovations have the potential to provide similar road friction conditions while having less impact on the environment. We need to investigate the cost-effective application of these alternatives and pavement innovations now, to prepare for the near-future when a substitute for road salt is desired and needed.

The outcome of this project is to investigate and enhance strategies that improve water quality by evaluating road salt alternatives and pavement innovations to reduce the chloride load from road runoff. The methods and tools developed during this project will inform state, municipal and private entities using chloride-based salt on roads and parking lots. A feasibility matrix will be developed to summarize high level economic, environmental, time frame, implementation & maintenance challenges and benefits for alternate strategies.

A better understanding of road friction for road salt alternatives, combined with knowledge of environmental impacts and application and infrastructure costs will enable an improved decision-making process for public and private entities. City, county and MnDOT engineers will soon be making decisions about the best road salt alternative for their application. In addition, commercial entities are salting parking lots to reduce liability. This research could be used by the legislature to limit this liability if proper practices are used. The need for this research and the information it will generate is great, and the timing is urgent.

Input and advice from several agencies will be utilized to ensure that the goals of this research are met, and that the findings are useful to, and shared with, decision-makers in Minnesota. First, we have partnered with the Minnesota Pollution Control Agency (Brooke Asleson) for many years on the impacts of road salt. Second, we have enlisted the assistance of the Minnesota Department of Transportation (Steven Lund), who directs the maintenance and operation unit of the Metro District. Finally, we will seek advice from the members of the Stormwater Research Council, who participate and are involved in much of the stormwater research in Minnesota.

II. OVERALL PROJECT STATUS UPDATES:

First Update January 31, 2019

The project team has met several times to discuss the activities and outcomes. The literature review is complete and is submitted with this project update. Effort towards the modeling and friction measurements have commenced.

Second Update June 30, 2019

The project team has met several times to discuss the activities and outcomes. A meeting with modeling experts was held to discuss capabilities of various model software and applicability to modeling road salt alternative impacts. Several meetings with the staff coordinating the experiments (Activity 3) resulted in the development of two separate protocols for measuring de-icing and anti-icing effectiveness of various road salt alternatives. The road salt alternatives currently under consideration include

conventional salt (NaCl) as a baseline for comparison, Magnesium Chloride (MgCl₂), Potassium Acetate (KAc), CF7 (commercial KAc mix), Propylene Glycol (organic chemical), Abrasives (de-icing only), and Pavement Technologies (pending availability).

Amendment Request (09/05/2019)

Re-budget for Lab Services, equipment, and lab supplies: We are requesting a re-budget of \$5,900 to allow for laboratory analysis of samples. Additional analytical services are needed to analyze road-side soil samples to compare the presence of sodium and chloride (conventional road salt) and soil properties that could be used to model breakdown of road salt alternatives such as organic chemicals. The analytical services will be provided by the Research Analytical Laboratory on the St. Paul Campus of the University of Minnesota because they provide soil analysis at a reduced rate for University of Minnesota projects. The reduced rates allow for more samples to be analyzed for more parameters. In addition, a friction measurement device was available for loan from the MN Dept. of Transportation. Thus, the purchase of a British Pendulum Tester is no longer necessary. We are requesting that the cost for the pendulum tester (\$9,000) be reallocated partially to pay for analytical services (\$5,900) and the remainder added to Equipment/Tools/Supplies (\$3,100). The additional funds for Equipment/Tools/Supplies will be used to expand the experiments to include measurement of adhesive strength of road salt alternatives. Many road salt alternatives are used as anti-icing to minimize adhesion of the snow and ice to the pavement, allowing for easier removal via plowing. These additional experiments will measure adhesive (shear) strength of ice to a surface in the presence of various road salt alternatives to simulate these real-world application techniques. Thus, the new budget for Equipment/Tools/Supplies is \$18,100. These changes are shown in the expenditures spreadsheet.

Amendment Approved by LCCMR 10/09/2019.

Third Update January 31, 2020

The project team has met several times to discuss the activities and outcomes. Several alternatives were discussed, and it was determined that only a few alternatives are used or would be considered for use by the industry; Potassium Acetate (KAc) and propylene glycol. As a result, these chemicals have been recommended for laboratory testing and Activity 2, Outcome 2 is complete.

Amendment Request (01/31/2020)

In meeting with the team members for Activity 2 (modeling environmental impacts) and Activity 3 (measuring friction), we have determined that the data results from Activity 3 should be used to inform and improve the modeling effort in Activity 2. As a result, we request that the deadline for Activity 2, Outcome 1 be extended through the duration of Activity 3 (3/31/2021) so they can be completed concurrently. Activity 2, Outcome 2 is complete as described in the status update.

Amendment Approved by LCCMR 2/8/2020.

Laboratory testing (Activity 3) of anti-icing has continued, measuring the effect of sodium chloride, magnesium chloride, and potassium acetate at four temperatures (-5 °C, -15 °C, -25 °C, -35 °C).

Fourth Update June 30, 2020

The project team has met several times to discuss the activities and outcomes. During these discussions, it was hypothesized that a hydrophilic (water-repellent) substance could weaken the bond between ice and pavement, thus reducing the need for road salt. Thus, a commercial hydrophilic substance commonly used on vehicles (RainX) was added to the list of alternatives to be tested as part of this research.

Activity 2, Outcome 1 continues concurrently with Activity 3, Outcome 1. Computer modeling using EPA SWMM has the potential of modeling runoff, application of rock salt, NaCl-based brine, and potassium acetate. More detail is provided in the activity below. This software will be used to complete Activity 3, Outcome 1.

Laboratory testing (Activity 3) consists of friction measurements for de-icing and friction enhancement (e.g., sand and grit) and anti-icing experiments which measure the ability of road salt and road salt alternatives to weaken the bond between ice and pavement. All anti-icing chemicals that were planned for testing (no treatment, Na-Cl-based brine, Magnesium Chloride, Potassium Acetate, RainX) have been tested at various temperatures (-15 °C, -25 °C, -35 °C). Friction measurements for de-icing and friction enhancement will resume in the next biennium (July – Dec 2020).

Fifth Update January 31, 2021

We responded by email on October 6, 2020 that this project has experienced COVID- related delays that have resulted in a need for an extension to our project funding in order to complete the designated outcomes. We could not get into the University to perform laboratory experiments for some months, which set back the entire project, and were occupied by COVID -related arrangements for our other projects, so we would appreciate having some more time to complete the project. We were updated on December 6, 2020, that our project was included in the request to extend funding and that the status still in process.

Activity 2, Outcome 1 continues concurrently with Activity 3, Outcome 1. Computer modeling has shown that EPA SWMM can model runoff, application of rock salt, NaCl-based brine, and potassium acetate. More detail is provided in the activity below. This software will be used to complete Activity 2, Outcome 1. Upon completion of Outcome 1, Activity 2 will be complete. There has been progress on this activity, but we were delayed due to Covid-19 related time conflicts.

Laboratory testing (Activity 3) consists of friction measurements for de-icing and friction enhancement (e.g., sand and grit) and anti-icing experiments which measure the ability of road salt and road salt alternatives to weaken the bond between ice and pavement. Experimental data collection is tentatively complete and data analysis is underway. Activity 3, Outcome 1 was delayed due to Covid-19 related time and access conflicts. Pending data analysis approval, Activity 3, Outcome 1 will be complete during this biennium (Jan – June 2021). Subsequent to completion of Outcome 1, Outcome 2 (develop ranking metrics) and Outcome 3 (write report) can then be completed.

Project extended to June 30, 2022 by LCCMR 6/30/21 as a result of M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 18, legislative extension criteria being met.

Sixth Update June 30, 2021:

Activity 2, Outcome 1 continues concurrently with Activity 3, Outcome 1. EPA SWMM is currently being used to model runoff, application of rock salt, NaCl-based brine, and potassium acetate. More detail is provided in the activity below. This software is being used to complete Activity 2, Outcome 1.

Laboratory testing (Activity 3) consists of friction measurements for de-icing and friction enhancement (e.g., sand and grit) and anti-icing experiments which measure the ability of road salt and road salt alternatives to weaken the bond between ice and pavement. Experimental data collection and data analysis are complete. Report preparation for Activity 3 is underway.

Seventh Update January 31, 2022:

Activity 2, Outcome 1 continues concurrently with Activity 3, Outcome 1. EPA SWMM is continuing to be used to model transport of chloride-based road salt and potassium acetate as an alternative. Preliminary analysis from this effort, combined with results from a concurrent synergistic project funded by the MnDOT Local Road Research Board (LRRB), suggest that potassium (K) may have more environmental impacts than Acetate (Ac). This is because the toxicity limit of potassium was discovered to be substantially lower than the toxicity limit for acetate. The modeling and analysis are nearly complete and will be finished and written into the final report by the project end date of June 30, 2022.

Laboratory testing (Activity 3) consists of friction measurements for de-icing and friction enhancement (e.g., sand and grit) and anti-icing experiments which measure the ability of road salt and road salt alternatives to weaken the bond between ice and pavement. Experimental data collection and data analysis are complete. Two manuscripts describing the results have been prepared; one submitted for publication and a second manuscript will be completed and submitted for publication during this biennium.

The literature review (Activity 1), results from the modeling effort (Activity 2), and the manuscripts describing the laboratory testing (Activity 3) will be combined into the final report for this project and submitted by the project end date, June 30, 2022.

April 21, 2022 Amendment Request

An amendment to the budget is requested to shift funds in order to approach zero balance in each of the categories. Items which are completed will have extra funds shifted to items that have a negative balance or to items that are still in progress.

Amendment Approved by LCCMR 7/5/2022.

Final Update June 30, 2022

Activity 1: Literature review was completed early in the project and revised for inclusion in this final report and status update. Topics in the literature include: alternatives to chloride-based road salt (acetate-based, formate-based, glycol and glycerol, succinate-based, and other road salt alternatives), performance of road salt alternatives (RSAs), environmental impacts, abrasives, pavement innovations (Pavement Heating, Deicers in the Pavement Mix Design, Hydronic Pavements, Hydrophobic Pavements, and other pavement innovations), and observations and recommendations.

Activity 2: Investigate water quality impacts of RSAs in Minnesota was completed during the last biennium of the project. During the previous biennium, the results of a model assessment of environmental impacts of potassium acetate for the Miller Creek Watershed near Duluth, MN was presented. During the last biennium, other RSAs and climate regimes (when they should be applied) were considered. The primary differences between the environmental impacts of acetate and other RSAs include climate regime, application rate, decay rate coefficient, and toxicity thresholds for the chemicals being considered. These variables are discussed in this final report and status update. The best approach for assessing environmental impacts is for end users to choose the conditions for which they want the environmental impacts and model those conditions specifically, following the example established by this research project (see example in the Seventh Update (January 31, 2022) for Activity 2).

The experimental data collection and analysis for Activity 3: Conduct friction tests on pavement cores to select promising techniques was completed during the Sixth Update (June 30, 2021). The project team has drafted two manuscripts for publication in peer-reviewed journals describing the methods and

results of these experiments. In summary, it was shown that 1) water-heated sand is an alternative to chloride-based road salt that can improve friction compared to bare ice or dry sand on bare ice, and 2) non-chloride RSAs can reduce the bonding strength of ice to a solid surface at colder temperatures. Thus, water-heated sand as an abrasive and organic or hydrophobic non-chloride RSAs can be used to reduce the use of chloride-based road salt and provide more winter benefit on Minnesota's roadways.

Overall Project Outcome and Results

Over 100,000 tons of road salt are applied to Minnesota's roads each year to prevent or reduce snow and ice cover during the winter season. Sodium chloride is typically used because it is inexpensive and effective, but it can corrode vehicles, pavement, and metal structures (e.g., bridges) and increases chloride concentration in surface and ground waters throughout the State. This results in additional costs for replacing roadway infrastructure and reduces water quality, habitat, and biodiversity in our natural resources. This project investigated alternatives to sodium chloride-based road salt that reduce snow and ice on roadways with less environmental impact. The project team reviewed scientific research papers, performed laboratory experiments, and used computer models to predict the potential environmental impacts of these chemicals on Minnesota's natural resources.

This project found several outcomes, including: 1) chloride-based road salt concentration can exceed the chronic and acute water quality standards during a typical year, 2) acetate-based alternatives only exceeded water quality standards for low flow rates (low dilution), 3) potassium-based chemicals can be toxic at low concentration and toxicity thresholds are exceeded when potassium is applied over all roadways for all winter storms, 4) other alternatives such as formate, glycol, glycerol, and succinate have varying performance, application rate, and toxicity thresholds, 5) water-heated sand improves friction compared to bare ice or dry sand on bare ice and can be removed from the environment with simple grit collection chambers, and 6) non-chloride alternatives can reduce the bonding strength of ice to a solid surface. Thus, water-heated sand as an abrasive and organic or hydrophobic non-chloride alternatives can be used to reduce the use of chloride-based road salt and provide more winter benefit on Minnesota's roadways, but modeling predicts that some of these chemicals could exceed toxicity thresholds if applied for all conditions.

III. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Synthesize past and current investigations.

Description: Past and current investigations of road salt alternatives, pavement innovations and road friction studies will be reviewed. We are aware that there are substantial research needs here and that sufficient information will not be available for all alternatives, but this review will limit duplication of effort and maximize progress towards essential knowledge gaps.

ENRTF BUDGET: \$27,596

Outcome	Completion Date
1. Synthesize past and current investigations	12/31/2018

Final Update January 31, 2019

The literature review is complete and is submitted with this project update.

ACTIVITY 2: Investigate water quality impacts of road salt alternatives in Minnesota.

Description: Information gathered in Activity 1 will be synthesized through the use of computer models to evaluate potential water quality impacts of road salt alternatives in Minnesota. Many of the non-chloride-based alternatives are organic compounds, which have a biological oxygen demand when released into the

environment. The amount of such alternatives required for anti-icing and de-icing will be estimated from literature values, and computer models will then be used to determine the water quality impacts of these amounts on common water resources in Minnesota.

ENRTF BUDGET: \$181,670

Outcome	Completion Date
1. Predict water quality impacts in Minnesota for alternatives	03/31/2021
2. Select alternatives for laboratory testing	12/31/2019

First Update January 31, 2019

The literature review provided input into the available models and past studies on the impact of road alternatives or similar organic chemicals on the environment. Modelling will commence in the next semi-annual period.

Second Update June 30, 2019

A meeting with modeling experts was held to discuss capabilities of various model software and applicability to modeling road salt alternative impacts. It was determined that a simple model and open source model is best for accessibility to various groups and industry professionals, but a more complex model may be used for calibration and comparison of impacts at different locations.

Third Update January 31, 2020

In reviewing the literature, talking with industry professionals, and discussing the options with the project team (modeling and experiments), it was determined that there are only a few road salt alternatives that are used or would be considered for use by the industry. The existing chloride-based road salts include NaCl and MgCl₂. The alternatives include Potassium Acetate (KAc) and propylene glycol. These alternatives will be modeled (Activity 2) and are recommended for laboratory testing (Activity 3) as part of this project. Thus, Outcome 2 is complete.

Meetings with modeling experts were held to discuss use of various model software to predict environmental impacts of road salt alternative impacts. The project team agreed that a simple and open source model will be developed for industry professionals and the more complex model will be improved by using information from Activity 3 to calibrate and verify the model to predict the environmental impacts at different locations. With the proposed amendment request (see above), outcome 1 of this activity would continue throughout the duration of Activity 3 to improve the outcomes for the entire project.

Fourth Update June 30, 2020

Activity 2, Outcome 1 continues concurrently with Activity 3, Outcome 1. EPA-SWMM has the capabilities to model snowfall, snow plowing, snowmelt, and KAc transport and decay. In addition, EPA-SWMM is freely accessible (<https://www.epa.gov/water-research/storm-water-management-model-swmm>) and commonly used by County, and City staff in Minnesota. This software will be used to complete Activity 3, Outcome 1. So far, rock salt (solid NaCl), salt brine (liquid NaCl & MgCl₂), and Potassium Acetate (liquid KAc) has been modeled using EPA-SWMM on an example watershed, as shown in Figure 1.

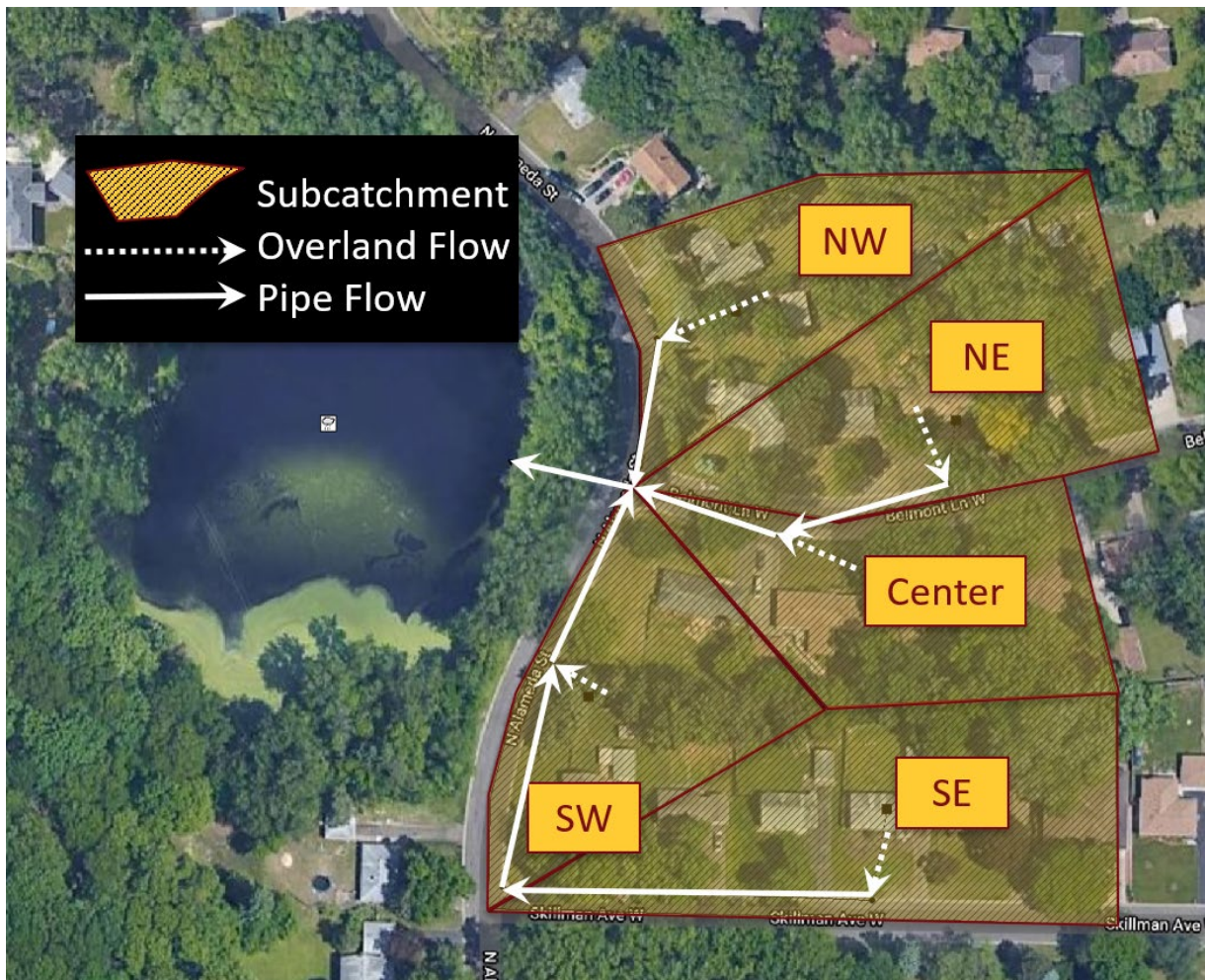


Figure 1: Schematic of hypothetical urban subwatershed modeled in EPA-SWMM.

EPA-SWMM was used to predict the response of a hypothetical scenario which spanned a period of 11 days with three precipitation events on days 2, 6, and 9 with total cumulative snowfalls of 125 mm (4.9 inches), 50 mm (1.97 inches), and 50 mm (1.97 inches), respectively. The temperature record was represented by a sinusoidal diurnal cycle with a max temperature of +15°C and a minimum temperature of -5°C. The climate data, unit area runoff (mm/hr), and maximum snow depth (mm) are shown in Figure 2. EPA-SWMM also transports snow from impervious surfaces (roadways) to pervious surfaces (lawns and ditches) in addition to snow accumulation, melt, and runoff (data now shown).

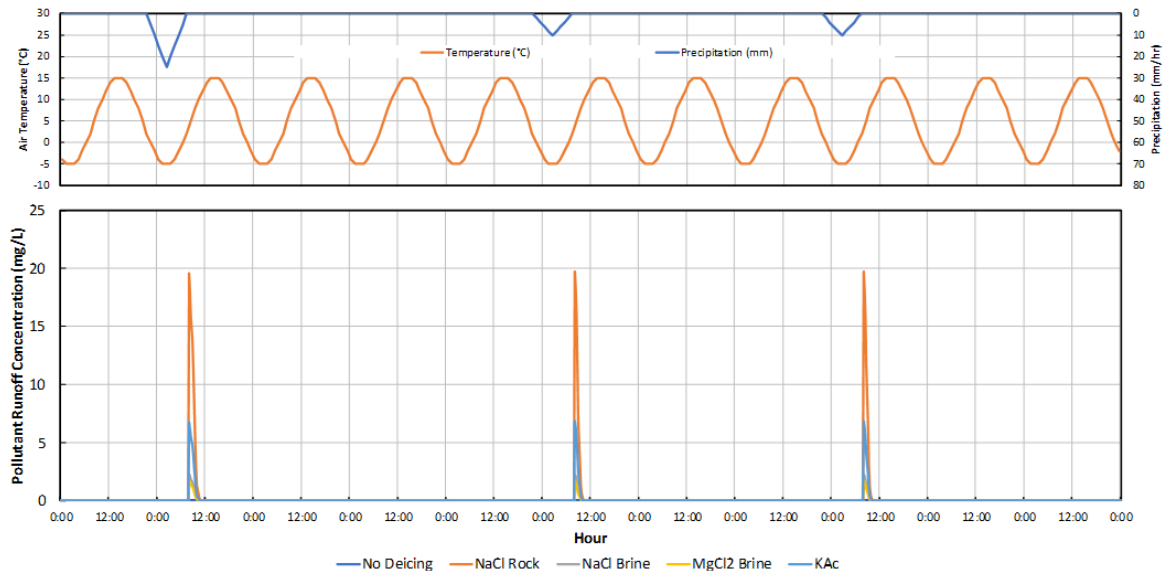


Figure 3: Pollutant runoff concentration (mg/L) for rock salt, liquid brine (NaCl and MgCl₂), and potassium acetate (KAc).

Finally, the transport of potassium acetate (KAc) also requires natural biodegradation of KAc in the environment during transport. This can be modeled within EPA-SWMM using the built-in first order decay rate equation or a user-defined decay process. The first-order decay rate equation was tested and found to function within EPA-SWMM as expected (results not shown). Values for first-order decay based on temperature for KAc will be assumed from literature values and used to calibrate the model to accurately model biodegradation of KAc. Other road salt alternatives, such as propylene glycol, will also be investigated and incorporated into the model if the appropriate modeling parameters are available to input in EPA-SWMM. This will be completed throughout the remainder of the project.

Fifth Update January 31, 2021

Three EPA-SWMM models that represent different regions in Minnesota have been selected to demonstrate the environmental impacts of road salt and road salt alternatives. These models including Miller Creek watershed, encompassing portions of Hermantown and Duluth, MN in the Toimi Drumlins and North Shore Highlands ecoregions. The Miller Creek watershed and model covers approximately 10 square miles, originating in the headwaters of Miller Creek in Hermantown and discharging into Lake Superior at 26th Ave. West in Duluth, just below Lincoln Park. The unique features of this model are the combination of undeveloped rural landscapes, developing areas, and fully-built areas such as downtown Duluth, shallow bedrock and clay subsoils, and a substantial elevation change of about 760 feet.

The second model selected to represent Minnesota is a portion of the City of Minneapolis, MN, which lies within the St. Croix Outwash Plain and Stagnation Plain ecoregion. This model will reflect ultra-urban, fully developed metropolitan areas throughout MN. The third model selected to represent Minnesota is located northwest of Rochester, MN and encompasses approximately 7.5 square miles within the Rochester/Paleozoic Plateau Upland ecoregion. The unique features of this model are the combination of undeveloped rural landscapes, developing areas, and fully-developed residential areas, karst geology, and a relatively flat topography.

These models will be used to assess the environmental impacts of road salt (e.g., NaCl, MgCl₂, CaCl₂) and road salt alternatives (e.g., K-Acetate, propylene glycol) as discussed in the previous status report (Jan – Jun 2020). Sensitivity analysis began during the current biennium (Jul – Dec 2020) but will be complete in the next biennium (Jan – Jun 2021). The sensitivity analysis will illuminate which input parameters

(e.g., application rate, biodegradation rate, hydraulic residence time) are most important for predicting environmental impacts. When sensitivity analysis is complete, then the models can be used to predict the environmental impacts based on various input conditions. The result of this modelling effort will be thresholds of road salt alternatives application rates at which environmental impacts are significant.

Sixth Update June 30, 2021:

The Miller Creek model in the Duluth region is proceeding well. We are expanding this project with the help of a Minnesota Department of Transportation project to study the impacts of potassium acetate on the environment in MnDOT Region 1, when applied as a road salt anti-icing alternative. We will model the environmental impacts of propylene glycol as well, which is not part of the MnDOT project.

We have had some challenges with currently selected inputs for the Minneapolis region and Rochester region models. Neither of the models had the objective of constituent transport, so their calibration criteria were dissimilar to ours. We have had to recalibrate the models, which is requiring some time. Calibration of the models is occurring currently.

Seventh Update January 31, 2022:

Full modeling details and results will be provided in the final report. The following is a synopsis of some of the results.

1 Scenario Analysis of Environmental Impacts of Potassium Acetate

The Miller Creek EPA-SWMM Model was used to model the environmental impacts from an individual subcatchment and from a tributary watershed in various potassium acetate (KAc) application scenarios. First, EPA-SWMM was used to model the runoff and outflow concentration of K and Ac from an individual subcatchment. It was hypothesized that runoff from some individual subcatchments could contain large concentrations of K and Ac due to high application rates and lack of dilution prior to entering receiving waters. It was also hypothesized that the concentration would be less within Miller Creek and in the outflow from Miller Creek due to dilution by the creek and contributions from other subcatchments with lesser anti-icer application rates. The results from these simulations are described in the following sections. All model runs simulated runoff and pollutant concentration using the above-mentioned model parameters and precipitation data from November 1, 1998 to April 30, 1999.

1.1 Runoff and Outflow Concentration from an Individual Subcatchment

The Miller Creek EPA-SWMM model was used to simulate runoff and K and Ac concentrations in the outflow from a single subcatchment (12.8 acres) when KAc application was assumed on all roadways. For the period of November 1, 1998 to April 30, 1999 (close to a median total snowfall for the last 30 years of record) there were 1023 hours of non-zero runoff values (Q) ranging from 0.01 cfs to 1.23 cfs. This data was sorted from smallest to largest flow rate and the percent exceedance (Erickson et al. 2013) was calculated and plotted as shown in Figure 4.

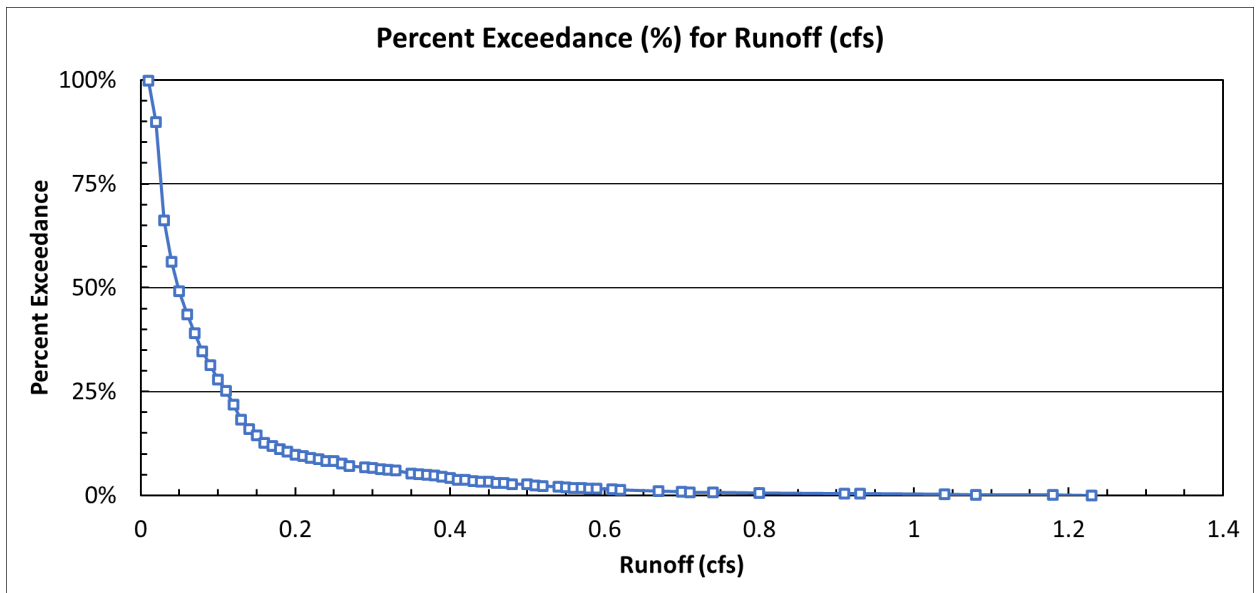


Figure 4. Percent exceedance for runoff data from an individual subcatchment within Miller Creek for the November 1998 through April 1999 period ($n = 1023$).

Approximately 50% of the simulated hourly runoff data is less than 0.05 cfs and 90% is less than 0.19 cfs. This logarithmic distribution of runoff data was separated into bins, which were used to analyze simulated concentration data for K and Ac as a function of small, medium, and large flow rate ranges. These data are shown in Figures 5-6 for K with an assumed toxicity limit of 0.13 g/L (130 mg/L) for K.

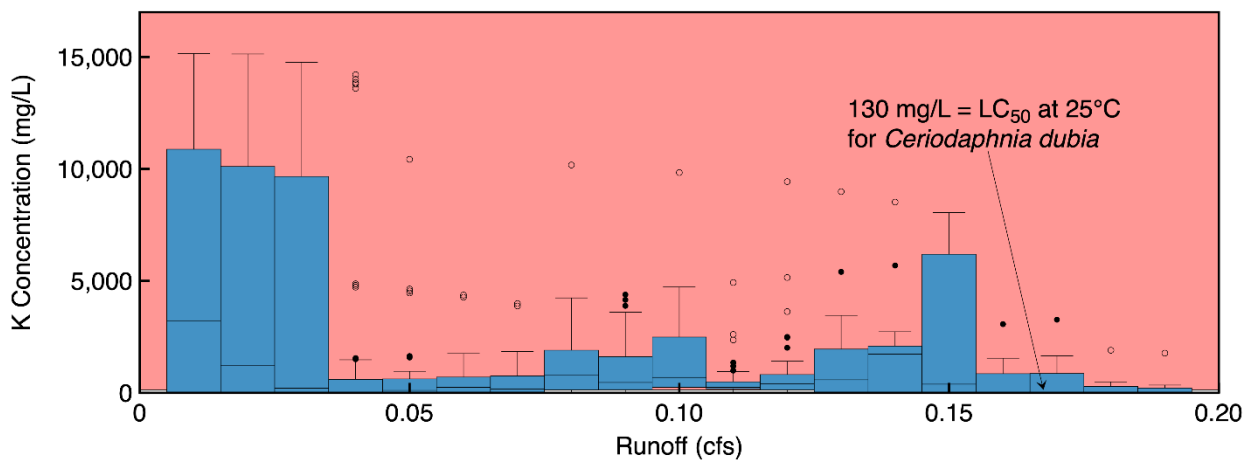


Figure 5. Potassium (K) concentration statistics for low flow rates (0 – 0.2 cfs) for an individual subcatchment as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. A toxicity limit of 0.13 g/L for K was assumed and the region of concentration above this value is shaded in light red.

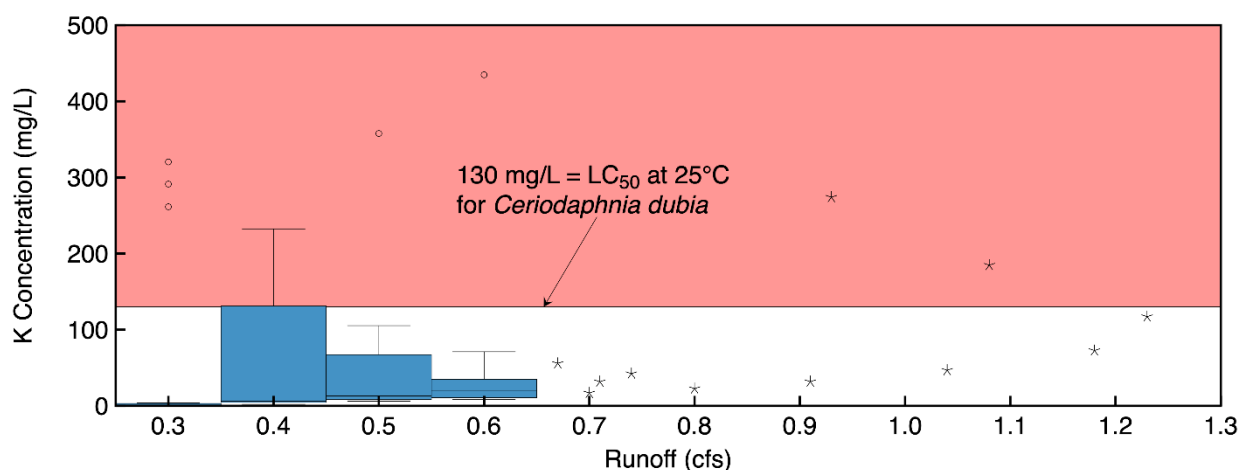


Figure 6. Potassium (K) concentration statistics for higher flow rates (0.3 – 1.3 cfs) for an individual subcatchment as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. Individual flow rate values > 0.65 cfs are shown as asterisks (*). A toxicity limit of 0.13 g/L for K was assumed and the region of concentration above this value is shaded in light red.

For low flow rates ($Q < 0.2$ cfs, Figure 5), the concentration statistics for K range from 0 to over 15,000 mg/L. It is apparent from Figure 5 that the median values of K concentration exceed the assumed toxicity limit (130 mg/L) for nearly all the flow rates within this range. For high flows (0.2 cfs $< Q < 1.3$ cfs), the K concentration statistics range from 0 to ~250 mg/L for the interquartile range (IQR) and ~450 mg/L including extreme values. Only some extreme outliers (within 3x beyond the IQR) and individual hourly values for flow rates > 0.65 cfs (asterisks) exceed the assumed toxicity limit (130 mg/L) for the high flow rate range. It is also apparent from Figures 5 and 6 that the concentration 1) varies substantially as a function of flow rate, and 2) decreases from low flow rates to high flow rates.

Acetate (Ac) data for low flow rates ($Q < 0.2$ cfs, Figure 7) and high flow rates (0.2 cfs $< Q < 1.3$ cfs) are shown in Figures 7 and 8, respectively. The toxicity limit for Ac is assumed to be 7.26 g/L (7260 mg/L). Similar to K (Figures 5 and 6), Ac concentrations vary substantially as a function of flow rate and decrease from low flow rates to high flow rates as shown in Figures 7 and 8. Though the assumed toxicity limit for Ac is substantially larger than that for K (7260 mg/L vs. 130 mg/L), the range of concentration values for low flow rates still exceed the toxicity limit below 0.03 cfs as shown in Figure 7. All Ac concentration values were below the assumed toxicity limit for high flow rates as shown in Figure 8.

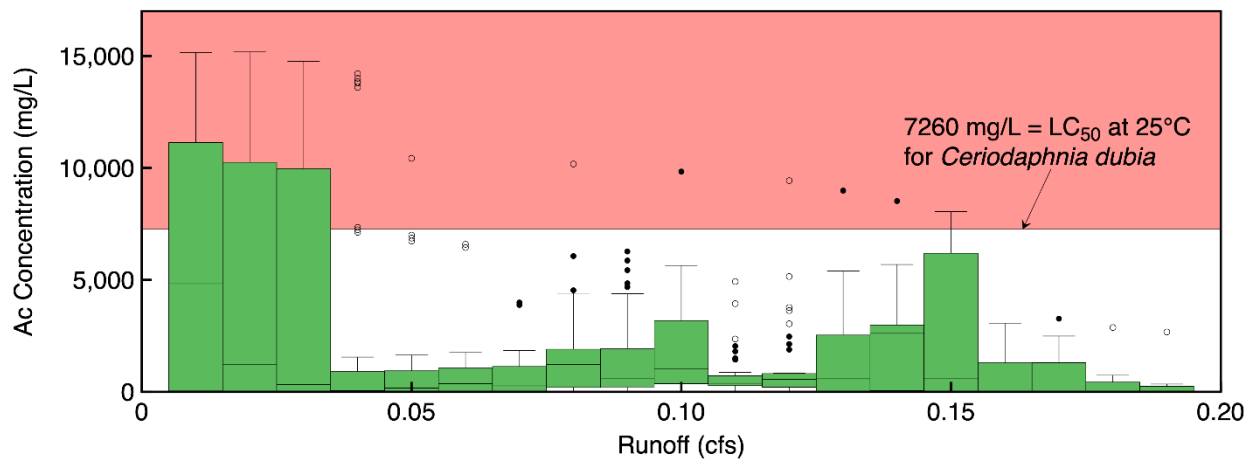


Figure 7. Acetate (Ac) concentration statistics for low flow rates (0 – 0.2 cfs) for an individual subcatchment as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. A toxicity limit of 7.26 g/L for Ac was assumed and the region of concentration above this value is shaded in light red.

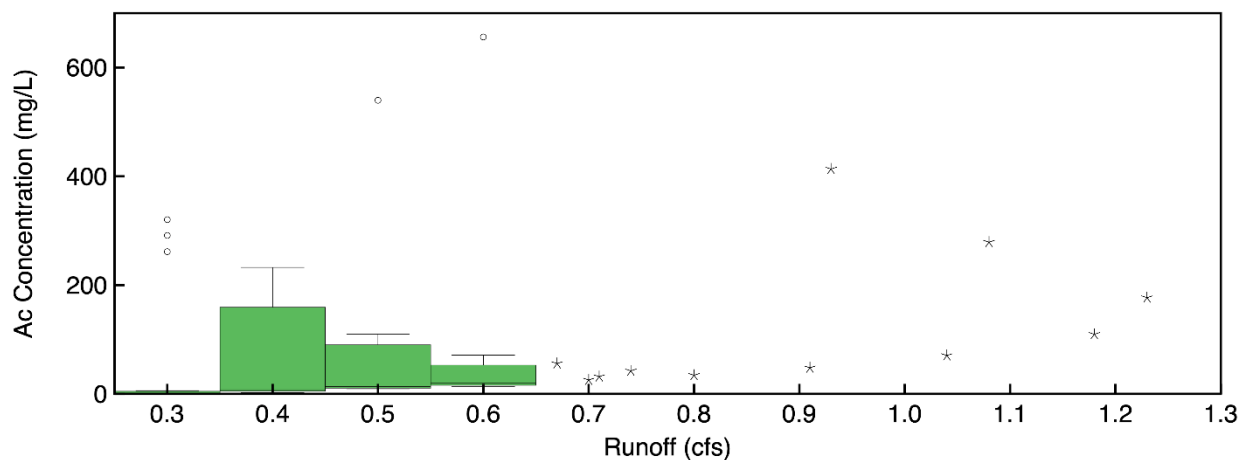


Figure 8. Acetate (Ac) concentration statistics for high flow rates (0.2 – 1.3 cfs) for an individual subcatchment as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. Individual flow rate values > 0.65 cfs are shown as asterisks (*).

1.2 Runoff and Outflow Concentration from Miller Creek

The Miller Creek SWMM model was also run for the entire Miller Creek watershed under several scenarios, corresponding to different levels of KAc anti-icer usage in the watershed for the time period of November 1, 1998 to April 30, 1999:

- Case I) KAc used only on 25% of all roadways
- Case II) KAc used on all roadways
- Case III) KAc used on all roadways and parking lots (all paved areas in the watershed)

The flow rate at the outlet of Miller Creek is substantially larger than outflow from an individual subwatershed as shown in Figure 9 for Cases I, II, and III. The flow duration curves for Cases I, II, and II

are nearly identical: the range of flow rates is 0 to 268 cfs for all three cases, with 50% of the data less than ~1.1 cfs and 90% of the data less than 27 cfs.

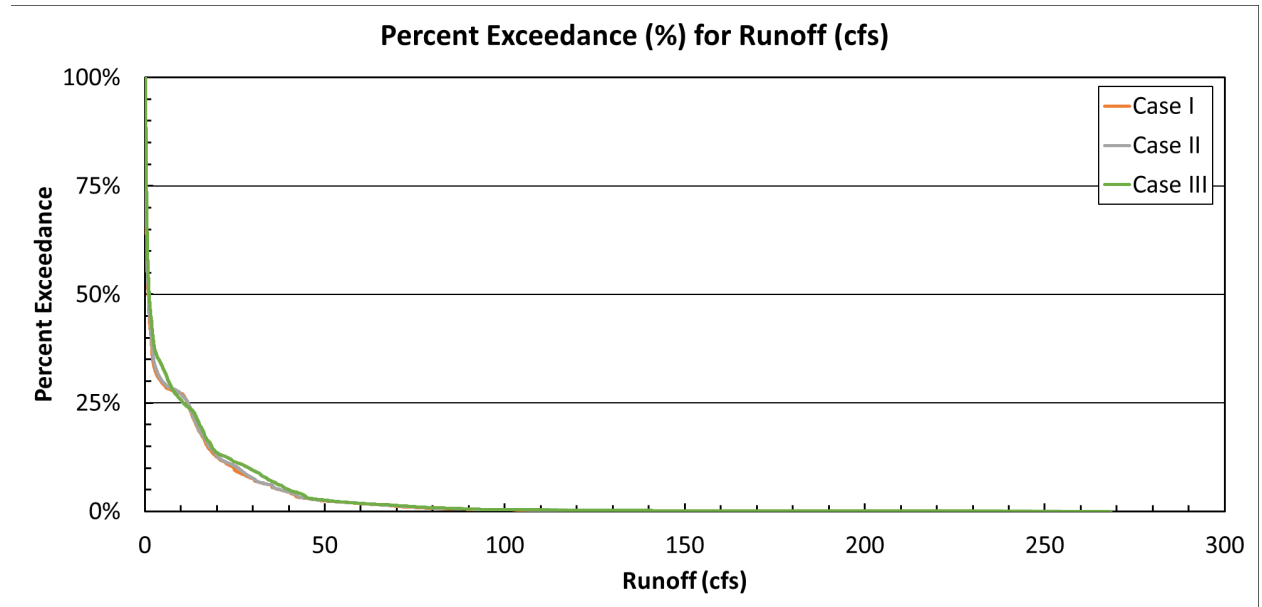


Figure 9. Percent exceedance for simulated non-zero outflow data from Miller Creek for Cases I, II, and III.

When KAc is used only on 25% of all roadways (Case I), the export of K and Ac from Miller Creek at the outlet is hypothesized to be less than the outflow concentration from an individual subcatchment (see section 3.2.1 above) and less than Cases II and III. Dilution within Miller Creek due to baseflow and by contributions from subcatchments with fewer roads and therefore lower KAc application will further dilute the concentration exported from Miller Creek at the outflow.

The simulated concentration of K in the outflow from Miller Creek for Cases I, II, and III for low flows ($Q < 10$ cfs) are shown in Figure 10, where flow rates are binned by unit cfs values. As expected, the increase in impermeable areas that receive KAc treatment results in an increase in K concentration in the outflow from Miller Creek, as evidenced by the increase in concentration statistics for Cases I, II, and III respectively (Figure 10). For Case I, only the interquartile range (IQR) and outliers for the lowest flow rate exceed the assumed toxicity limit of 130 mg/L for K (Figure 10). For Case II, more simulated concentration values at the lowest flow rate exceed the assumed toxicity limit for the low flows. For Case III, some median concentration values exceed the assumed toxicity limit through the entire range of 0 – 10 cfs flows.

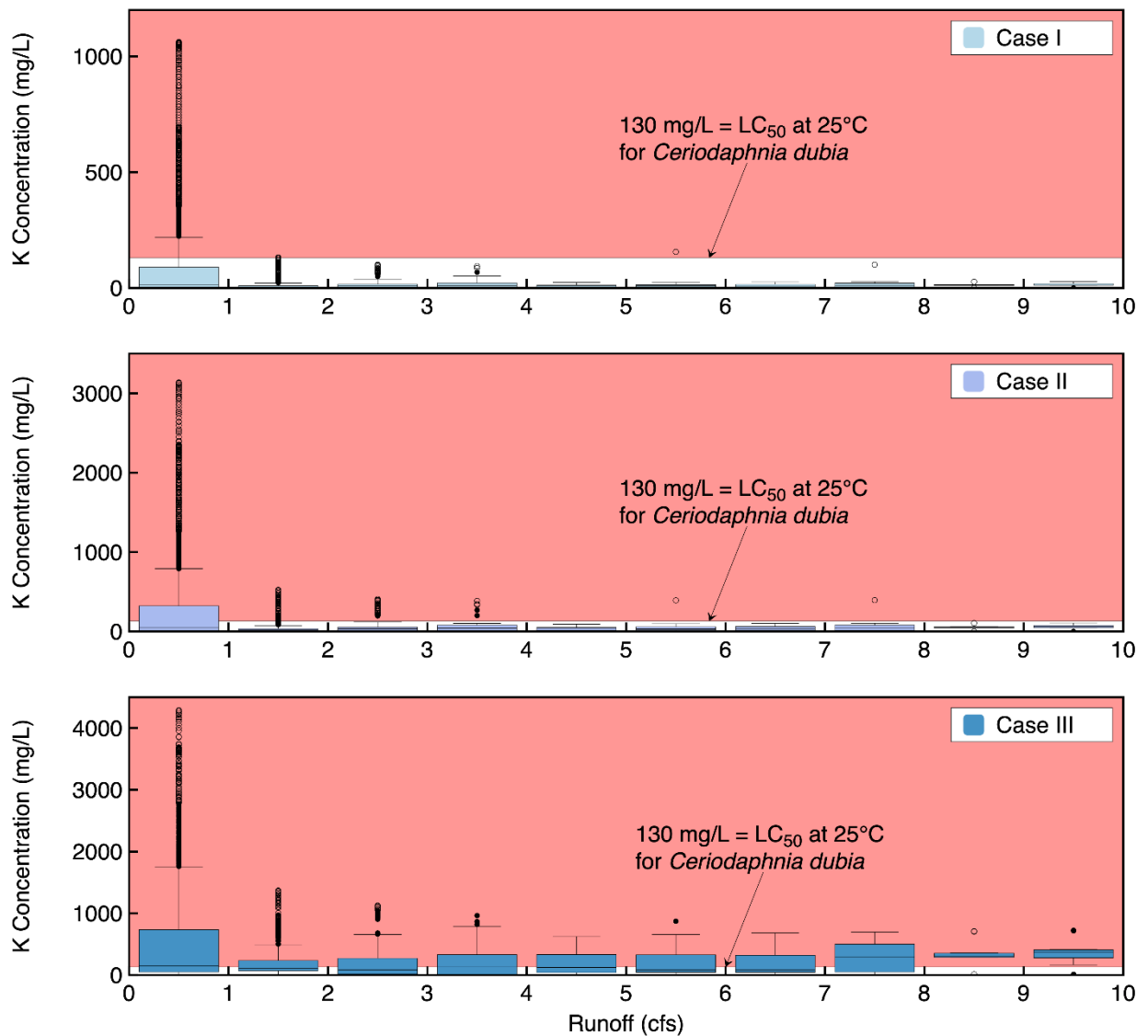


Figure 10. Potassium (K) outflow concentration statistics for low flow rates (0 – 10 cfs) for Case I (top), II (middle), and III (bottom) of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. A toxicity limit of 130 mg/L for K was assumed and the region of concentration above this value is shaded in light red.

K Concentration statistics for Cases I, II, and III for medium flow rates (10 – 45 cfs) are shown in Figure 11, where flow rates are binned by unit cfs values. Similar to the low flows, the K concentration increases from Case I to Case II and from Case II to Case III. Compared to the low flows, the K concentrations for all three cases are less for medium flows, demonstrating a decrease in concentration as the flow rate increases. This is expected because higher flow rates indicate more runoff that is likely disproportionate to the amount of KAc applied to the roadways, resulting in more dilution as flow rate increases. Nonetheless, some interquartile ranges and median values exceed the assumed toxicity limit for medium flow rates in Cases II and III.

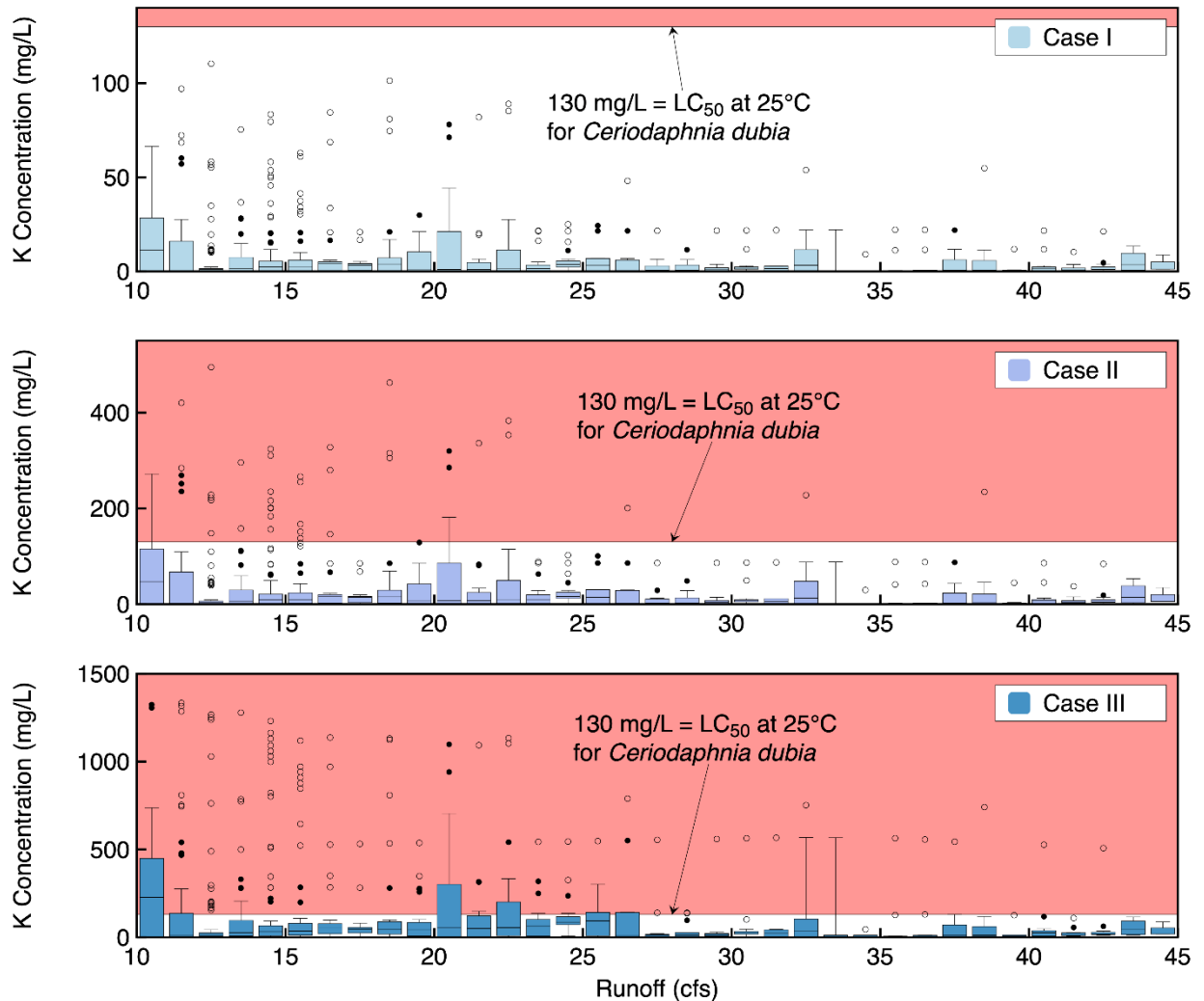


Figure 11. Potassium (K) outflow concentration statistics for medium flow rates (10 – 45 cfs) for Case I, II, and III of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. A toxicity limit of 130 mg/L for K was assumed and the region of concentration above this value is shaded in light red.

K Concentration statistics for Cases I, II, and III for high flow rates (45 – 280 cfs) are shown in Figure 12, where flow rates between 45 and 95 cfs are binned into 10 cfs groups. Similar to the low and medium flows, the K concentration increases from Case I to Case II and from Case II to Case III. High flows also exhibit less concentration compared to medium flow rates, further demonstrating a decrease in concentration as the flow rate increases. Despite the overall decrease in concentration range for the high flow rates, some interquartile range values exceed the assumed toxicity limit for high flow rates in Case III. All values of K concentration in the outflow from Miller Creek for Cases I and II at the high flow rates are below the assumed toxicity limit of 130 mg/L (Figure 12).

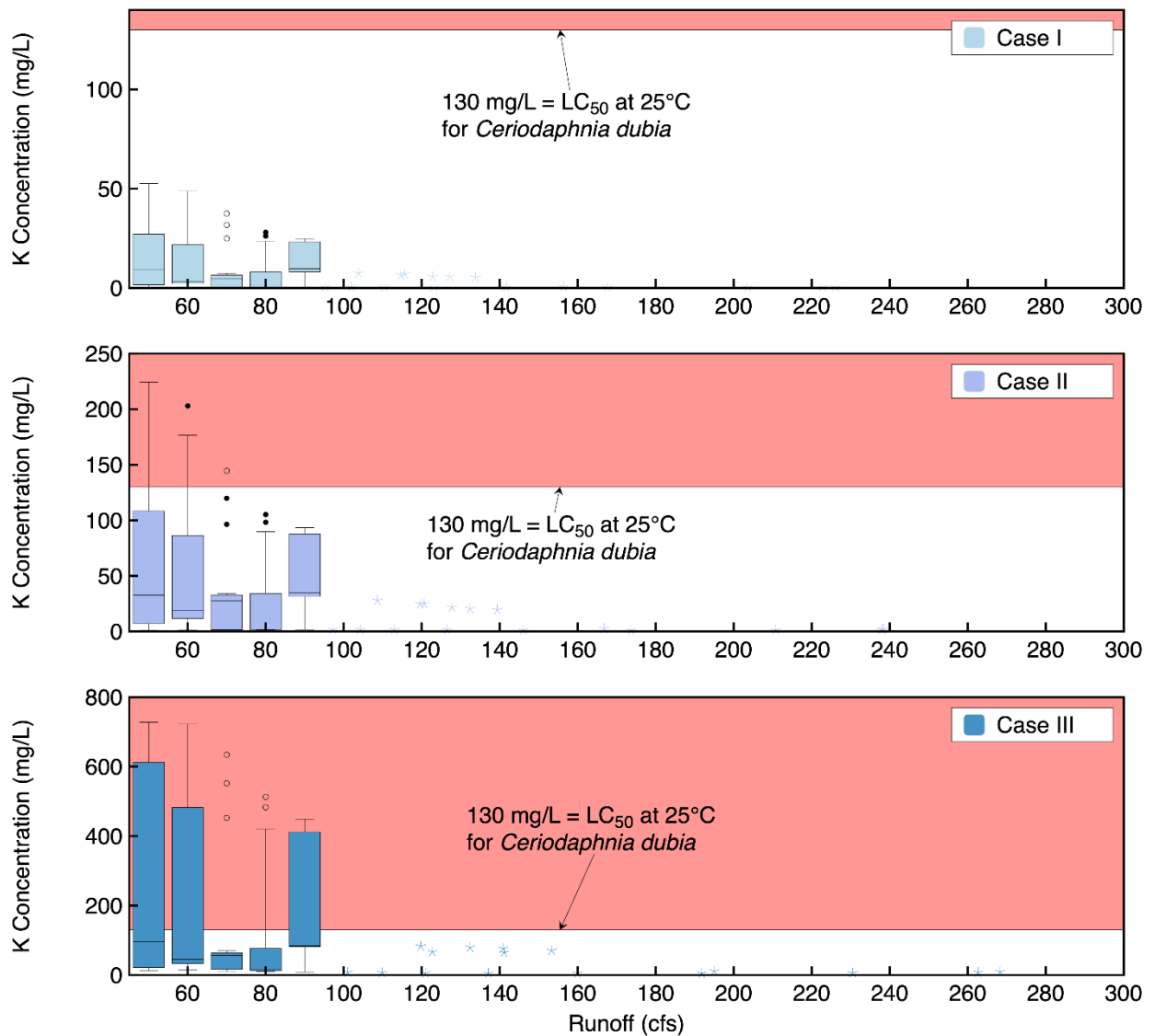


Figure 12. Potassium (K) outflow concentration statistics for high flow rates (45 – 270 cfs) for Case I, II, and III of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. Individual flow rate values > 95 cfs are shown as asterisks (*).

The simulated concentration of Ac in the outflow from Miller Creek for Cases I, II, and III for low flows ($Q < 10$ cfs) are shown in Figure 13, where flow rates are binned into unit cfs values. As expected, the increase in impermeable areas that receive KAc treatment results in an increase in Ac concentration in the outflow from Miller Creek, as evidenced by the increase in concentration statistics for Cases I, II, and III respectively (Figure 13). The toxicity limit for Ac is assumed to be 7,260 mg/L, but no low flow data exceeded this limit. Similar to K concentration data, Ac data decreases as flow rate increases and values for outflow from Miller Creek are substantially less than simulated values for an individual subcatchment (Figures 11 & 12).

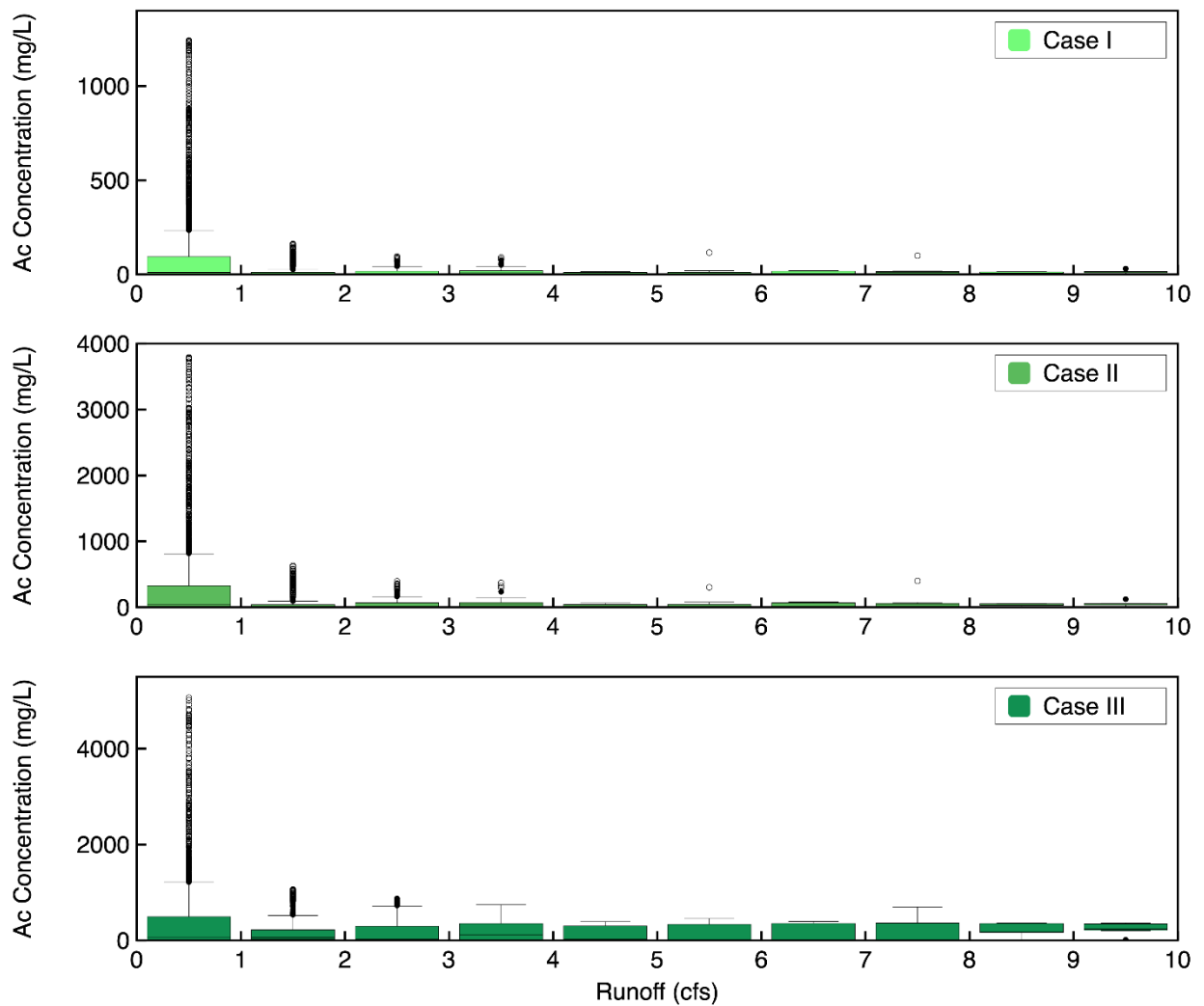


Figure 13. Acetate (Ac) outflow concentration statistics for low flow rates (0 – 10 cfs) for Case I, II, and III of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles.

Ac concentration statistics for Cases I, II, and III for medium flow rates (10 – 45 cfs) are shown in Figure 14, where flow rates are binned into unit cfs values. Similar to the low flows, the Ac concentration increases from Case I to Case II and from Case II to Case III. Compared to the low flows, the Ac concentrations for all three cases are less for medium flows, demonstrating a decrease in concentration as the flow rate increases. While all Ac concentration values are below the toxicity limit, it is still apparent that the difference in application rates between Cases I, II, and III produces a substantial increase in Ac concentration in the outflow from Miller Creek.

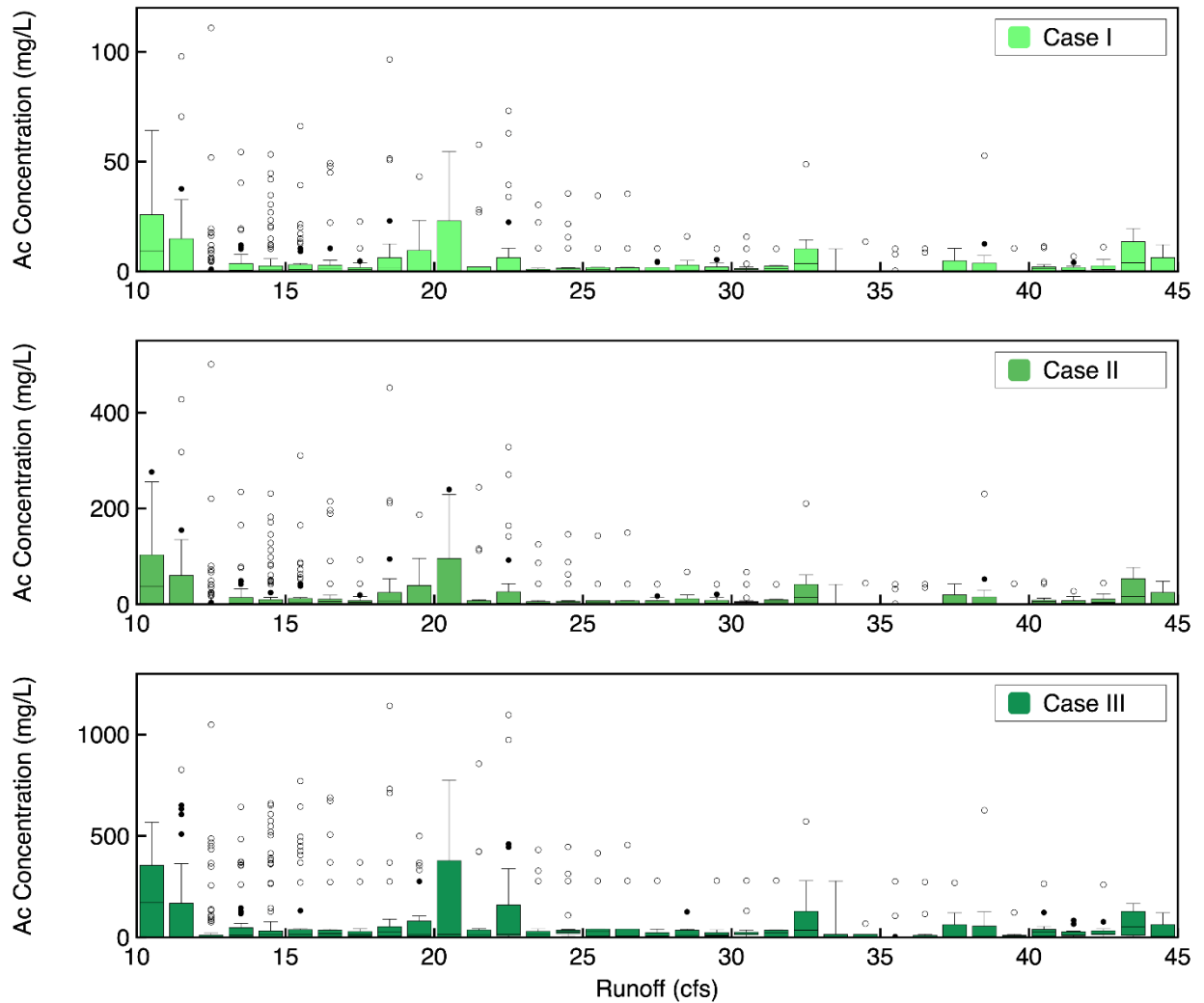


Figure 14. Acetate (Ac) outflow concentration statistics for medium flow rates (10 – 45 cfs) for Case I, II, and III of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles.

Ac Concentration statistics for Cases I, II, and III for high flow rates (45 – 280 cfs) are shown in Figure 15, where flow rates between 45 and 95 cfs are binned into 10 cfs units. Similar to the low and medium flows, the Ac concentration increases from Case I to Case II and from Case II to Case III. High flows also exhibit less concentration compared to medium flow rates, further demonstrating a decrease in concentration as the flow rate increases. While all Ac concentration values are below the toxicity limit, high flow rates in combination with moderate Ac concentration could produce substantial Ac load delivered to downstream water bodies.

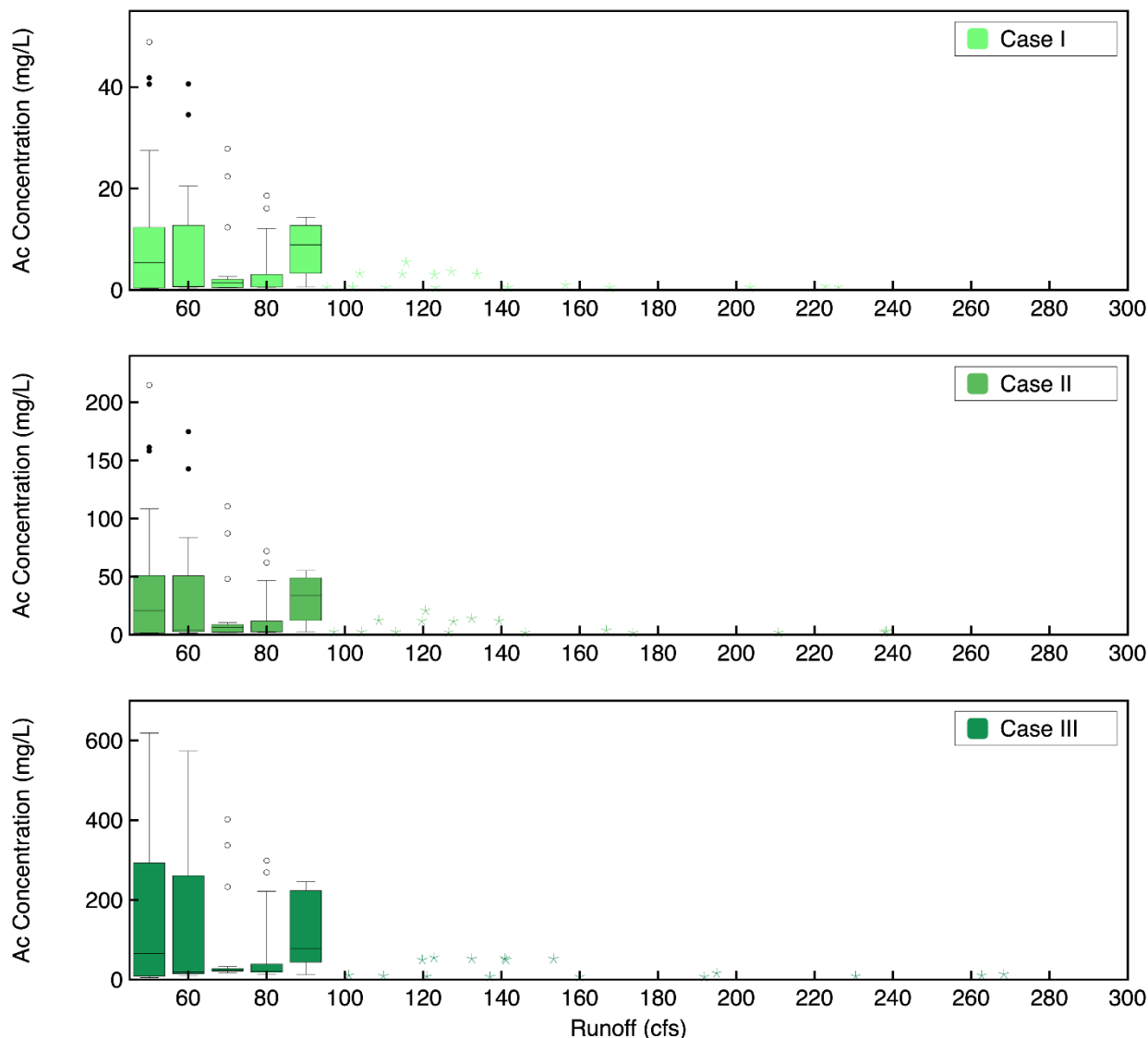


Figure 15. Acetate (Ac) outflow concentration statistics for high flow rates (45 – 270 cfs) for Case I, II, and III of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the interquartile range (IQR), outliers (within 1.5x beyond the IQR) are drawn as filled circles and extreme outliers (within 3x beyond the IQR) are open circles. Individual flow rate values > 95 cfs are shown as asterisks (*).

The de-icer concentration statistics for the Miller Creek outlet are summarized in Table 1. It is apparent from the difference in toxicity limit between Potassium (130 mg/L) and Acetate (7260 mg/L) that potassium will have more environmental impacts if the concentration of K and Ac are similar in magnitude. For K, the mean concentration exceeds the toxicity limit for Cases II and III, suggesting that less than 100% of the roadways can be treated with KAc without exceeding the toxicity limit. This is consistent with the data shown in Figures 10 – 12. The 90th percentile and max K concentrations exceed the toxicity limit for all three Cases, suggesting that even when limited to 25% of the roadways, there is still potential for environmental impacts of potassium.

By contrast, Acetate does not exceed the toxicity limit in the mean, 90th percentile, or maximum concentration for any of the three cases at the outlet of Miller Creek. This is consistent with the data shown in Figures 13 – 15. Thus, it is apparent that potassium has more potential for environmental impacts than acetate when considering toxicity. It is important to note, however, that acetate is an

easily biodegradable substance and can create a substantial biological oxygen demand (BOD) impact on receiving waterbodies. This may become an issue of low dissolved oxygen if the acetate concentration is too high. Storm sewers, however, typically have a number of opportunities for reoxygenation (Huisman, et al. 2004), and the most likely impact would be in the downstream water body.

Table 1. Summary of Scenario Cases and Simulated Anti-icer Concentrations at the Miller Creek outlet. Anti-icer concentration statistics based on November 1, 1998 to April 30, 1999. All concentrations are mg/L. Values in bold italics exceed the assumed toxicity limit.

	Case I (25% of Roadways)	Case II (100% of All Roadways)	Case III (All Roadways and Parking Lots)
Total Connected Pavement Area Anti-iced (acres)	39.8	159.1	600.4
Potassium (K)			
Assumed K Toxicity Limit	130	130	130
Mean K Concentration	54.8	171.1	334.3
90 th Percentile K Concentration	137.5	454.0	1034
Max K Concentration	1062	3136	4289
Acetate (Ac)			
Assumed Ac Toxicity Limit	7260	7260	7260
Mean Ac Concentration	54.6	171.6	260.8
90 th Percentile Ac Concentration	137.5	489.8	711.7
Max Ac Concentration	1242.1	3790.9	5062.1

Time series of flow rate, K concentration, and Ac concentration for Case II are shown in Figure 16. The time series of flow rate, K, and Ac concentration are beneficial for illustrating the changes over time for these parameters at the outlet of Miller Creek. In Case II, 100% of the roadways are treated with KAc, which represents a median treatment strategy that could be employed by road maintenance crews. When comparing the K concentration to the K toxicity limit (130 mg/L), it is apparent that there are at least ten simulated events during the winter of 1998/99 in which the K toxicity limit was exceeded. Some events exceeded the toxicity limit by more than 10x. By contrast, the toxicity limit for Acetate is above the range for Figure 16 and thus is not exceeded during this simulated winter.

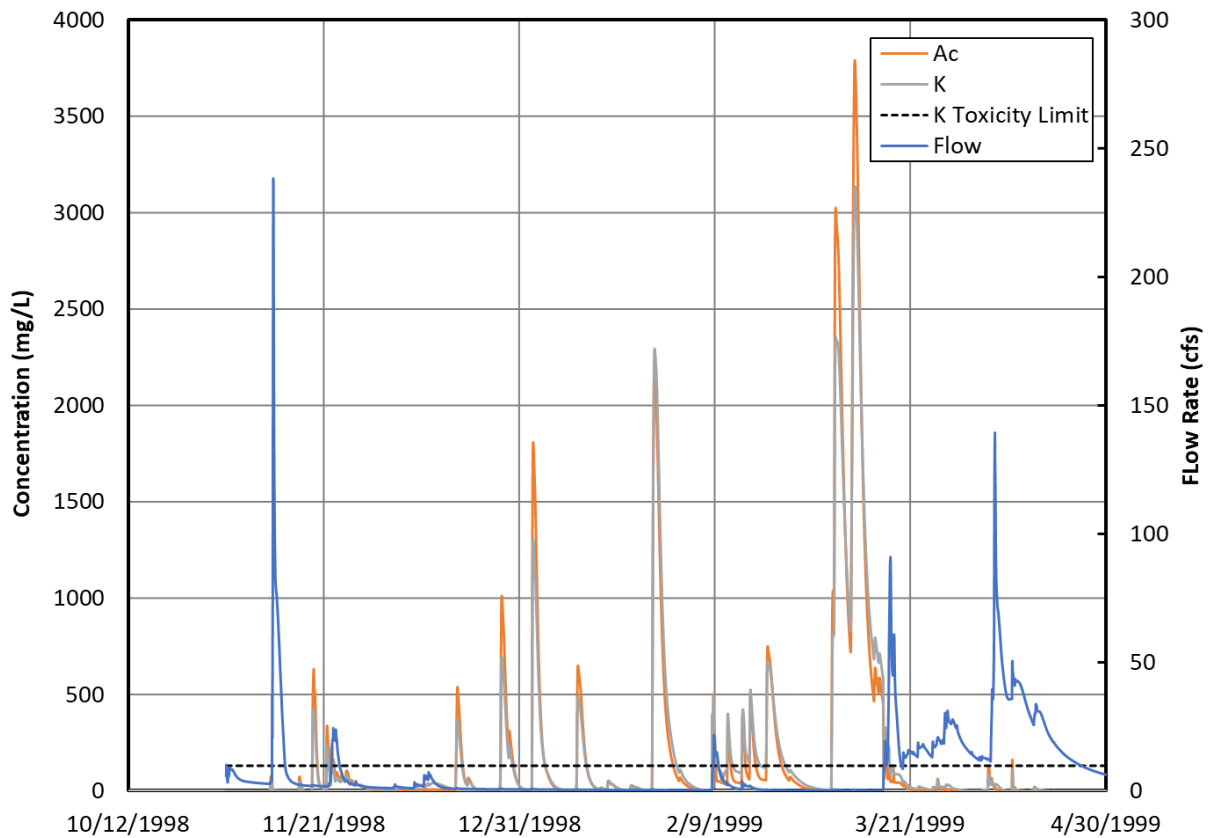


Figure 16. Simulated flow rate and K and Ac concentration at the outlet of Miller Creek for Case II (KAc applied to all roadways).

The time series of K concentration for the three cases are shown in Figure 17. This demonstrates the substantial differences in management strategies for Cases I, II, and III. Applying KAc on 25% of the roadways produces peak K concentrations of ~1150 mg/L. Increasing the application area to 100% of the roadways increases the peak K concentration to ~3150 mg/L and including the parking lots increases the peak K concentration to ~4300 mg/L. This is, however, for the highest concentration event. When considering the number of events, applying KAc on only 25% of the roadways produced only three events that exceeded the toxicity limit, whereas Case II (100% of roadways) produced at least ten events with exceedances. Including parking lots in Case III produced conditions in which the concentration did not drop below the toxicity limit between events, resulting in extended periods of time when the toxicity limit was exceeded. The environmental impacts of such conditions are substantial.

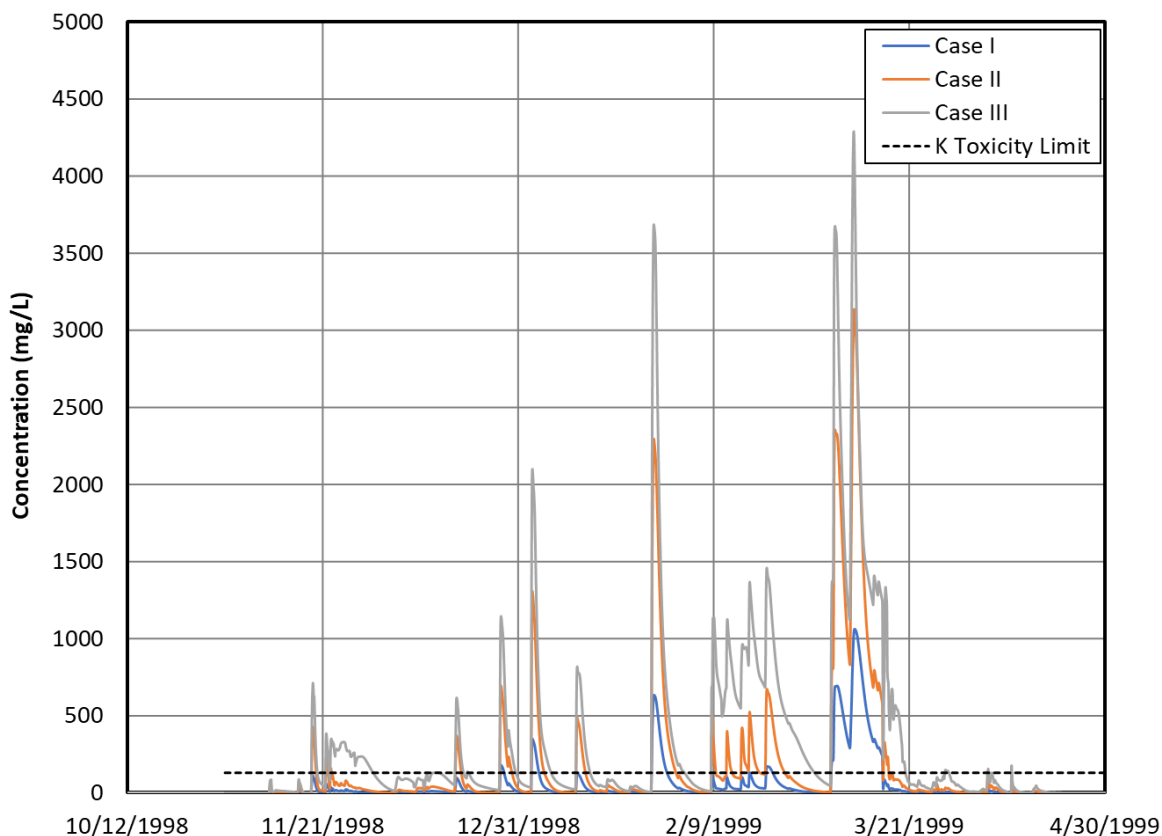


Figure 17. Simulated K concentration at the outlet of Miller Creek for Cases I, II, and III.

2 Preliminary Assessment

The K concentrations due to potassium acetate application as an anti-icer to 25% of the roads in the Miller Creek watershed were predicted to be above toxic concentrations for water fleas. Potassium, especially, is a chemical with a low LC_{50} and is a concern for the broad application of KAc anti-icer. We believe that KAc could be used in the most precarious winter driving safety locations, but not over all watershed roads or for all storms. Acetate could be used as a general organic anti-icer, but in combination with another cation, such as sodium or magnesium. These alternative ions do not, however, possess the low temperature effectiveness of KAc.

The results of this task focus on estimating concentrations of potassium acetate in surface waters, and do not consider the accumulation of potassium and acetate in roadside soils or in groundwater. The KAc in-stream concentrations simulated in this task assume that KAc is not transported through shallow groundwater, and therefore there is no background KAc concentration in baseflow. Some previous studies have shown, for example, relatively low degradation rates of acetate infiltrating to groundwater in winter conditions of 0.02 per day. Thus, it is possible that some acetate could appear in baseflow. If, however, the acetate concentration is similar to or lower than current chloride concentration in baseflow, it is not expected to cause impairments or toxicity exceedances.

It is important to note that the results given in this update are based on an analysis of the Miller Creek watershed in Duluth, MN. Other watersheds with similar climate conditions, watershed response to precipitation, and application rates of deicers and anti-icers are expected to have similar results.

Further work is needed in other parts of the state to extend and generalize the results for different climate regions and watershed characteristics.

Final Update June 30, 2022

The literature review (Activity 1) describes previous and recent literature on road salt alternatives, including chemicals (e.g., acetate, formate, glycol, glycerol) and abrasives (e.g., sand, heated sand) and the Seventh Update (January 31, 2022) for Activity 2 shared a thorough analysis of environmental impacts of potassium acetate as one road salt alternative. These results can be extended to represent other chemicals and for other watersheds or locations (given some assumptions) by considering the following differences:

1. Varying climate regime for other locations and watersheds,
2. Varying application rates for the chemicals,
3. Varying decay rate coefficients for organic chemicals, and
4. Varying toxicity thresholds for the chemicals being considered.

The best approach for assessing environmental impacts is for end users to choose the conditions for which they want the environmental impacts and model those conditions specifically, following the example established by this research project. Modeling every combination of toxicity, decay rate, application rate, and climate regime for all road alternatives and climate regimes in Minnesota is beyond the scope of this work. The following sections outline how these conditions vary and how the results can be interpreted to ascertain environmental impacts of various chemicals under various conditions.

Varying Climate Regimes for other Locations and Watersheds

Miller Creek in Duluth, MN was used as the primary study site for analyzing de-icer/anti-icer concentrations in surface runoff. To check if the Miller Creek results are representative of other areas of the state, snow fall data for Brainerd, Duluth, Minneapolis, and Rochester, MN were analyzed. For the 30-year period 1991-2020, Duluth received significantly more snowfall, on average, compared to Brainerd, Minneapolis and Rochester, and more days with 1 inch or greater snowfall (Figure 18). The median (50th percentile) snowfall depth for Duluth was 90.2 inches, compared to 46, 52.7, and 47.4 inches for Brainerd, Minneapolis, and Rochester, respectively.

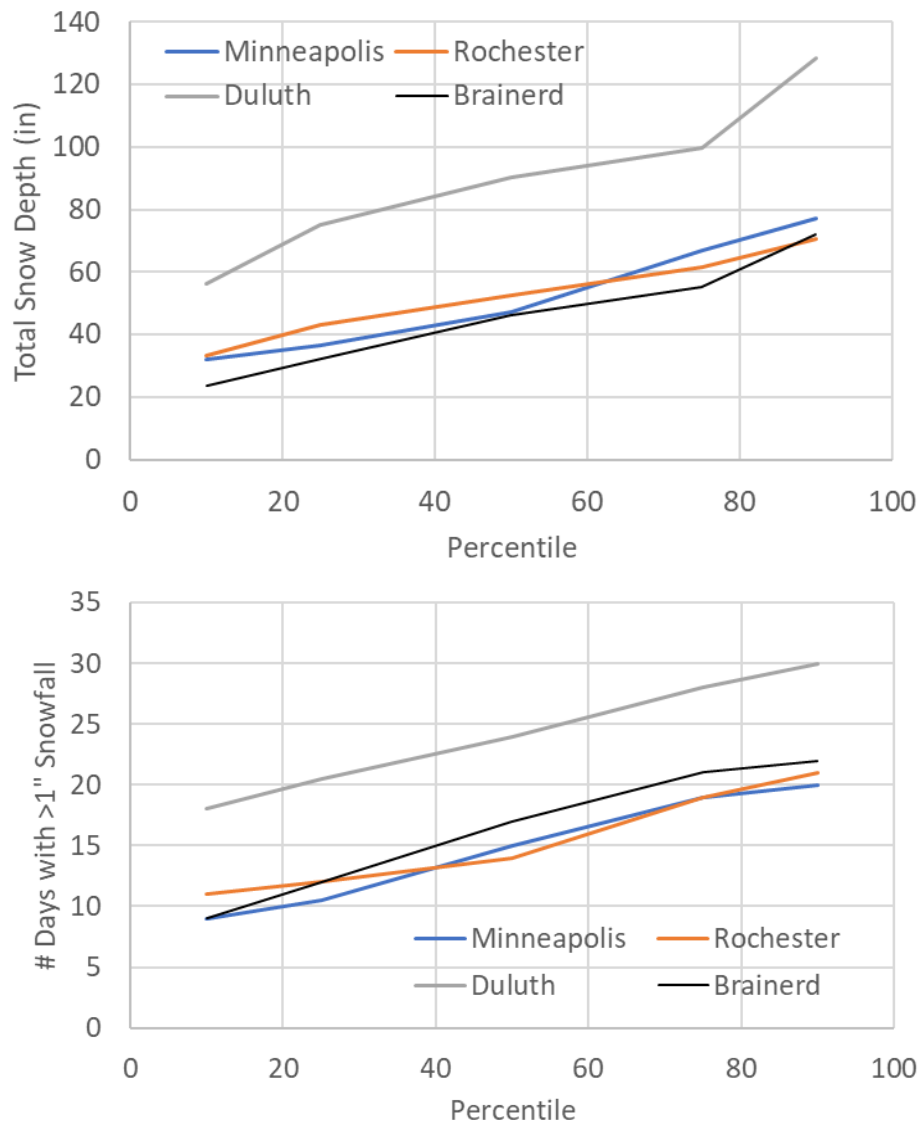


Figure 18. Statistics of total snowfall (upper panel) and number of days with at least 1 inch of snowfall (lower panel) for the winter seasons (October – April) from 1991-2020, for Brainerd, Duluth, Minneapolis, and Rochester.

To examine whether these differences in snowfall lead to significant differences in de-icer/anti-icer concentrations in surface runoff, 31 years of climate data (1990-2020) for Duluth and Minneapolis were used as input to the Miller Creek SWMM model to simulate 30 winter seasons. As before, potassium acetate was applied to the roadways on each day with at least one inch of snowfall. The SWMM model was run for a 31-year continuous simulation between January 1, 1990 and December 31, 2020 for each city. Simulated runoff and the concentrations of potassium and acetate were compiled for the outlet of Miller Creek for 30 winter seasons, starting with October 1, 1990 through April 30, 1991 and ending with October 1, 2019 through April 30, 2020. The simulation results for Duluth and Minneapolis are summarized in Table 2 and Figure 19. Although both snowfall and anti-icer application were higher for Duluth, the concentrations of anti-icer in surface runoff were similar for Minneapolis and Duluth (Table 2), suggesting that the larger snowfall depth in Duluth dilutes the higher total anti-icer application. However, 60% higher total application of anti-icer in Duluth compared to Minneapolis (Table 2) would lead to correspondingly higher total loading of anti-icers to downstream water bodies.

Year-to-year variability of the mean concentration in runoff is high at both sites (Figure 19). The year-to-year mean anti-icer concentration was found to be correlated to mean flow rate ($r^2=0.87$) at both sites, with similar inverse relationships (Figure 20). Higher flow rates tend to dilute the anti-icer concentrations, with an order of magnitude change in both flow rates and concentration over the 30 winter seasons.

Table 2. Summary of SWMM simulation results for runoff concentrations of potassium and acetate over 30 winter seasons (1990-91 to 2019-20) in Duluth and Minneapolis, MN. Mean concentrations are flow-weighted.

Variable	Duluth	Minneapolis
Flow Rate, Mean (cfs)	5.2	3.4
Acetate, Total Application per Winter, Mean (kg)	6890	4223
Acetate Conc., Mean (mg/L)	37.8	41.7
Acetate Conc., Max (mg/L)	2794	2183
Potassium, Total Application per Winter, Mean (kg)	4570	2799
Potassium Conc., Mean (mg/L)	39.0	42.6
Potassium Conc., Max (mg/L)	2573	1893

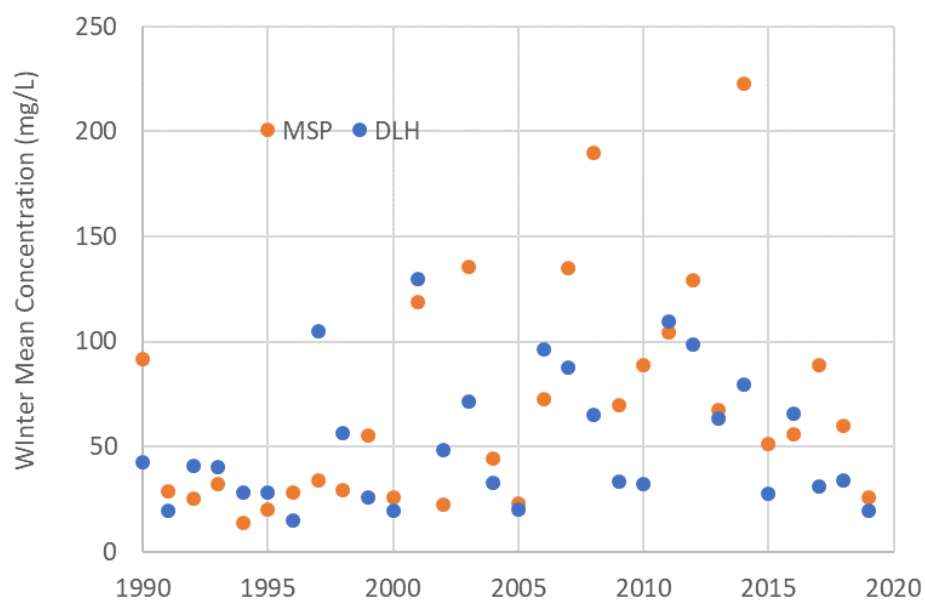


Figure 19. Simulated flow-weighted mean acetate concentration for each winter season (1990-91 to 2019-20) in Minneapolis and Duluth.

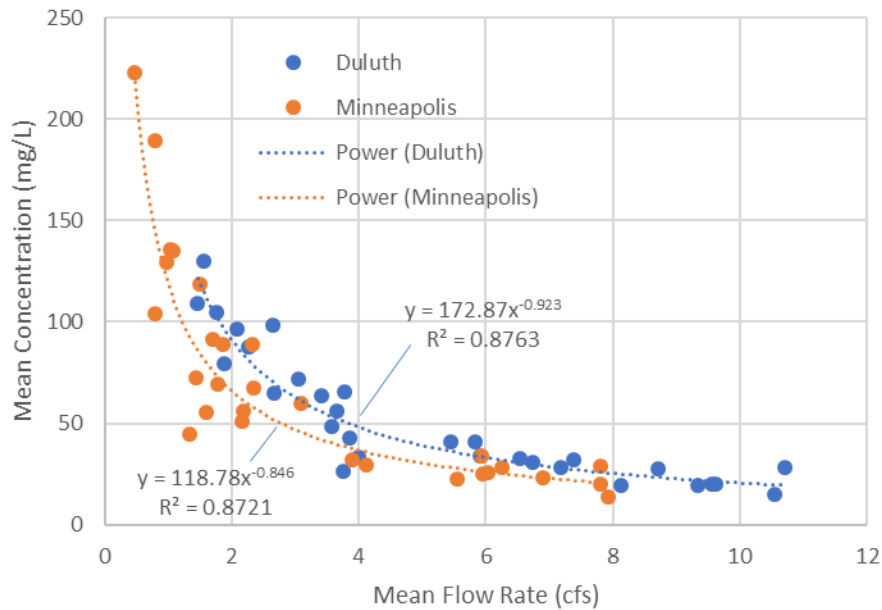


Figure 20. Relationship between flow-weighted annual mean acetate concentration and annual mean flow rate for 30 winter seasons in Minneapolis and Duluth, MN.

Varying Application Rates

More details and the ranges of the application rates for various road salt alternative chemicals is provided in the literature review (Activity 1), but Table 3 below provides a summary for several chemicals. For comparison, the modeling described in the previous status update assumed Potassium Acetate application as liquid at 42.5 gal/lane mile.

Table 3. Summary of Application rates for various road salt alternatives.

Road Salt Alternative	Application Rate	Reference
Sodium Acetate (NaAc)	190-320 lbs/lane-mile when near 32°F.	Fay et al. 2015
	600-1500 lbs/lane-mile at 10°F (1" of ice)	
Calcium Magnesium Acetate (CMA)	250-400 lbs/lane-mile	
Potassium Acetate (Kac)	25-60 gal/lane-mile as an anti-icer, 60-80 gal/lane mile as deicer	
Sodium Formate (NaFo)	125-250 lb/lane-mile near 32°F and thin ice, 400-1000 lb/lane-mile at 10°F and 1" ice.	
Potassium Formate (KFo)		
Ethylene Glycol	50-2000 gal/lane mile	
Propylene Glycol		
SnowMelt (a fully bio-based product), Fusion (a mixture of a bio-based product and chloride salt), and Caliber M1000 (another mix of a bio-based product and chloride)	3, 6, 9 liters per 1000 ft²	Hosseini et al. 2017
Sodium Chloride (NaCl) and liquid Potassium Succinate (KSu)	Typical anti-icing application rates used by state DOTs range from 40 to 75 gal/lane-mile.	Fay and Akin 2018

Fay, L., Honarvarnazari, M., Jungwirth, S., Muthumani, A., Cui, N., Shi, X., Bergner, D., Venner, M. 2015. *Manual of Environmental Best Practices for Snow and Ice Control. Clear Roads and Minnesota DOT.*

Fay, L., and M. Akin, 2018. *Investigation of Alternative Deicers for Snow and Ice Control*, Center for Environmentally Sustainable Transportation in Cold Climates, University of Alaska Fairbanks, Fairbanks, AK, USA.

Hosseini, F., Hossain, S.M.K., and L.P. Fu, 2017. *Bio-based materials for improving winter pavement friction*, *Canadian Journal of Civil Engineering*, 44(2):99-105.

In general, most road salt alternative chemicals are applied at rates greater than 42.5 gal/lane-mile. Thus, assuming similar decay rates and other modeling parameters as described above, one could assume that road salt alternatives applied at greater rates will produce greater acetate outflow concentrations compared to the results displayed in the Seventh Update (January 31, 2022) for Activity 2.

Varying Decay Rate Coefficients

Organic compounds such as acetate, formate, glycol and glycerol will experience natural biodegradation during transport in the environment. This was modeled within EPA-SWMM using the built-in first order decay rate equation. Values for first-order decay coefficient (k) will depend on temperature and compound, though EPA SWMM guidance recommends 0.11 per day (US EPA 2016) for general modeling of biochemical oxygen demand (BOD) processes such as this. This assumes, however, normal summer temperatures (~20°C), which are not appropriate for winter and spring conditions during which organic road salt alternatives will be transported through the environment. In the modeling described in the Seventh Update (January 31, 2022) for Activity 2, acetate was assigned a decay coefficient (k) of 0.03 per day based on values measured at 34°F, 39°F, and 46°F (1°C, 4°C, and 8 °C) (Revitt and Worrall, 2003). Little information is available for organic road salt alternatives at low temperatures, but this value is likely appropriate for formate, glycol and glycerol in addition to acetate. For accurate environmental impact assessments, however, biodegradation rates should be measured for the chemicals of interest and the temperatures at which they will be transported through the environment after anti-icing or de-icing application.

Revitt, D. M., & Worrall, P (2003). *Low temperature biodegradation of airport de-icing fluids*. *Water Science and Technology*, 48(9), 103–111.

U.S. Environmental Protection Agency. (2016). *Storm water management model reference manual. Volume III – water quality*. Retrieved from <https://www.epa.gov/water-research/storm-water-management-model-swmm>

Varying Toxicity Thresholds

The environmental impacts and toxicity considerations for Calcium Magnesium Acetate (CMA) include 2500 mg/L to 3000 mg/L does not affect plant growth directly but may be deadly to seedlings (Horner 1988). A concentration of 5000 mg/L of CMA was found to slightly delay the hatching of rainbow trout but it did not affect the number of eggs hatched (Winters et al. 1984). Water flea reproduction was significantly inhibited at 250 mg/L CMA but there was no harmful impact to algae at concentrations under 50 mg/L CMA (Winters et al. 1984).

Though no numeric values were given, Ice-B-Gone (pellet form of CMA) was found to have a low level of toxicity for acute oral toxicity, sub-chronic toxicity, acute inhalation toxicity, acute dermal toxicity, skin irritation, eye irritation, and skin sensitization when tests were performed on rats and the latter

two tests were also performed on human volunteers (Buteau et al 1992). CMA was found to be a slight eye irritant but not a skin irritant or skin sensitizer.

Goldman and Lubnow (1992) found that concentrations of 10 mg/L CMA appeared to increase chlorophyll in one lake and a concentration of 1 mg/L resulted in statistically higher chlorophyll concentrations in another lake. During the summer, eight out of the ten lakes showed no response to CMA at doses of 0.1, 1.0, and 10 mg/L CMA but bioassays in the late spring and early winter showed slight responses to CMA.

Joutti et al. (2003) tested sodium chloride, calcium chloride, magnesium chloride, potassium formate, potassium acetate, and CMA with different bioassays. Bioassays were an onion plant root elongation test, a duckweed growth inhibition test, an enzyme inhibition test, and a microbial test (luminescent bacteria, BioTox test). Overall, the organic chemicals were more toxic than the inorganic salts. The rank of toxicity, according to the root elongation and growth inhibition tests, were, from most toxic to least toxic: potassium formate, potassium acetate, CMA, calcium chloride, sodium chloride, and magnesium chloride. CMA could not be tested for the other two bioassays due to the turbidity of the samples.

Dougherty and Smith (2006) investigated the effect of sodium chloride, magnesium chloride, calcium acetate, magnesium acetate, sodium ferrocyanide, and sodium formate on tadpoles of two frog species and one toad species. Some salt compounds negatively affected some tadpoles but the acetates, sodium ferrocyanide, and sodium formate did not. All the concentrations tested were less than 170 mg/L and it was noted that higher concentrations may result in more of an impact.

Hanslin (2011) found that increasing concentrations from zero to 13.3 mmol/L soil caused negative responses, but results varied with five plant species investigated. Root growth decreased in two species and leaf biomass decreased in four of the five species. There was no impact on specific leaf area, relative chlorophyll content, height increase, or chlorophyll fluorescence. Overall, the organic deicers did not have less impact on saplings than sodium chloride did during active growth.

In summary, toxicity varies amongst chemicals and species. Thus, conditions must be chosen to determine the extent of environmental impacts. As described above, climate regime, application rate, and decay rate for organic chemicals will affect the concentration of road salt alternatives. When modeled appropriately and specifically for the chemicals of interest, then outflow concentrations can be compared to toxicity thresholds to determine what environmental impacts may occur, as exemplified by the modeling results described in the Seventh Update (January 31, 2022) for Activity 2.

ACTIVITY 3: Conduct friction tests on pavement cores to select promising techniques.

Description: Blocks of several different pavement types will be treated with approximately 12 road salt alternatives and pavement innovations, and exposed to typical winter conditions in a climate-controlled room. The temperature, humidity, and ice cover will be controlled to make direct comparisons between alternatives. One of several road friction testers will be selected for these experiments and used to measure road friction in simulated winter conditions with pavement innovations and road salt alternatives. Ranking metrics will be developed based on cost and environmental impact of the alternatives, as well as road friction results for various simulated winter conditions.

ENRTF BUDGET: \$190,734

Outcome	Completion Date
1. Laboratory road friction tests completed in various conditions for road salt alternatives	12/31/2020
2. Develop ranking metrics from cost and predicted road friction results for all alternatives	3/31/2021
3. Write report on laboratory results	6/30/2021

First Update January 31, 2019

The project team has met several times to discuss the objectives and outcomes of the laboratory friction measurements. A preliminary plan and instrumentation for the measurements has been developed and a preliminary experimental procedure has been developed and tested. The measurements will commence in the next semi-annual period.

Second Update June 30, 2019

1. We've developed a novel protocol for measuring de-icing effectiveness of various road salt alternative chemicals related to skid resistance (friction) in laboratory conditions. The surface of the pavement is simulated by a special arrangement of cylindrical specimens that form a much larger area of testing on which a dynamic friction tester can effectively measure friction coefficient at various speeds and temperatures.
2. We have also developed a protocol for measuring anti-icing effect by measuring the shear strength (adhesion) of the interface between surfaces treated with various road salt alternatives and ice. A servo-hydraulic testing machine equipped with an environmental chamber and special fixtures were used for the testing.
3. The road salt alternatives currently under consideration include conventional salt (NaCl) as a baseline for comparison, Magnesium Chloride (MgCl₂), Potassium Acetate (KAc), CF7 (commercial KAc mix), Propylene Glycol (organic chemical), Abrasives (de-icing only), and Pavement Technologies (pending availability).

Third Update January 31, 2020

1. The measuring anti-icing effect protocol was further refined to improve the precision of the measurements. A more consistent application method was set in place in order to replicate the field application rate of the anti-icing chemicals.
2. Control samples without anti-icing treatment and samples treated with three anti-icing chemicals, conventional salt (NaCl), Magnesium Chloride (MgCl₂), and CF7 (commercial KAc mix) were prepared. All of them were tested at four temperatures: -5 °C, -15 °C, -25 °C, -35 °C.

Fourth Update June 30, 2020

Laboratory testing (Activity 3) consists of friction measurements for de-icing and friction enhancement (e.g., sand and grit) and anti-icing experiments which measure the ability of road salt and road salt alternatives to weaken the bond between ice and pavement. All anti-icing chemicals that were planned for testing (no treatment, Na-Cl-based brine, Magnesium Chloride, Potassium Acetate, RainX) have been tested at various temperatures (-15 °C, -25 °C, -35 °C). Friction measurements for de-icing and friction enhancement will resume in the next biennium (July – Dec 2020).

Fifth Update January 31, 2021

Experimental data collection for Laboratory testing (Activity 3) was completed, and data analysis is underway. Pending data analysis approval, Activity 3, Outcome 1 will be complete during this biennium (Jan – June 2021). Subsequent to completion of Outcome 1, Outcome 2 (develop ranking metrics) and Outcome 3 (write report) can then be completed.

Sixth Update June 30, 2021:

The experimental analysis and the data analysis are complete. We are currently writing up the results for the final report.

Seventh Update January 31, 2022:

Two manuscripts describing the results of Activity 3 have been prepared; one submitted for publication and a second manuscript that will be completed and submitted during this biennium.

Final Update June 30, 2022

Two manuscripts describing the results of Activity 3 have been prepared. One was previously submitted for publication and a second manuscript is drafted and will be submitted.

IV. DISSEMINATION:

Description: Dissemination and transfer of new knowledge and technology will be directed towards homeowners, practitioners, regulatory units of government, and other interested stakeholders. The project team has a long history of providing training and dissemination of science through the Water Resource Center, the Erosion and Stormwater Certification Program and the MN Road Salt Applicator training. Information learned in this study will be incorporated into this and other certification curricula. The team is well-equipped to communicate and disseminate results and outreach will occur through a variety of established formats. The results will be incorporated into MPCA chloride reduction programming and policy.

Knowledge transfer will also occur through written and electronic communication streams including St. Anthony Falls Laboratory's UPDATES, a stormwater research newsletter distributed to over 2,400 subscribers and the University of Minnesota Extension Water Resources News published 4-6 times per year. The team will also seek to include information in the Minnogram and Confluence newsletters, published by the Water Resources Center. In addition, one or more journal articles will be submitted for publication from the results of this project.

The team is also well-equipped to engage in dialogue and collaboration with public entities including watershed districts, municipalities, counties, universities, the Minnesota Cities Stormwater Coalition, and statewide entities working on stormwater management. Finally, the team is able to collaborate and communicate with researchers and educators across multiple campuses spread throughout the state.

First Update January 31, 2019

The project is currently in the data collection and measurement phase and thus no data or results are available for dissemination. However, the existence and intentions of the project have been communicated with stakeholders and target audiences (cities, homeowners, associations, etc.) and will continue throughout the project. The following presentations have discussed the project and preliminary results:

- <https://twin-cities.umn.edu/news-events/umn-experts-winter-weather-driving>

Second Update June 30, 2019

The project is currently in the data collection and measurement phase and thus no data or results are available for dissemination. However, the existence and intentions of the project have been communicated with stakeholders and target audiences (cities, homeowners, associations, etc.) and will continue throughout the project.

Third Update January 31, 2020

The project is currently in the data collection and measurement phase and thus no data or results are available for dissemination. However, the existence and intentions of the project have been communicated with stakeholders and target audiences (cities, homeowners, associations, etc.) and will

continue throughout the project. The following presentations have discussed the project and preliminary results:

- October 24, 2019. Invited to present "Recent, in progress, and future research on salt pathways, pavements, water softening, and all things chloride." Oral Presentation. 20th Annual Minnesota Road Salt Symposium. Vadnais Heights, MN.

Fourth Update June 30, 2020

The project is currently in the data collection and measurement phase and thus no data or results are available for dissemination. However, the existence and intentions of the project have been communicated with stakeholders and target audiences (cities, homeowners, associations, etc.) and will continue throughout the project.

Fifth Update January 31, 2021

The project is currently in the data collection and measurement phase and thus no data or results are available for dissemination. However, the existence and intentions of the project have been communicated with stakeholders and target audiences (cities, homeowners, associations, etc.) and will continue throughout the project.

Sixth Update June 30, 2021:

The following presentations have discussed the project and preliminary results:

- August 4, 2021. Invited to present "How Anti-icing Chemicals Affect Ice Bonding to Pavement at Different Temperatures." Oral Presentation. 2021 Road Salt Symposium. Virtual.

Seventh Update January 31, 2022:

The following publications and presentations have discussed the project and preliminary results:

- January 9–13, 2022. Invited to present "Increasing Friction on Roadway Ice with Water Heated Sand." Poster Presentation. 2022 Transportation Research Board Annual Meeting. Washington, D.C. Road Salt Symposium. Virtual.
- Erickson, A., Turos, M., Weiss, P., Gulliver, J. and Marasteanu, M. (2022, submitted). "Increasing friction on roadway ice with water-heated sand."
- Erickson, A., Turos, M., Weiss, P., Gulliver, J. and Marasteanu, M. (2022, in preparation). Effectiveness of Organic Anti-Icing Alternatives.

Final Update June 30, 2022

The following publications and presentations have discussed the project and preliminary results:

- December 7, 2021. Interviewed for "[Good Question: How Does Salt Melt Ice?](#)" with Jeff Wagner, WCCO 10 o'clock news.
- February 17, 2022. Invited to present "Urban Stormwater Runoff Research: Innovating Practice to Improve Water Quality." Oral Presentation. MPCA Minnesota GreenCorps. Virtual.
- February 18, 2022. Invited to lead "St. Anthony Falls Laboratory; A tour for participants of 2022 IECA Annual Conference and Trade Show." Oral Tour. 2022 International Erosion Control Association 50th Annual Conference. Minneapolis, MN.
- April 19, 2022. Invited to lead "Urban Stormwater Runoff Management." Oral presentation with Poornima Natarajan. St. Anthony Falls Laboratory; A tour for UMN CSE Dean Andrew G. Alleyne. Minneapolis, MN.

- May 6, 2022. Invited to present "Urban Stormwater Runoff Management." Oral presentation with Poornima Natarajan. 2022 St. Anthony Falls Laboratory Research Retreat. Minneapolis, MN.
- May 19, 2022. Invited to lead "St. Anthony Falls Laboratory; A tour for MN GreenCorps Members." Oral tour. St. Anthony Falls Laboratory. Minneapolis, MN.
- June 8, 2022. Invited to lead "St. Anthony Falls Laboratory; A tour for MN Watershed Partners." Oral tour. St. Anthony Falls Laboratory. Minneapolis, MN.
- June 28, 2022. Invited to present "Stormwater Research in Minnesota" Oral presentation. 2022 Water Environment Federation (WEF) Stormwater Summit. Minneapolis, MN.
- Erickson, A., Turos, M., Weiss, P., Gulliver, J. and Marasteanu, M. (2022, in preparation). "Increasing friction on roadway ice with water-heated sand."
- Erickson, A., Turos, M., Weiss, P., Gulliver, J. and Marasteanu, M. (2022, in preparation). Effectiveness of Organic Anti-Icing Alternatives.

V. PROJECT BUDGET SUMMARY:

A. Preliminary ENRTF Budget Overview: See attached budget spreadsheet

Explanation of Use of Classified Staff: N/A

Total Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation:

Enter Total Estimated Personnel Hours: 5166	Divide by 2,080 = TOTAL FTE: 2.5
---	----------------------------------

Total Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation:

Enter Total Estimated Personnel Hours: 930	Divide by 2,080 = TOTAL FTE: 0.45
--	-----------------------------------

B. Other Funds:

None.

VI. PROJECT PARTNERS:

A. Partners receiving ENRTF funding

Name	Title	Affiliation	Role
Peter T. Weiss	Professor	Valparaiso University	Visiting Professor to St. Anthony Falls Laboratory and subject matter expert.
Connie Fortin		Fortin Consulting	Subject matter expert.

B. Partners NOT receiving ENRTF funding

Name	Title	Affiliation	Role
Brooke Asleson	Water Pollution Prevention Coordinator	Minnesota Pollution Control Agency	State regulatory leadership coordinating issues related to the overall chloride management strategies underway at the MPCA

VII. LONG-TERM- IMPLEMENTATION AND FUNDING:

The long-term implementation of the results of this project includes the dissemination of lessons learned, as described in section IV above. In addition, the project team is soliciting the Clear Road program for funds to match this effort, which would allow the project team to expand the research with field measurements and experiments of road salt alternatives in natural winter conditions. The project team is also pursuing opportunities to collect friction measurements of roadway surface throughout Minnesota, to better understand the friction of various pavements during winter conditions with, and without road salt applications. The information gained from this project will propel these future endeavors towards a robust understanding of road safety in cold Minnesota winters that also protects the environment from harmful anti-icing and de-icing chemicals.

VIII. REPORTING REQUIREMENTS:

- The project is for 4 years, will begin on July 1, 2018, and end on June 30, 2022.
- Periodic project status update reports will be submitted January 31 and June 30 of each year.
- A final report and associated products will be submitted between June 30 and August 15, 2022.

IX. SEE ADDITIONAL WORK PLAN COMPONENTS:

A. Budget Spreadsheet



Project Title: Investigation of Road Salt Alternatives and Pavement Innovations

Legal Citation: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04c

Project Manager: John S. Gulliver

Organization: University of Minnesota

College/Department/Division: St. Anthony Falls Laboratory

M.L. 2018 ENRTF Appropriation: \$400,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to investigate road-salt alternatives and pavement innovations to reduce lake, stream, and groundwater degradation caused by road-salt chlorides. This appropriation is available until June 30, 2021, by which time the project must be completed and final products delivered.

Project Length and Completion Date: 4 Years ending June 30, 2022

Date of Report: August 15, 2022

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Revised Budget 4/21/22	Amount Spent (2022/06/30)	Activity 1 Balance	Activity 2 Revised Budget 4/21/22	Amount Spent (2022/06/30)	Activity 2 Balance	Activity 3 Revised Budget 4/21/22	Amount Spent (2022/06/30)	Activity 3 Balance	TOTAL BUDGET	Total Amount Spent (2022/06/30)	TOTAL BALANCE
BUDGET ITEM												
Personnel (Wages and Benefits)												
Personnel: Professor (J. Gulliver), Supervisory and Analysis, 6.7% FTE (75% salary, 25% benefits) each year for 3 years. \$58,835	\$6,259	\$6,259	\$0	\$28,189	\$28,189	\$0	\$24,386	\$24,386	\$0	\$58,834	\$58,834	\$0
Personnel: Professor (B. Wilson), Supervisory and Analysis, 1.9% FTE (75% salary, 25% benefits) each year for 3 years. \$11,124	\$0	\$0	\$0	\$5,964	\$5,964	\$0	\$5,160	\$5,160	\$0	\$11,124	\$11,124	\$0
Personnel: Professor (M. Marasteanu), Supervisory and Analysis, 1.9% FTE (75% salary, 25% benefits) each year for 3 years. \$16,896	\$1,342	\$1,342	\$0	\$6,042	\$6,042	\$0	\$9,512	\$9,512	\$0	\$16,896	\$16,896	\$0
Personnel: Research Associate (A. Erickson), Literature review, computer modeling, laboratory experiments, and analysis, 36% FTE (75% salary, 25% benefits) each year for 3 years. \$176,976	\$11,497	\$11,497	\$0	\$51,778	\$51,778	\$0	\$113,703	\$113,703	\$0	\$176,978	\$176,978	\$0
Personnel: Research Associate (M. Turos), laboratory experiments and analysis, 16.7% FTE (75% salary, 25% benefits) each year for 3 years. \$44,573	\$4,781	\$4,781	\$0	\$21,531	\$21,531	\$0	\$18,261	\$18,261	\$0	\$44,573	\$44,573	\$0
Personnel: Junior Engineer Trainee, Laboratory experiments, 4.8% FTE (100% salary) each year for 3 years. \$2,534	\$419	\$419	\$0	\$1,885	\$1,885	\$0	\$230	\$230	\$0	\$2,534	\$2,534	\$0
Personnel: Junior Scientist (A. Ketchmark), Experimental apparatus and laboratory experiments, 15% FTE (79% salary, 21% benefits) each year for 3 years. \$3,298	\$3,298	\$3,298	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$3,298	\$3,298	\$0
Professional/Technical/Service Contracts												
Professional/Technical/Service Contracts: Contract with Peter Weiss (Visiting Professor) to provide oversight and expertise with laboratory experiments. 10% FTE (100% salary) each year 3 years. \$45,700	\$0	\$0	\$0	\$25,090	\$25,090	\$0	\$20,610	\$20,610	\$0	\$45,700	\$45,700	\$0
Professional/Technical/Service Contracts: Contract with Fortin Consulting to provide expertise and experience with data collection and analysis related to road salt alternatives. 4.8% FTE (100% Salary) each year for 3 years. \$32,136	\$0	\$0	\$0	\$17,230	\$17,230	\$0	\$14,905	\$14,905	\$0	\$32,135	\$32,135	\$0
Lab analytical services. Analytical services to analyze road-side soil samples to compare the presence of sodium and chloride (conventional road salt) and soil properties that could be used to model breakdown of road salt alternatives such as organic chemicals. \$6,058		\$0	\$0		\$0	\$0	\$6,058	\$6,058	\$0	\$6,058	\$6,058	\$0
Equipment/Tools/Supplies												
Equipment/Tools/Supplies: Supplies for experimental setup and analysis. \$1,507		\$0	\$0		\$0	\$0	\$1,507	\$1,507	\$0	\$1,507	\$1,507	\$0
Capital Expenditures Over \$5,000												
Printing												
Travel expenses in Minnesota												
Travel: Collect information and pavement cores. 500 miles @ \$0.56/mi \$363	\$0	\$0	\$0	\$363	\$363	\$0	\$0	\$0	\$0	\$363	\$363	\$0
COLUMN TOTAL	\$27,596	\$27,596	\$0	\$158,072	\$158,072	\$0	\$214,332	\$214,332	\$0	\$400,000	\$400,000	\$0

ROAD SALT ALTERNATIVES AND PAVEMENT INNOVATIONS

A Literature Review

Project: Investigation of Road Salt Alternatives and
Pavement Innovations

By: Peter T. Weiss and John S. Gulliver

December 2018

Funded by the Legislative-Citizens Committee on Minnesota Resources
(LCCMR) 2018

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Introduction

This report is Activity 1 of the Legislative-Citizens Committee on Minnesota Resources (LCCMR) 2018 funded project entitled “Investigation of Road Salt Alternatives and Pavement Innovations.” The objective of the project is to investigate road salt alternatives (RSAs) and pavement innovations to reduce or eliminate the transport of chlorides into Minnesota’s lakes, streams, and groundwater. According to the project work plan, Activity 1 is a review of previous research on road salt alternatives, pavement innovations, and pavement friction.

Previous studies have investigated the performance of RSAs with regards to the prevention of ice formation on the pavement surface (anti-icing), the reduction or elimination of ice or snow cover on the pavement surface (deicing), their environmental impact, their cost, production processes, and various other related topics. To maintain alignment with the focus of the funded project with respect to RSAs, this report focuses on their performance, environmental impact, and cost. With regards to pavement innovations, this report focuses on concrete and asphalt pavement innovations that are intended to enhance anti-icing, deicing, and road friction.

The organization of this report is such that it first introduces and discusses RSAs investigated and reported in the literature. Studies that specifically investigated the performance of RSA with respect to anti-icing, deicing, or road friction follow. Although the previously mentioned sections on RSAs include a general discussion of their environmental impacts such as biochemical oxygen demand (BOD) and corrosivity, some studies focused specifically on the impact of RSAs on specific environmental aspects (e.g. toxicology). These studies are reviewed in a separate section on environmental impact, which also includes a review of studies that have modeled the fate, transport, or impact of RSAs, mainly the BOD of calcium magnesium acetate (CMA) in streams and lakes.

Lastly, previous research on pavement innovations are discussed. This discussion includes a description of the pavement innovation technique and, depending on the study, covers issues such as anti-icing, deicing, road friction, energy requirements, and cost.

Road Salt Alternatives

To minimize the environmental impact of salts, many RSAs have been investigated over the past several decades on the basis of water solubility, their ability to lower the freezing point

of water, corrosiveness, toxicity, cost, environmental impact, and flammability (Boice 1986). This section introduces and discusses these materials, most of which are organic compounds, and covers such issues as their cost, effectiveness, and general environmental impacts. Please note that there is a subsequent section devoted solely to studies that investigated a specific environmental impact of RSAs and that the current section presents a general overview of environmental concerns and findings for each of the RSAs presented.

Before beginning the discussion of RSAs that are intended to melt snow and ice, it is worthwhile to note that research has determined that abrasives (i.e. sand and grit) can be more effective at increasing road friction (Perchanok 2010) and provide longer lasting road friction if the abrasives are pre-wetted as they are placed on the road, heated to ~82 °C (~180 °F) just prior to placement, or mixed with hot water just prior to placement (Nixon 2001). These techniques help more abrasive stay on the road upon placement (i.e. not bounce off) and it helps abrasives stay on the road for a longer period of time because, upon placement without such treatment, a large fraction of the abrasives bounce off the road surface, are blown off by natural winds (D'Itri 1992), or are swept off in 10 to 100 vehicle passages (Nixon 2001).

Concerning the organic RSAs discussed in the literature, much focus has been on acetates-based products, formate-based products, glycol and glycerol, and succinate-based products. A discussion of these RSAs begins immediately below.

Acetate-Based Alternatives

As previously mentioned, one organic RSA is acetate (Boice 1986, Baltrenas and Kazlauskiene 2009), which includes potassium acetate, sodium acetate, and calcium magnesium acetate (CMA) (Fay and Muthumani 2017). Although most of the research has been completed on CMA, potassium acetate is currently favored in cold climates because of its improved level of service, i.e., it will melt snow and ice at lower temperatures than road salt and most other RSAs. The main advantage of acetate-based alternatives is that they are not as corrosive to most metals as salts (Ihs and Gustafson 1996, MDOT and Tetra Tech 2006, Fay and Muthumani 2017) and Ihs and Gustafson (1996) have stated that CMA also causes less freeze/thaw damage to pavements. Acetates are, however, corrosive to galvanized steel and they can cause damage to concrete and asphalt through alkali-silica reactions on aggregates and emulsification of asphalt

binder (Fay and Muthumani 2017). With regards to steel, Baltrenas and Kazlauskiene (2009) found that magnesium acetate was three times less corrosive than calcium chloride and two times less corrosive than magnesium chloride. Boice (1986) found that the corrosiveness (and ice melting ability) of CMA depends on the ratio of calcium to magnesium, with optimum values from three to seven. In one study investigating aluminum corrosion, the potassium acetate corrosion rate was equal to that for chloride, although the corrosion rate for CMA was lower (Levelton Consultants 2008). Levelton Consultants (2008) also pointed out that many studies that have investigated the corrosivity of CMA were done on steel bars submersed in CMA, not of steel bars embedded in concrete exposed to CMA, which would more accurately represent the true exposure process. They also noted that concrete scaling is more dependent on the quality of concrete than on the deicer used.

With regards to cost, acetates are significantly more expensive than chloride-based deicers and, therefore, are mostly used at airports and where steel corrosion is a concern, such as at bridges. In fact, only 10-15% of department of transportations that responded to a survey indicated they use acetate in some way (Fay and Muthumani 2017). Acetates can be up to 20 times more expensive than chloride-based deicers (Boice 1986, Fay and Muthumani 2017) and Albright (2009) found that CMA is still more expensive than salts even when factoring in the cost of corrosion damage caused by salts. The lack of an economic and reliable production method of CMA contributes to the high cost (Boice 1986). Albright (2009) noted, however, that future advances in CMA production could result in a price drop of 20%. In one such method, Jin et al. (2010) converted a vegetable waste product into acetic acid and CMA. Electrodialysis was used to condense CMA from the acetic acid with 22% of the total organic carbon in the vegetable waste being converted to CMA.

In a study that investigated methods with the potential to reduce the total negative impact of deicing by considering the total life-cycle impact, Fitch et al. (2013) showed that CMA has higher total life-cycle environmental impacts than conventional rock salt and preemptive treatment of roads with salt brine and/or CMA. Most of the total life-cycle environmental cost of CMA was due to CMA production, which uses more energy and water and produces more greenhouse gases than chloride-based methods. As previously discussed, it also has a higher BOD.

Another drawback of acetates is that they are less effective than chloride-based deicers (Bang and Johnston 1998). For example, Boice (1986) found that it took 1.65 times the CMA to obtain an equivalent melting power of salt. Others have found or estimated different amounts of CMA are required to equal the effectiveness of chloride-based deicers, but every study has found more CMA (or acetate) is needed. For example, MDOT and Tetra Tech (2006) found that up to two times the amount of CMA was required for equal effectiveness and Fay and Muthumani (2017) stated values ranging from 1.3 to 1.5 times are typical when the temperature is below - 6.7 °C (20° F).

Acetates also work more slowly compared to salts such as sodium chloride, they are less effective in freezing rain, dry snow, and light traffic and they also don't work well when applied to thick accumulations of snow or ice (Fay and Muthumani (2017). Ihs and Gustafson (1996), however, found that, in some cases, the effectiveness of CMA lasted longer than that of sodium chloride.

D'Itri (1992) noted that, in practical applications, powdered CMA was blown off the road surface due to winds (either natural or vehicle induced) and Boice (1986) noted that because CMA is lightweight it cannot penetrate snow and ice. CMA also absorbs moisture and can form sticky conglomerations (Boice 1986). The use of CMA in pellet form prevented winds from blowing the material off the surface of the road (D'Itri 1992) and allowed the Michigan Department of Transportation to more optimally use CMA. In a different application, acetates can also be used to pre-wet salts, which increases the effectiveness of the salt (MDOT and Tetra Tech 2006).

A summary of acetate-based deicers is shown in Table 1 below.

Table 1. Summary of information on acetates (modified from Fay et al. 2015).

Form	Application Rate	Cost*	Effectiveness
Sodium Acetate	Near 32° F (thin ice): 190-320 lbs/lane-mile. 10° F (1" ice): 600-1500 lbs/lane-mile	\$1000-\$1500 per ton or \$95-\$240 per lane mile	Excellent at melting. Works more quickly and at lower temperatures than NaCl
CMA	250-400 lbs/lane-mile	\$600-\$2000 per ton or \$75-\$400 per lane-mile	Similar to NaCl but requires more CMA to achieve similar results. Works more slowly. Not as effective in freezing rain and light traffic
Potassium Acetate	Deicing: 60-80 gal/lane-mile. Anti-icing: 25-60 gal/lane-mile.	\$600-\$1200 per ton or \$192-\$512 per lane-mile**	Activates quickly. Works more quickly than glycol and is less slippery

* Product cost only (does not include labor or other application related costs)

**Assumes density of 10.7 lbs per gallon

Environmental concerns regarding the use of acetates as RSAs include impact to soils, vegetation, aquatic life, and water bodies. Most studies have found or estimated minimal or no environmental impact of acetates when they are used as an anti-icing or deicing agent. For example, Albright (2009) concluded that CMA would cause negligible changes to soil permeability and fertility even at concentrations much higher than those expected in road runoff and there would be no negative impact on vegetation on land or on aquatic organisms. The only environmental threat, according to Albright (2009), would be BOD in “poorly flushed” waters in which CMA accumulates. Similarly, Baltrenas and Kazlauskiene (2009) stated that calcium acetate and magnesium acetate do not affect water bodies and do not build up over time and that the calcium and magnesium can improve both soil structure and fertility. The Transportation Research Board (1991) stated that CMA is likely to have no adverse effect on humans and few negative environmental impacts. CMA produced from alternative sources, such as municipal solid waste, however, could cause contamination and introduce other problems.

Other studies have found, however, that there could be some environmental impacts. For example, at high concentrations, CMA could affect certain kinds of algae and it could free

aluminum and iron ions from the soil. The calcium and magnesium ions, however, when released through microbial degradation, could help neutralize acid rain (Boice 1986). The Minnesota Stormwater Manual (2018) also states that acetates would characteristically be absorbed by the soil but if they made it to the groundwater, they would be mobile, and they could impact surface waters. Small ponds and slow moving waters are the most likely water bodies to be impacted by acetates, especially from sodium acetate and potassium acetate, which are more mobile. Bang and Johnston (1998) noted that CMA may increase water hardness but that these ions tend to precipitate, which reduces the risk of groundwater contamination. Others, however, have reached different conclusions. For example, Ihs and Gustafson (1996) stated that CMA infiltration to groundwater can be significant and these substances should not be placed near groundwater. D'Itri (1992) found that CMA did not mobilize metal ions in the soil. In fact, it decreased the mobility of some.

Fay and Muthumani (2017) stated that the biggest environmental concern of acetates is BOD. Also, the Western Transportation Institute (2017) found that, in general, non-chloride deicers can temporarily impact BOD but will have limited or no long-term impact on water quality and aquatic species. If an acetate-based product were to have a high BOD and it was used frequently it could, however, have a greater environmental impact for an extended period. Ihs and Gustafson (1996) stated that the oxygen demand and decomposition of CMA is strongly dependent on temperature and, at low temperatures, CMA may last long enough to be carried to receiving water bodies. D'Itri (1992) found that CMA biodegradation in a soil was complete when temperatures were between 10 and 20°C (50 and 68 °F) but results were variable when temperatures were near 2 °C (35 °F). BOD due to acetate road application may also impact wastewater treatment plants (WWTP). Rabideau et al. (1987) found that if CMA were to replace chloride deicers in whole or in part, it would have significant impacts on WWTPs in Buffalo, NY due to increased aeration requirements (caused by the increased in BOD) and increased sludge handling.

A table (in modified form) from McKenney (2015) that summarizes negative environmental impacts of CMA (and, for comparison, sodium, calcium, and magnesium chlorides) on surface water, groundwater, soil, vegetation, and other aspects is shown in Table 2.

For studies that have investigated specific environmental impacts of BOD and other issues, see the “Environmental Impact” section later in this report.

Table 2. Negative environmental impact of CMA compared to conventional deicers (modified from McKenney 2015).

Deicer Environmental Impact on:	Calcium Magnesium Acetate (CMA)	Sodium Chloride	Calcium Chloride	Magnesium Chloride
Soils	Ca and Mg ions may exchange with metals in soil, which may release metals. Ca and Mg improve soil structure	Na ions can bind to soil, break down soil, and decrease permeability. Cl may form complexes with metals, increasing metal mobility	Cl may form complexes with metals, increasing metal mobility. Ca improves soil structure	Cl may form complexes with metals, increasing metal mobility. Mg improves soil structure.
Groundwater	Metals have potential to contaminate groundwater	Elevated chloride levels in groundwater	Metals have potential to contaminate groundwater	Metals have potential to contaminate groundwater
Surface Water	BOD can decrease oxygen levels in water, especially in lower waters of stratified bodies.	Elevated chloride levels, especially in small water bodies with high residence times near heavily salted areas. Can cause stratification and anoxia in bottom waters.	Elevated chloride levels, especially in small water bodies with high residence times near heavily salted areas. Can cause stratification and anoxia in bottom waters.	Elevated chloride levels, especially in small water bodies with high residence times near heavily salted areas. Can cause stratification and anoxia in bottom waters.
Vegetation	Little impact. Osmotic stress can occur at high concentrations.	Negative impact through traffic spray, osmotic stress, and nutrient imbalance. May influence spread of salt-tolerant non-native species	Osmotic stress and leaf scorch	Osmotic stress and leaf scorch
Wildlife	Little or no impact	Linked to salt poisoning in birds	Little or no impact	Little or no impact
Vehicles and Highway Structures	Increases conductivity which can increase corrosion. Less impact than chlorides	Initiates and accelerates corrosion of exposed metals. Exacerbates scaling	Similar to sodium chloride	Similar to sodium chloride. Cement paste deterioration due to reactions with Mg

Formate-Based Alternatives

Formates, like acetates, are a potential non-chloride based organic alternative to road salt. They have been researched much less than acetates and, therefore, there is much less available literature corresponding to the use of formates as an RSA. Like acetates, their main advantage is

that they are not as corrosive as road salts (Baltrenas and Kazlauskiene 2009) and they can help reduce dependence on chloride-based products.

Common forms are sodium formate and potassium formate, which are commonly used at airports for deicing airplanes. Formates are also corrosive to galvanized steel and damage concrete and asphalt but their main disadvantage is high cost.

With regards to environmental impacts, sodium formate can have some of the same negative environmental impacts as sodium chloride due to the release of the sodium ion (D'Itri 1992). Formate, like acetate, can increase water turbidity, hardness, and alkalinity. Formates will breakdown in topsoil, which can have a positive impact on plants at low concentrations but would be harmful at high concentrations.

Formates degrade in water and have a high BOD, which is more of a concern during spring runoff and warm weather (Fay and Muthumani 2017). BOD may be temporarily impacted but if the BOD and application rates are high, it could have a longer impact (Western Transportation Institute 2017).

A summary of formate-based RSAs is shown in Table 3 below.

Table 3. Summary of formate-based road salt alternatives (Modified from Fay et al. 2015).

Form	Application Rate	Cost	Effectiveness
Sodium Formate	Near 32° F (thin ice): 125-250 lbs/lane-mile. 10°	\$200-\$350 per ton or \$12-\$44 per lane mile (near 32° F, thin ice) \$40-\$175 per lane mile (10 °F, 1" ice)	Excellent at melting. Works more quickly and at lower temperatures than NaCl
Potassium Formate	F (1" ice): 400-1000 lbs/lane-mile	\$1000-\$1600 per ton or \$62-\$200 per lane mile (near 32o F, thin ice) \$200-\$800 per lane mile (10 oF, 1" ice)	Similar to NaCl but requires more CMA to achieve similar results. Works more slowly. Not as effective in freezing rain and light traffic

Glycol and glycerol are other organic, non-chloride based deicers that deice well and are typically used at airports. Both glycol and glycerol, which is a byproduct of biodiesel production, are not corrosive to steel and exert BOD when they break down in the environment (Fay and Muthumani 2017, Fortin et al 2014, Western Transportation Institute 2017). These products may be a carcinogen to plants, although the corresponding observations may have been influenced by airport sites that experienced high concentrations and high frequency of use. They can also negatively impact asphalt and concrete.

Overall, glycerin is less toxic than chloride, but in some situations they may affect plant cell metabolism, the functioning of enzymes, and fish fertility among other environmental impacts (Fay and Muthumani 2017).

Like the previous organic deicers discussed, these products are more expensive than chloride-based deicers and exert BOD in aquatic environments. The impact of BOD is not expected to be long-term, however, if a product has a high BOD and is used a lot, the BOD impact could exist for longer periods.

A summary of glycol and glycerol deicers is shown in Table 4 below.

Table 4. Summary of glycol and glycerol deicers (Modified from Fay et al. 2015).

Form	Application Rate	Cost	Effectiveness
Ethylene Glycol	50-2000 gal/lane-mile	\$14-\$40 per gallon or \$700-\$80,000 per lane mile	Very effective at deicing
Propylene Glycol		\$10-\$20 per gallon or \$500-\$40,000 per lane mile	
Glycerin	Varies depending on blend ratio. Typically used as an additive	\$10-\$30 per gallon	Used as ice inhibiting additive. Also provides anti-caking effect. Less expensive than glycols.

Succinate-Based Alternatives

Succinate, or succinic acid, is a dicarboxylic acid that is used in the food and pharmaceutical industries. Succinate salts exist in nature and can be produced from fermentation,

corn processing, and other processes. With regards to deicing, the most effective deicer has been potassium succinate (Fay and Muthumani 2017). Like the other organic deicers previously discussed, succinate is not corrosive to steel. It also is not corrosive to aluminum and causes no (or minimal) spalling of concrete (Fay and Muthumani 2017). In fact, when mixed with salt brine at 2% it reduced the corrosivity of the brine by 40%. Succinate BOD values are similar to values for acetate and formate and, like those materials, dissolved oxygen in receiving water bodies may temporarily be affected. Long-term impact is not expected unless application rates are high (Western Transportation Institute 2017).

A company, BioAmber, is working on producing a commercial potassium succinate deicer (Fay and Muthumani 2017). Because product manufacturing is not full-scale, the price of commercial potassium succinate has not yet been determined but BioAmber estimated that it could be similar to the cost of formate based deicers (Western Transportation Institute 2017). Fortin et al. (2014) has estimated costs could be up to \$75 per lane-mile and \$2.50 per gallon.

A summary table of the above RSAs and, for comparison, chlorides, is shown below in Table 5. Table 6 lists more detailed environmental impacts of some RSAs. Other literature that contains information similar to that discussed in this section and is related to general environmental impacts of RSAs include Fritzsche (1992), Fischel (2001), Ramakrishna et al. (2005), Fay and Shi (2012), and Fortin et al. (2014), among others.

Table 5. Summary of deicers (modified from Western Transportation Institute 2017).

Deicer	Low Temperature Effectiveness (°F)	Relative Cost	Relative Toxicity	Environmental Impacts	Infrastructure Impacts
Chlorides	NaCl: 15 MgCl ₂ : -5 CaCl ₂ : -15	Low	High	Accumulates in the environment. Impacts water quality and aquatic flora and fauna	Pavements and metals
Acetates	Kac: -26 NaAc: 0 CMA: 0	Moderate	Moderate	Moderate BOD	Pavements and galvanized steel
Formates	NaFm: 0 KFm: -20	High	Moderate	Moderate BOD	Pavements and galvanized steel
Glycols	-20	Moderate	High	High BOD	Limited
Succinates	Unknown	Unknown	Moderate	Moderate BOD	None known

Table 6. Environmental impacts of some RSAs (modified from Fay and Shi 2012).

Context Deicer	Soil	Flora	Fauna	Surface & Ground Water	Human
Chloride-based	Cl, Ca, & K can mobilize metals. Na can ↓ permeability & ↑ density. Ca can ↑ permeability & aeration. Mg can ↑ stability & permeability. NaCl can ↓ fertility (which can ↓ plant growth & ↑ erosion)	Can cause leaf singe, browning, senescence, & osmotic stress	Little or no impact when ingested unless at extremely high concentrations. Can cause behavior changes and toxicity in birds and mammals by direct ingestion. > 250 mg/L can cause changes in community structures	Can ↑ hardness. Can cause density stratifications which can cause low DO at depth. Ca & K can mobilize metals. K can cause eutrophication	Skin & eye irritant. Sodium in drinking water can lead to high blood pressure. Can ↑ Cl, Ca, K, and Na concentrations above recommendations. Anti-caking agents may contain cyanide, a known carcinogen
Acetates & Formates	Ca & Mg can mobilize metals, ↑ stability & permeability. CMA degradation can ↑ pH	At low concentrations, acts as fertilizer. High concentrations can cause low yield, leaf browning, & senescence	High BOD can cause anoxic conditions in water. Can promote bacteria and algae growth. Kac & NaAc appear more toxic than CMA	Can leach metals into water. High BOD can lead to low DO. Can ↑ hardness and turbidity	Skin & eye irritant. Ca & Mg can increase water hardness
Glycols	Propylene glycol degradation may ↓ hydraulic conductivity in anaerobic soil	Can inhibit plant growth	Disrupts endocrine. Ingestion of concentrated fluid can cause death	Higher BOD than other deicers.	Disrupts endocrine. Ingestion of concentrated fluid can cause death
Urea	Can ↑ nitrate concentrations	Little information available	Little information available	Can ↑ nitrate. Urea additives can be toxic	Can ↑ nitrate concentrations in water

Other Road Salt Alternatives

The previously discussed RSAs are the most commonly mentioned and researched materials in the literature. Other materials, however, have been suggested and studied. Information on products such as urea, molasses, agricultural byproducts such as beet extract, and various commercial products consisting of different materials or material blends is available in the literature and is summarized below.

Laurinavicius et al. (2011) investigated potential RSAs and listed urea as potentially viable. D'Itri (1992) and Fortin et al. (2014) also discuss urea as a possible RSA. Urea is not corrosive to steel. Urea breaks down in the environment and will not accumulate, although it has a higher BOD than the other organic RSAs and is a fertilizer that contains nitrogen (Fortin et al 2014). According to Fortin et al. (2014), urea is most effective at melting ice from -10 to -5 °C (15 to 23 °F). Urea, however, could be a significant source of nitrogen input to the environment (Findlay and Kelly 2011) and the nitrogen could act as a fertilizer. As a fertilizer, urea could cause algal blooms and other undesirable plant growth in water bodies (D'Itri 1992). Also, ammonia, which has relatively high toxicity to aquatic life, and nitrate formation from urea is of concern (D'Itri 1992) due to soil and water contamination. Laurinavicius et al. (2011) concluded that another material containing nitrate, calcium magnesium nitrate, is a potential RSA, but again, groundwater and soil contamination is a concern due to nitrate.

Molasses, an organic byproduct from sugar production, has also been used as a RSA. A patented molasses product called Geo-Melt in the United States and Safecote in Europe has been used in the United States, Great Britain, and Europe. Baltrenas and Kazlauskiene (2009) state that this product, when added to sodium chloride, helps the solution remain on the road seven times longer and can reduce salt use by 30-50%. It doesn't require any additional salt spreading or applicator equipment, which is convenient for road maintenance crews and municipalities. Adding 10% Geo-Melt to sodium chloride for road deicing increases the cost by 1.5 to two times. Geo-Melt should not be applied to low volume roads because, with low traffic volumes it can form a slippery layer before it mixes with the snow. No mention was made of environmental impact of Geo-Melt but the product does meet all British water quality standards (Baltrenas and Kazlauskiene 2009). McCullough (2010) investigated the use of Geo-Melt and found that users

of the product felt it didn't last long enough on the road surface and, therefore, always required salt application in addition to Geo-Melt.

Harris et al. (1965) investigated low corrosivity deicers for airports and determined that the prime candidate was a mix of 75% tri-potassium phosphate and 25% formamide. Field testing was recommended as was further investigation into the effect the mixture had on concrete spalling. No other information on this mix was found in the literature.

Johnston and Huft (1992) suggested that mixtures of sodium salts and fatty acids with low molecular weights could be attractive RSAs. Advantages include the materials being non-toxic, non or only mildly corrosive, and biodegradable. Listed disadvantages include the cost and the release of sodium ions.

Jungwirth et al. (2014) developed and tested locally sourced brine alternatives for anti-icing winter roads in Alaska. The most successful mixes contained 2% potassium succinate, potassium acetate, or urea and corrosion inhibitors (potassium gluconate and sodium metasilicate). While most mixes lost their effectiveness over time due to evaporation, two mixes that contained urea and an organic proprietary product called Boost, increased their effectiveness as time elapsed. The successful mixes were high-performing anti-icers with low corrosivity compared to conventional deicers and were made with byproducts from local distilleries or breweries.

In a report that summarized the experiences of the Michigan Department of Transportation's use of an agricultural (primarily from corn processing) byproduct based anti-icing agent in southwest lower Michigan from 1999 to 2002, Kahl (2002) noted that some drivers thought that, due to its black color, the product used was black ice that had formed on the road surface. The agricultural byproducts were used as anti-icers and were initially applied at a rate of 35 gallons per lane-mile (~\$30/lane-mile). Results showed these anti-icing practices maintained bare pavement longer, that salt use was reduced by 61%, and that the use of pure CMA with no salt would have cost \$120/lane-mile. The study recommended that liquid agricultural byproducts be used as anti-icing agents prior to snowfall and the onset of ice formation, not as deicers.

In another study that investigated the use of bio-based RSAs, Nazari et al. (2016) developed a product that was designed to be environmentally friendly, contained no metals, and

could be derived from an eco-friendly and cost-effective process. Locally sourced agricultural materials were mixed with 23% (by weight) salt brine and commercial additives that had little or no toxicity and the mixes were tested for their ice-melting capacity, ice-penetration rate, ability to protect asphalt and concrete, impact on friction coefficient of iced asphalt pavement, and anti-corrosion performance. A 23% by weight salt brine was used as the control. The main criteria for choosing the best performing anti-icer were the ice-melting capacity and the ability to increase the friction coefficient of iced asphalt pavement.

The top performing mix was a water-based solution made of 3% (by weight) of sugar beet extract, 0.67% sodium metasilicate, and 23% sodium chloride. This mix had a high ice-melting capacity and ability to increase the friction coefficient of iced asphalt at 25° F. This mix also had a decent ice-penetration rate and low impact on Portland cement mortar scaling. It also had little impact on asphalt binder.

In his literature review, Albright (2009) discussed another agricultural based product, Ice Ban (or Magic Minus Zero). According to Albright (2009), Ice Ban was found to be an effective prewetting agent. Compared to salt it melted ice more quickly, penetrated more deeply, and was effective at lower temperatures than salt alone. The product has high concentrations of phosphorus and, although this phosphorus initially did not appear to be bioavailable, it was subsequently released through microbial action.

McCullough (2010) gave a more thorough summary of Ice Ban and its performance as an anti-icer and deicer. That investigation reported that Ice Ban melted more ice than magnesium chloride at all temperatures tested and it also melted ice more quickly. Furthermore, as the temperature dropped, all products became less effective at melting ice, but this effect was less for Ice Ban. Ice Ban melted as much or more ice than magnesium chloride even when Ice Ban was applied at temperatures 5.5 °C (10 °F) colder than magnesium chloride. Findings from McCullough (2010) include:

1. Ice Ban penetrated ice more quickly and deeper than magnesium chloride,
2. Ice Ban did not appear to be corrosive to metals or asphalt,
3. Friction test results after Ice Ban application on asphalt and concrete pavements had results similar to wet pavement results,

4. Dried Ice Ban on pavement did not decrease the skid resistance of asphalt but with concrete pavement skid resistance decreased slightly but remained within acceptable safety limits,
5. Field tests showed Ice Ban provided equal or better performance in all applications except one. That application was in Nebraska when Ice Ban was sprayed in a freezing rain (no liquid application is recommended, however, during a freezing rain),
6. Field tests confirmed previous lab experimental results that showed Ice Ban melts more ice more quickly than magnesium chloride,
7. Field tests confirmed previous lab experimental results that showed Ice Ban is less corrosive than salt, and
8. Salt that is pre-wet with Ice Ban is more effective than salt alone.

ASCE (1999) is an extensive study that investigated the effectiveness, corrosivity, and ease of use of Ice Ban. This report also notes that Ice Ban provided equal or better performance than control materials in almost every case. The low corrosivity of Ice Ban was also noted as was the fact that, in some cases, Ice Ban lowered corrosion rates to values less than the corrosion rate of pure water. The impact on concrete scaling was similarly low and was much better than the other deicing agents tested (chlorides and acetates). ASCE (1999) does note, however, that users sometimes had difficulty in using and applying Ice Ban due to its high viscosity and presence of solids, both of which lead to clogged nozzles and applicators.

A study by Roosevelt and Fitch (2000) determined that the Virginia DOT should not use Ice Ban M50 as a pre-wetting agent for snow and ice control because of the cost and operational problems associated with its use. The study found that Ice Ban M50 was more effective than a similar amount of magnesium chloride or sodium chloride and it was less stressful to roadside vegetation than any other chemical tested. There were problems, however, with consistency (product composition would change from batch to batch), mold, and product stability. Although the product was not recommended for use, it was recommended to conduct further tests on Ice Ban. McCullough (2010) found that users of Caliber, another commercial product, believed it was cleaner and much improved compared to Ice Ban. No further information on Caliber, however, was found in the literature.

Beet products and byproducts have also been investigated and used as RSAs. For example, in Arkansas, rock salt pretreated with BEET 55C ®, a natural beet product, has been used (McKenney 2015). Also, many states in the mid-west have used "Beet Heet", a sugar beet molasses-based commercial product that increases the ability of rock salt to melt ice (Rhodan and Sanburn 2014). It was estimated that about 175 municipalities in the mid-west were using "Beet Heet" in 2014.

Some RSA products investigated were a combination of previously discussed materials. For example, researchers at the South Dakota Department of Transportation developed Ice Shear TM which is a deicing mixture of equimolar sodium acetate and sodium formate (Bang and Johnston 1998). It has low corrosivity and is an effective deicer (Johnston and Huft 1992). The sodium ion in Ice Shear TM is more soluble than the calcium and magnesium in CMA and both acetate and formate promote bacterial growth. Drawbacks to this product include the fact that Ice Shear TM may deplete oxygen with its high BOD. Bang and Roseland (1989) found that Ice Shear TM decomposed quickly when temperatures were warm but decomposition rates were slow when temperatures were near freezing. Bang and Johnston (1998) evaluated the environmental effects of Ice Shear TM and investigated its behavior in soil and water. Their results indicated that Ice Shear TM chemical compounds are biologically oxidized and that biodegradation during transport is quick enough to dilute the concentrations of organic salts in highway runoff. Thus, concentrations reaching receiving waters were expected to be reduced. The tolerance of aquatic life to the product is high (overall it has a low toxicity) and it causes no harm to lab animals through skin contact or inhalation (Bang and Roseland 1989). Also, Bang and Johnston (1998) found that Ice Shear TM is relatively harmless to Rainbow Trout and roadside vegetation. At low concentrations in soils the product may act as a fertilizer for plants. Lettuce, however, is not tolerant of Ice Shear TM but other broadleaf vegetation is tolerant.

Finally, some reports suggested that methanol may have potential as an RSA (Dunn and Schenk 1980; D'Itri 1992) but methanol has limited effectiveness due to relatively rapid evaporation (D'Itri 1992).

Performance of Road Salt Alternatives

This section reviews literature in which the performance of RSAs has been directly evaluated. Performance with regards to anti-icing, deicing, road friction, corrosivity, and other

performance related issues have been investigated by various authors. Some of the investigations have been performed under controlled laboratory conditions while other studies have been conducted in the field. It is important to note that Muthumani et al. (2014) and Fay and Shi (2011) state that laboratory test results don't always accurately portray performance in the field due to varying temperatures, traffic, wind, differences in snow properties, pavement type, and pavement condition, etc. Because ice melting ability is a key performance issue of any RSA, a summary of the conditions that drive the ice melting process is given immediately below, just before the review of research that has investigated the performance of RSAs.

Wahlin and Klein-Paste (2017) investigated ice melting rates and the corresponding driving forces of deicers. The ability of a material to melt snow or ice is linked to the freezing point of the material. In general, a lower freezing point should mean a greater ability to melt snow and ice. There are, however, large differences in ice melting performance among materials with the same freezing point. These differences appear to be due to differences in the diffusivity of the material in water. The diffusive flux, which is a product of the driving force and diffusivity, correlated well with the rate of ice melt. This indicates that the chemical melting rate was rate-limited by mass diffusion. Fick's Law for diffusion, which is valid for very dilute solutions, however, could not be related to the rate of ice melting. The correlation between diffusive flux and ice melting rate existed only when using methods appropriate for non-ideal solutions in which the chemical potential, not the concentration gradient as used in Fick's Law, is the driving force. This indicates that properties such as chemical potential and activity are better descriptors of ice melting than concentration. With that background information, a review of the performance of RSAs follows.

Performance of Acetates, Formates, Glycol/Glycerol, and Succinates

Fay and Shi (2011) tested chloride-based products, a sodium acetate/sodium formate blend, CMA, and other RSAs for ice melting, ice penetration, ice undercutting, and their impact on freeze-thaw resistance of Portland cement concrete. Road friction following deicer application was also assessed as was corrosivity and thermal properties. Four deicers, all liquids, were identified as best performing. Two of the best performing were magnesium chloride based products, one was an agricultural product (containing magnesium and/or calcium chloride), and one was potassium acetate.

The magnesium chloride and CMA products had the least impact on Portland cement concrete and the potassium acetate product had the coldest effective temperature (followed by a magnesium chloride product). The agricultural product resulted in the lowest friction coefficient on both ice covered and deiced concrete. Acetates were not corrosive to steel but were corrosive to galvanized steel.

Based on the results of Western Transportation Institute (2017), Fay and Akin (2018) investigated the effectiveness of potassium succinate as a RSA. Results indicated that potassium succinate is similar to sodium chloride with regards to improving winter road friction. Potassium succinate, however, was found to be effective only down to -5 °C (23 °F), whereas salt brine was effective down to -10 °C (15 °F). This result is contrary to the value published by the Western Transportation Institute (2017) that lists the effective low temperature for succinates as -20 °C (-4 °F), although this result was based on results of just one test method. The Western Transportation Institute (2017), however, also states that the effective low temperature for succinates is “unknown” due to the uncertainty in the single value of -20 °C (-4 °F) obtained from just one test method. Also, the ice melting rate of potassium succinate was slightly less than that of salt brine. Based on these results, Fay and Akin (2018) suggest that potassium succinate can be a viable RSA at or above -5 °C (23 °F).

Fortin et al. (2014) stated that potassium acetate works at the lowest temperature of all acetates (-28.9 to 0 °C; -20 to 32 °F) while formates and potassium succinate are also effective in this temperature range with formates having the lowest BOD of all the non-chloride deicers. Urea has one of the highest BODs of non-chloride deicers and is effective from -9.4 to 0 °C (15 to 32 °F).

Shi et al. (2009) evaluated the performance of potassium acetate, sodium acetate/formate-blends, and potassium formate as compared to sodium chloride, magnesium chloride, and sand-salt mixes. Lab tests were conducted for ice melting, penetration, and undercutting of ice. Like Fay and Shi (2011) found, the four best performers were liquids. The best performers from high to low rank were 1. A magnesium chloride blend, 2. Apex Meltdown (which is magnesium chloride based), 3. A blend of magnesium chloride and Ice Ban, and 4. CF7 (a commercial product that is potassium acetate based). CF7 had the coldest effective temperature (followed by

Apex Meltdown) but CF7, sodium chloride, and IceSlicer (another commercial product) were the most harmful to concrete.

Wahlin and Klein-Paste investigated the effect of deicing chemicals on the hardness of snow. Dendritic snow was mixed with six different solutions in equilibrium with ice and then compressed. After compression, hardness of the snow was measured. Snow mixed with potassium formate was 25% softer than snow mixed with sodium chloride whereas the urea/snow mix was 20% harder than the sodium chloride/snow mix. This could impact the required amount of chemicals needed to achieve the same hardness, which could impact chemical usage in practical applications.

Performance of Other RSAs

Some studies have investigated the performance of other RSAs such as molasses-based products or agricultural products. For example, Fu et al. (2012) compared two liquid molasses-based materials with salt brine for use as pre-wetting agents and, in separate tests, as anti-icing agents. Pre-wetting involved spraying salt with a solution of the molasses-based product before road application. Pre-wetting the salt helps the salt adhere to the road surface and provides moisture, which salt needs for effective deicing, on cold, dry days. When used as an anti-icing agent, the materials were sprayed directly on the road surface before a snowfall event. Results showed that, when used as pre-wetting agents, none of the materials performed better than the others for 85% of the tests. For the remaining 15% of the tests, results were mixed and there was no consistent material that outperformed the others. When used as anti-icing agents, the two molasses-based products resulted in higher friction values than salt brine. The molasses materials were applied at a lower rate yet outperformed the salt brine by up to 10% with regards to friction.

Muthumani, et al. (2015) compared agriculturally derived products and complex chloride minerals in a laboratory investigation by measuring the degree to which products lower the freezing point of water and improve the ice melting capacity, weaken the ice bond to pavement, improve product longevity on the road surface, prevent ice formation, influence absorbance of sunlight on performance, and reduce corrosion of carbon steel. A best practices manual was developed which included storage guidelines, material handling and loading, storage and mixing,

brine production equipment, application methods and guidelines, anti-icing and direct liquid application, and identified issues with agriculturally derived products.

Hosseini et al (2017) compared the road friction performance of RSAs with conventional brine (a 23% sodium chloride solution). The RSAs tested were Snowmelt (a fully bio-based product), Fusion (a mixture of a bio-based product and chloride salt), and Caliber M1000 (another mix of a bio-based product and chloride). Tests, which were performed in a parking lot in Ontario, Canada, were done at three different application rates (3, 6, and 9 liters per 1000 ft²). The application rate did not affect product performance and treated sections had from 10 to 40% increased friction as compared to untreated control sections. There was no statistical difference, however, in the performance of each of the three products.

Lee et al. (2017) investigated the performance of chloride-based and organic-based materials mixed with chlorides with respect to ice melting and their impact on steel and concrete. Hazardous components of the products were also compared. Field tests showed that most of the organic products met South Korea's corrosion, concrete freeze-thaw, and environmental requirements. Field tests also showed that chloride products were more effective than the organic products except when temperatures were below -17.2 °C (1 °F), at which point no product was effective. Lab test results agreed with field test results in that the organic-based materials were not as effective as chloride products. Liquid organic-based materials were effective deicers, however, but solid organic-based materials were not.

Specific Environmental Impact of RSAs

Although environmental impacts of RSAs were previously discussed, many studies investigated specific impacts of RSAs on water bodies, soil, or organisms. A thorough review of such studies was beyond the scope of the previous sections and would have cluttered the broad discussion in those sections. The work, however, is significant, relevant, and contributes much to the field of RSAs and, as such, is reviewed in this section. A sub-section at the end of this section covers studies that involve modeling the fate of RSAs (mainly CMA) in the environment.

In a general study that investigated three different deicing management techniques to determine possible methods to reduce phosphorus and sediment export to a lake, Albright (2009) investigated the impact of: 1. Abrasives with just enough salt to avoid clumping (the abrasives

were fines with high phosphorus content), 2. Reduced abrasives and increased salt use along with liquid Ice Ban applied in spot applications, and 3. Use of only pre-wetted salt and Ice Ban applied in spot applications. Each of the three strategies were implemented for a period of one to six years and phosphorus and sediment export to the lake was recorded. The third technique (only pre-wetted salt with some Ice Ban application) resulted in the lowest phosphorus and sediment loading. It was noted, however, that chloride concentrations in the lake were increasing and this strategy would likely increase this trend.

Horner (1988) investigated CMA in the environment and recommended that, to prevent DO depletion, CMA not be used in watersheds where road runoff can directly reach receiving water bodies that have less than 100:1 dilution available in the runoff season. Other recommendations and conclusions included:

1. Provide a vegetated drainage course between roads where CMA is applied and receiving water bodies (at least 25% of acetate and butyrate can be removed in five meters of overland flow in vegetation but cation removal cannot be assumed in three meters),
2. Avoid CMA use where coarse soils overlay sensitive aquifers,
3. Avoid CMA use where soils are contaminated with metals because CMA may mobilize metals,
4. Dilute CMA by at least 4-times in order to keep concentrations below water quality standards,
5. CMA can increase soil permeability by up to 20 times depending on the soil type and CMA concentration,
6. Complete CMA degradation occurs in soils within two weeks at 10 and 20 °C (50 to 68 °F) but it takes two to four weeks at 2 °C (35.6 °F),
7. A soil depth of 3 cm was enough to degrade CMA in lab experiments,
8. There can be a lag of up to one week before CMA degradation begins,
9. Plants can withstand 2500 mg/L of CMA in soil but this concentration may be deadly to seedlings if immediately exposed,
10. Spraying or flooding plants with water containing 3000 mg/L of CMA does not affect the plants, and
11. In water, the ultimate BOD is about 75% of the CMA added.

Brenner and Horner (1992) investigated the impact of CMA, with respect to DO, on terrestrial and water ecosystems. Specific goals were to determine the BOD of CMA, determine the effect of temperature on degradation rate, determine if there is any BOD from contaminants in corn-based CMA, compare lab results to field results, and predict impact of full-scale CMA application on the DO of receiving waters and recommend ways to minimize the impact. It was estimated that the high range of CMA in road runoff could be 100 mg/L. This concentration completely depleted DO within two days at 20 °C while 10 mg/L of CMA depleted 4.5 mg/L and 7.0 mg/L of DO for reagent grade CMA and corn-based CMA, respectively. This indicates a larger BOD in corn-based CMA, which could be attributed to butyrate that was present in the corn-based CMA (both CMA products had equal acetate concentrations).

The DO depletion rate was a strong function of temperature and seemingly followed an Arrhenius relationship. Tests were conducted at 2 °C, 6 °C, 10 °C and 20 °C (35.6 °F, 42.8 °F, 50.0 °F and 68.0 °F). The standard, first-order BOD equation did not fit well at low temperatures (2 °C and 6 °C) due to a lag, however, and an alternative log curve was proposed. DO depletion due to CMA was tested in microcosms and in ponds and, although DO depletion occurred, it did not occur to the same extent as in lab experiments. This was likely due to reaeration of the microcosm, which could occur in the field but did not occur in the laboratory. In support of this theory, one pond, when ice covered, experienced a much larger drop in DO with a relatively small inflow of CMA. Recommendations to limit the impact of CMA included no application in areas where receiving water bodies are close to the road, where or when water bodies are ice covered, where CMA will not be diluted, and where there are fish that are sensitive to low DO. No application was also recommended when there may be late spring storms because water temperatures would be higher and this would likely lead to increased degradation rates and greater DO depletion.

To assess for DO depletion, Brenner and Horner (1992) suggested obtaining information on typical winter snowfall, water content of snow, typical amounts of deicer applied, volumes of runoff and runoff patterns after a thaw, distance from roads to receiving water bodies, permeability of soil, volumes of lakes and flow rates of streams, types of fish and spawning habits in nearby water bodies, and knowledge of potential for under-ice DO depletion in water bodies.

Horner and Brenner (1992) focused on environmental impacts of CMA other than BOD and DO depletion and included such topics as CMA transport characteristics, CMA fate in the environment, and its impact on terrestrial and aquatic ecosystems. With respect to soil, the only significant impact found was that CMA increases soil permeability. Lab studies showed potential acetate mobility, but field studies showed only minor evidence of this. CMA can also, through ion exchange with calcium and magnesium, release certain metals from the soil. Field results showed less of a tendency to do so and less consistency than lab studies. Also, the amount of metals released would not cause environmental problems. The authors noted, however, that the actual behavior in roadside soils is not known. At concentrations in the soil that were much higher than those expected in road runoff, no adverse effects were observed except when the high concentration was in the root zone, which killed seedlings.

Through a literature review and limited laboratory studies, Winters et al. (1984) reviewed the toxicity of CMA and found that it is less toxic to rainbow trout and fathead minnows than sodium chloride. A concentration of 5000 mg/L of CMA was found to slightly delay the hatching of rainbow trout but it did not affect the number of eggs hatched. Water flea reproduction was significantly inhibited at 250 mg/L CMA and at 125 mg/L sodium chloride. CMA, however, was found to be more toxic to algae than sodium chloride, but at concentrations under 50 mg/L CMA there was no harmful impact to algae. Overall, sodium chloride did more damage to plants than CMA, although one plant (Russian Olive) was damaged less by sodium chloride. CMA transport through the soil resulted in some removal of iron, aluminum, and nutrients from the soil. At concentrations likely to be generated in deicing applications, CMA may have less of a negative impact on the environment than sodium chloride.

Buteau et al. (1992) performed toxicity tests on Chevron's Ice-B-Gone® Deicer, which was a pellet form of CMA. Acute oral toxicity, sub-chronic toxicity, acute inhalation toxicity, acute dermal toxicity, skin irritation, eye irritation, and skin sensitization tests were performed on rats and the latter two tests were also performed on human volunteers. All tests showed a low level of toxicity. CMA was found to be a slight eye irritant but not a skin irritant or skin sensitizer.

Goldman and Lubnow (1992) investigated the impact of CMA on 10 lakes in northern California with respect to microbial processes. Concentrations of 10 mg/L CMA appeared to

increase chlorophyll in one lake and a concentration of 1 mg/L resulted in statistically higher chlorophyll concentrations in another lake. During the summer, eight out of the ten lakes showed no response to CMA at doses of 0.1, 1.0, and 10 mg/L CMA but bioassays in the late spring and early winter showed slight responses to CMA. Temperature, weather, and the standing stock of microbial populations were the most important variables that influenced algae populations. The authors theorized that increases in water temperature likely increased microbial activity and bacterial mineralization, which, in turn, could have caused the increases in chlorophyll.

Tanner and Wood (1999) investigated the effect of CMA application by the Oregon Department of Transportation on Bear Creek, which is in the Cascade Mountains. The road on which CMA was applied and Bear Creek run parallel to each other for about one mile and the creek is close to the road. At the time of the study, the road received CMA applications several times a year. The creek is small with a flow rate of approximately 4 cfs and it receives runoff directly from the road and shoulder. CMA (96% pure) was mixed with water at a dilution factor of 0.33 by weight and applied at 35 gallons per mile. Streamflow, rainfall precipitation, stream DO, pH, specific conductance, and water temperature were monitored continuously through the winter of 1998-99. No effect was observed with respect to calcium concentration, BOD, or magnesium concentration. BOD was small in water samples taken before CMA application and also in those taken after CMA application. Five-day BOD was 0.1 to 1.5 mg/L and twenty-day BOD was 0.2 to 2.0 mg/L.

Some studies have investigated the impact of RSAs on groundwater quality. For example, Granato et al. (1995) took groundwater samples at test sites next to Route 25 in Massachusetts and analyzed them for major trace chemicals. Groundwater concentrations were higher down gradient from the road as compared to samples taken up gradient. This suggests that the road (and possibly deicing agents) are affecting groundwater quality. One site was particularly impacted by both CMA and road salt. Results suggest, but are not conclusive, that there is potential mobilization due to winter recharge, ion exchange, acidification from road salts, and mineral weathering caused by deicing chemicals. No chemical concentrations exceeded national primary drinking water standards, but chloride and manganese exceeded secondary standards and surface water recommendations were exceeded for chloride, cadmium, and copper.

Hellstén and Nystén (2003) investigated the migration of sodium chloride, calcium chloride, magnesium chloride, CMA, potassium acetate, and potassium formate in aquifers. Potassium formate caused fewer negative impacts to infiltrated water than chloride and acetate. For example, overall results showed more metals were leached from the soils by sodium chloride than by acetate or formate. CMA, however, leached more arsenic, lead, nickel, and zinc than formate and formate leached more molybdenum and chromium than acetate or chloride. Although metals were leached from the soil, only manganese and sodium exceeded European Union drinking water standards.

Jain (2018) used experimental mesocosm to investigate the impact chloride and acetate salts of sodium and calcium had on soil permeability and the retention of copper in the soil. Results showed that chloride-based salts reduced permeability and acetate-based salts had minimal impact on permeability. Acetate-based salts, however, increased organic removal in the soil (as measured by chemical oxygen demand), which may indicate microbial growth. Also, less copper was retained by the soil when salt was included in the runoff.

Hellstén et al. (2005) monitored groundwater chemistry in an aquifer to determine the fate of potassium formate on an aquifer scale. Formate did not enter the saturated zone through the vadose zone because of biodegradation in the topsoil. Thus, no undesirable changes in groundwater chemistry were observed.

Some studies have specifically investigated the impact of deicers on metal mobility in soils. For example, Amrhein et al. (1992) investigated the impact of deicers on metals leaching from roadside soils. Roadside soil samples were taken, placed in 50 mL syringes that acted as columns, and tested under laboratory conditions. Two sets of experiments were performed. In one set, 175 mL of a sodium chloride-CMA solution was run through the columns followed by 105 mL of distilled water (to represent snow melt water). In the second set of experiments, 90 mL of the sodium chloride-CMA solution was run through the soil columns followed by 90 mL of distilled water. Slightly more nickel, chromium, cadmium, lead, and iron were leached when high CMA concentrations were used. This suggests effects of ligand complexation (chloride versus acetate) and competitive ion exchange on metal mobilization. Solubilization of cadmium was mostly controlled by competitive cation exchange and complexation by chloride and acetate. High concentrations of CMA leached more cadmium than sodium chloride leached and more

than dilute salt solutions leached. Concentrations of lead, chromium, nickel, cadmium, and copper in leachate never exceeded drinking water regulations but copper, nickel, and iron concentrations often exceeded limits set to protect freshwater life. Sodium tends to destroy soil structure and increase organic matter mobility, thereby increasing chances of metal mobility. The calcium and magnesium in CMA increases soil permeability and soil structure and reduces the dispersion of organic matter and clays. Horner and Brenner (1992), however, found that there was less tendency and consistency for the release of metals through ion exchange due to CMA application in the field as compared to laboratory studies.

Burkett and Gurr (2004) followed up on a modeling study performed by Scarsbrook et al. (1996; discussed below) by performing field tests. Preliminary field tests indicated that, of the four streams modeled, the smallest stream (baseflow of 1.8 cfs; $0.05 \text{ m}^3/\text{s}$) would need a CMA application of 110 g CMA/m^2 on a nearby road to result in a 20% reduction in DO from saturation. In full-scale field tests an average application rate of 30 g CMA/m^2 was applied to the road and the stream DO never dropped below 90% saturation. There was also no noticeable effect on benthic growth or aquatic invertebrates. No impact was noticed on a beech or tea tree forest or in fernland or grassland. No impact on soil chemistry was observed and increases in phosphorus and exchangeable calcium and magnesium were insignificant with decreases in values being as common as increases. Observed benefits of CMA application over sand/grit application were 1. A reduction in accidents, 2. A decrease in travel time during icy conditions, 3. A 24% increase in friction when CMA was used in place of sand, and 4. Less road closures.

Finally, Rasa et al. (2005) investigated the impact of sodium chloride and potassium formate on the mobility of cadmium in roadside soils. Formate elevated the soil pH, which increased the fraction of cadmium adsorbed onto oxide surfaces to up to 80%. Sodium chloride, however, increased the water soluble fraction of cadmium due to cation competition and the formation of cadmium-chloride complexes.

Deicer Impact on Specific Species

Other studies on the impact of RSAs have investigated their impact on a specific species of plant or organism. For example, Robidoux and Delisle (2001) investigated the environmental impact of sodium formate, CMA, sodium chloride, on three plants (barley, red fescue grass,

Kentucky bluegrass) and an earthworm (*Eisenia fetida*). It was concluded that, overall, the toxicological impact of sodium formate was approximately the same as sodium chloride with both having a larger impact than CMA. The authors noted, however, that due to the fact that more CMA is required for the same deicing effect as sodium chloride or sodium formate, the total impact of using any of the three deicers may be similar.

Joutti et al. (2003) tested sodium chloride, calcium chloride, magnesium chloride, potassium formate, potassium acetate, and CMA with different bioassays. Bioassays were an onion plant root elongation test, a duckweed growth inhibition test, an enzyme inhibition test, and a microbial test (luminescent bacteria, BioTox test). Overall, the organic chemicals were more toxic than the inorganic salts. The rank of toxicity, according to the root elongation and growth inhibition tests, were, from most toxic to least toxic: potassium formate, potassium acetate, CMA, calcium chloride, sodium chloride, and magnesium chloride. CMA could not be tested for the other two bioassays due to the turbidity of the samples.

Dougherty and Smith (2006) investigated the effect of sodium chloride, magnesium chloride, calcium acetate, magnesium acetate, sodium ferrocyanide, and sodium formate on tadpoles of two frog species and one toad species. Some salt compounds negatively affected some tadpoles but the acetates, sodium ferrocyanide, and sodium formate did not. All the concentrations tested were less than 170 mg/L and it was noted that higher concentrations may result in more of an impact.

Hanslin (2011) investigated the impact of CMA, potassium formate, and sodium chloride on the growth and stress responses of tree saplings. Tests were conducted in pots with five species of saplings and different concentrations of the deicers. Increasing concentrations (zero to 13.3 mmol/L soil) caused negative responses but results varied with species. Root growth decreased in two species and leaf biomass decreased in four of the five species. There was no impact on specific leaf area, relative chlorophyll content, height increase, or chlorophyll fluorescence. Overall, the organic deicers did not have less impact on saplings than sodium chloride did during active growth.

Harless et al. (2011) conducted 96 hour acute toxicity tests on larval wood frogs for urea, sodium chloride, magnesium chloride, potassium acetate, calcium chloride, and CMA. Larval were least sensitive to urea, sodium chloride, and magnesium chloride and were most sensitive to

CMA, potassium acetate, and calcium chloride. Toxicity varied greatly and the authors suggested more research be done to determine effects on other species.

Schuler et al. (2017) investigated the effect sodium chloride, magnesium chloride, ClearLane TM and two salts mixed with GeoMelt TM (a proprietary blend containing beet juice) and Magic Salt TM (a proprietary blend of magnesium chloride mixed with a distillation byproduct) had on food webs in experimental aquatic communities. Sodium chloride had little effect but the organic additives reduced DO and, after microbial breakdown, transformed phosphorus to a usable form that resulted in an increase in algae. More algae lead to more zooplankton. Magnesium chloride reduced compositional differences of zooplankton and, at low concentrations, increased the number of amphipods. The authors concluded that RSAs can alter ecosystems.

A summary of the studies that investigated specific environmental impacts of RSAs is given in alphabetical order in Table 7 below.

Table 7. Major conclusions from studies investigating specific environmental impacts of RSAs.

Study Citation	Major Conclusions	Comments
Albright 2009	Pre-wetted salt with Ice Ban was best of three methods to reduce phosphorus export to a lake.	Increase in Cl^- in lake would be accelerated.
Amrhein et al. 1992	CMA can leach metals from soil.	
Brenner & Horner 1992	Should not use CMA where water bodies are close to road, are ice covered, are not diluted, and where fish are sensitive to low DO.	Suggest obtaining additional watershed info such as typical snowfall, water content of snow, soil permeability, etc.
Burkett & Gurr 2004	Field tests showed that road application of 30 g CMA/m ² did not drop BOD of 1.8 cfs stream below 90% saturation. Also had limited or no other environmental impacts.	
Buteau et al. 1992	Ice-B-Gone form of CMA has low level of toxicity.	
Dougherty & Smith 2006	Salts negatively impacted tadpoles but acetates and sodium formate did not.	
Goldman & Lubnow 1992	CMA did not affect 8 of 10 lakes in summer but CMA impacted algae populations in late spring & early winter.	
Granato et al. 1995	Groundwater adjacent to road can be impacted by CMA and road salt.	
Hanslin 2011	During active growth, organic deicers did not have less impact on saplings than sodium chloride.	
Harless et al. 2011	Larval wood frogs were most sensitive to CMA, potassium acetate, CaCl_2 , and were least sensitive to urea, NaCl , and MgCl_2 .	Recommended additional tests on other species.
Hellstén & Nystén 2003	In soil, acetate and formate leach less metals than sodium chloride. Potassium formate causes less negative environmental impact on infiltrated water quality than chloride and acetate.	
Hellstén 2005	Potassium formate was degraded in soil and did not impact groundwater.	
Horner 1988	Should not use CMA where road runoff directly enters water body with dilution factor < 100.	See body of this report for additional conclusions.
Horner and Brenner 1992	CMA increases soil permeability and can release metals.	
Joutti et al. 2003	Organic deicing chemicals are more toxic than non-organic salts	
Rasa et al. 2005	Formate application to soil increased pH, which increased the fraction of cadmium bound to the soil.	
Robidoux & Delisle 2001	Toxicological impact of sodium formate is about equal to sodium chloride and both have larger impact than CMA.	More CMA is needed to get the same deicing effect.
Schuler et al. 2017	Organic deicers can alter ecosystems.	
Tanner & Wood 1999	CMA road application had no impact on a small creek (~4 cfs) that ran parallel to the road.	Investigated impact on BOD and calcium and magnesium concentrations.
Winters et al. 1984	CMA is less toxic to rainbow trout and fathead minnows than NaCl . CMA is more toxic to algae than NaCl but, overall, NaCl is more toxic to plants.	

Environmental Modeling Studies

Some documents reported on model studies to determine the fate and/or impact of roadway deicers in the environment. For example, Lindstrom (2006), who modeled the fate of chloride using a model for the unsaturated groundwater zone and a different model for the

saturated zone, showed that aquifer chloride concentrations will increase and take several decades to decrease even if all chloride use is stopped. The only model studies found in the literature that investigated RSA fate, transport, and/or impact focused on CMA. Since Task 2 of this project involves such a model, a discussion of those studies is included below.

D'Itri (1992) modeled the effect of CMA road applications on surface waters by using rate and empirical coefficients from other studies and assuming that CMA applied to a road surface is either: 1) Transported by runoff to adjacent soil where it begins to degrade, or 2) Stored in a snow bank until it is released into the ground via snowmelt. Direct runoff from the road to receiving water bodies was not considered. The loss of acetate in the soil was modeled using the non-point source model *Simulator for Water Resources in Rural Basins-WQ* (SWRRBWQ). CMA degradation in receiving water bodies was modeled using first order equations for CMA and DO, again with rate constants from previous studies. Model results showed a 70% loss of CMA per 10 feet of runoff distance if CMA is applied directly to the soil or 50% if it is added to the snow pack. D'Itri (1992) plotted percent CMA remaining versus distance from the edge of a two-lane road with shoulder assuming the road runoff is delivered to a 10 foot wide buffer zone. This plot, which is reproduced as Figure 2, shows that CMA is totally degraded after 40 feet. D'Itri (1992) concluded that CMA input to a water body is not likely to be significant unless the water body is close to the road.

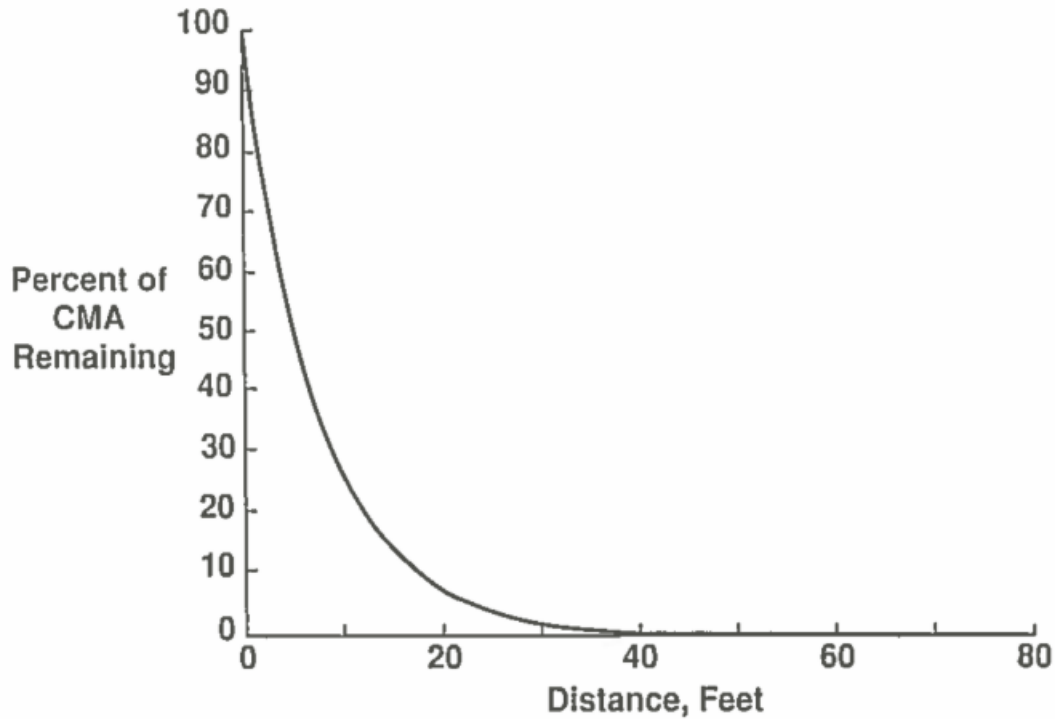


Figure 1. CMA remaining from distance of roadway assuming a two-lane road with shoulder delivers runoff and CMA to a 10 foot wide buffer (D'Itri 1992).

Additionally, the D'Itri (1992) model was conservative in that it ignored flow through the receiving water body, which could bring in more oxygen and, thus, help replenish some of the depleted DO. Model runs were conducted for receiving ponds from 1 to 14 hectares in size and from 2 to 8 meters in depth. Biodegradation was simulated by adjusting the biodegradation rate for a temperature of 20 °C (68 °F) with temperature dependence functions from other studies. Results showed that a 1 acre pond with a depth of 2 m (i.e. the worse case scenario) with an annual loading of 60 g BOD/m² would have a maximum DO deficit of about 2 mg/L. This deficit would occur during the winter when other DO sinks would not be present and the results would not be compounded. D'Itri (1992) also found there would be no significant impact of CMA on lake phytoplankton. This research indicates that, once CMA or other organic alternatives enters the soil, it will have a limited influence upon DO concentration in receiving water bodies.

Scarsbrook et al. (1996) modeled the impact of CMA road application in a national park area in New Zealand. The model, which implemented a Streeter-Phelps DO model for CMA impact on four streams, was used to test six scenarios. Four scenarios used estimates of BOD delivery rates (directly to the streams) and BOD values based on data from two rain events in

1995 to model CMA impact on stream DO levels. The two other scenarios estimated the mass of CMA road application required to cause a 20% drop in stream DO (from saturation) under average flood conditions and under short duration floods.

Model results showed the two largest streams were not at any risk even for the worst case scenario of 100% CMA delivery to the stream in a 5 hour runoff event. But the critical CMA burden (i.e. causing a 20% drop in DO from saturation) for the smallest stream (baseflow of 0.05 m³/s; Burkett and Gurr, 2004) was only 35 g CMA/m². For larger streams, this value was 153 g CMA/m² or above. Also, of the first four scenarios, the smallest streams were significantly impacted under three of the four model scenarios. Scarsbrook et al. (1996) recommended that field investigations be performed in order to estimate the amount of CMA carried to the streams by runoff, the amount lost in the soil, and the resulting DO values in the streams (so that the model could be refined and critical CMA values be reassessed). As previously discussed, Burkett and Gurr (2004) did some additional field tests related to Scarsbrook et al. (1996).

These two modeling studies indicate that the most important impact upon DO concentration would be due to direct runoff into the receiving water body.

Abrasives

Historically, sand has been applied to road surfaces in an attempt to increase friction between the road surface and vehicle tires. Numerous studies, however, have found that any increase in friction caused by sand placed on the road surface is usually quickly diminished due to the particles bouncing off or being blown off the road due to winds induced by passing vehicles (e.g. Salimi et al 2014, Saltan et al. 2014). Dahlen and Vaa (2001), for example, found that sand removal from the road surface can occur after the passing of just 50 vehicles. Nixon (2001) stated that this can occur with “light” vehicle passage, especially in colder weather. Schlup and Ruess (2001) also found this to be true and added that abrasives visible on the road surface can give drivers a false sense of security and cause them to drive too fast for conditions. Finally, Keyser (1973) found that abrasives less than 300 microns in size do almost nothing to increase road friction.

Studies have also found abrasives cost more than salts and cause more negative environmental impacts. For example, Fay and Shi (2012) stated that, in order to attain a

reasonable level of service, the environmental impacts of abrasives are more detrimental than that of salt. Abrasives can exacerbate the stress on roadside vegetation and soil (Fay and Shi 2012) and they are a significant risk to water quality and can threaten aquatic species (Staples et al. 2004). They can also increase water turbidity, clog streams and drains, reduce water body oxygenation, affect food chains, and reduce fish reproduction (Staples et al. 2004). Abrasives less than 10 microns in size can contribute to air pollution (Fay and Shi 2012) and their use can be limited in air quality non-attainment regions (Chang et al. 2002). Schlup and Ruess (2001) concluded that salts have less overall negative impact on the environment than abrasives and that, in a study of three Swiss cities over two winters, the cost of abrasives was six to 10 times more than that of salts. These studies have not considered the long-term impact of chloride on toxicity in fresh water bodies. In the Minneapolis-St. Paul metropolitan area, for example, the U.S. Environmental Protection Agency's chronic (~long-term) chloride toxicity criteria are frequently surpassed, and some water bodies have also surpassed the acute (~short term) toxicity criteria (MPCA, 2014).

Although many studies have found that sand, when applied using conventional methods, does not last long on the road surface, other studies have determined that alternative placement methods can increase the longevity of the impact of abrasives on road surfaces. For example, Nixon (2001) stated that prewetting sand at the tailgate of the truck just prior to placement can help the sand stay on the road and that heating the sand just prior to placement can have the same effect. When the sand is prewet the water, upon freezing, can freeze the particles to the road surface and when abrasives are heated it will cause a small portion of ice to melt, which, upon refreezing, will help adhere the sand to the surface. Ihs (2002) also noted this effect when spraying sand with hot water just prior to distribution.

FinnRA (1991) found that heating the sand to 80 °C (176 °F) prior to placing it in a truck for distribution did not make a statistical difference in friction. They also found that heated abrasives of up to 250 °C (482 °F) increased the coefficient of road friction from 0.22 to 0.37 but the value dropped back to 0.22 in less than 24 hours. Hallberg and Henrysson (1999) found that an application method called Hottstone®, which applied 2 to 5 mm aggregate at greater than 180 °C (356 °F) could increase friction for several days. Another method called Friction Maker™ applied 0 to 8 mm sand with hot water at 90 °C (194 °F) and also increased friction for

several days. The Friction Maker TM was cheaper than applying a salt/sand mix on a per application basis and the Hottstone [®] method was about 30% more expensive than applying a salt/sand mix on a per application basis. Nixon (2001) recommended that field trials be performed in Iowa to test application of abrasives using three different methods. The methods were 1. Pre-wetting the abrasives at the back of the spreader, 2. Heating abrasives to ~180 °C (356 °F) prior to placement, and 3. Mixing abrasives with hot water at ~90 °C (194 °F).

Dahlen and Vaa (2001) found that using heated abrasives or adding warm water to sand can allow the sand to stay on the road even after more than 2000 vehicles pass by and that using warm-wetted sand can reduce overall sand use by 40% to 50%. The most extensive report on using warm and/or wet sand was Perchanok et al. (2010) who reported on the Hot Water Sander, a material spreader developed in Sweden that prewets sand with water at 95 °C (203 °F) as it's being spread on the road. Tests in Scandanavia demonstrated that the sand could stay on the road for more than 10 hours whereas conventionally applied cold and dry sand would be blown away within minutes. Based on tests in Norway, this method is expected to increase the coefficient of friction values by 0.1 and this increase is expected to last two times longer than conventionally applied sand. Overall O&M costs and environmental footprints are also expected to be lower, although the authors also estimated the capital and operating cost over the equipment life span to be 1.5 times conventional equipment.

Perchanok et al. (2010), however, did note that the method has several practical concerns. The listed concerns were:

1. While in operation, a fog cloud formed around the spinner, severely reducing visibility behind the spreader. This is a safety concern.
2. The operational speed is 15 mph (24 km/hr), which is lower than conventional spreaders. This is another safety concern.
3. Sand is discharged at the rear end of the spreader, which means the vehicle could be on an unsanded road.
4. The operating range of the spreader is reduced by 40 % compared to conventional spreaders of the same load capacity, due to the load of water.
5. In order to prevent sand from freezing in unheated stockpiles, conventional sand with approximately 3% added salt was used.

Abrasives can still be an effective means of winter road maintenance. For example, Ihs (2002) stated that Sweden uses crushed stone aggregate (0-5 mm) in urban areas and they also

use sand (0-8 mm) with ~3% salt by weight. On roads with speed limits above 43.5 mph (70 km/hr), the maximum size of abrasive used is 4 mm. Norem (2009) studied traffic accident data from Sweden to determine the effectiveness of winter maintenance options. The study found that salted roads were more accessible than sanded roads, but no conclusions could be drawn nationwide regarding a safety comparison between salted and sanded roads. That is because roads were safer on salted roads in central and southern Sweden but in the cold winters of northern Sweden, the number of accidents was higher on salted roads. Norem (2009) recommended that salting should be avoided in areas and in periods when the frequency of road surface temperatures below -8°C (18°F) exceeds 20%. In these climates, the warm-wetted sand method, Norem (2009) concludes, is likely better for improved friction. Norem (2009) also stated that warm-wetted sand is favorable on roads with traffic volumes less than 2,000 average annual daily traffic and in periods with stable winter conditions.

In an investigation into the impact of sand spreading rates, Salimi et al. (2014) found that sand spread at a low rate (354 lb/lane-mile; 100 kg/lane-km) did not improve friction but sand spread at a medium rate (886 lb/lane-mile; 250 kg/lane-km) and a high rate (1428 lb/lane-mile; 420 kg/lane-km) did improve friction by 23% and 43%, respectively.

Wang et al. (2015) investigated the wear of asphalt pavement due to the application of winter sand and winter salt. By simulating applications and wear, it was determined that sand removed bitumen from the pavement and polished the aggregate, which reduced road friction of the bare pavement over the long-term. Salt only impacted the bitumen on the surface of aggregate and the aggregates were only minimally polished. Thus, the salt treated specimens had a higher friction coefficient than the sand treated specimens.

Finally, Saltan et al. (2014) evaluated a new machine, the Ice Melter Experiment Mechanism (IMEM), that evaluated the impact abrasives have on snow or ice surfaces. The IMEM measures the amount of ice melted as the pressure from an experimental wheel is rotated over abrasives on the ice surface. As the wheel rolls over abrasive particles, it pushes them into the ice, which can melt a portion of the ice. The IMEM was used to evaluate a conventional limestone sand and, for comparison, a new abrasive, which was a pumice waste from the Isparta-Karakaya region of Turkey. The limestone sand performed better in that it melted more ice. At wheel loads of 3, 4, 5, and 6 kg, the sand melted 93%, 105%, 59%, and 48% more ice,

respectively. The sand, however, was removed from the ice surface by the simulated traffic. Although the pumice melted less ice, once broken into small pieces by the wheel, it remained on the ice surface where it had a longer impact on road friction. Saltan et al. (2014) suggested that, since pumice is used as a fertilizer, rain runoff containing pumice may be beneficial to roadside vegetation. It should be noted, however, that it would also likely add to nutrient loads, which are a main target of most stormwater management plans.

Pavement Innovations

To prevent ice formation on roads and melt or otherwise remove snow and ice from road surfaces, researchers have looked beyond what can be applied to the road surface to what can be done to improve pavement designs to achieve this objective. Most of the research has focused on the following four innovations: 1. Adding materials to the pavement mix design so the pavement can be more effectively heated, 2. Adding deicing agents to the mix design, which are released over time and aid in deicing, 3. Adding pipes to the pavement cross-section so that the pipes can be heated, often by warm liquid moving through them, which can melt snow and ice on the pavement surface, and 4. Applying a hydrophobic coating to the surface of the pavement in order to reduce ice adhesion strengths. These, and one other study which investigated making asphalt with a polyurethane binder instead of conventional asphalt, are reviewed below.

Pavement Heating by Adding to the Mix Design

Yang et al. (2012) investigated placing manufactured carbon fiber tape in concrete sidewalks to heat the tape with electricity. The system was effective in melting snow and ice on the surface. With an electricity cost of \$0.20/kW-hr, the average cost of heating the pavement when the air temperature was -11 °C (11.5 °F) was \$0.0292/m²-cm. Units are per square meter of pavement area and per centimeter of accumulated snow depth. Costs would increase with colder temperatures and greater wind chill, but the authors concluded that the method could be viable for bridge decks, parking lots, and sections of road that are susceptible to icing.

A similar technique for heating pavement, called electrically conductive concrete, involves adding conductive materials to the pavement mix design. This allows the pavement to be more efficiently heated by an external power source. Typical conductive materials are steel fibers, graphite powder, or carbon particles (Abdualla et al. 2016), among others. Additional

required components include electrodes, a power supply, and temperature sensors. In this design, an electric current applied through electrodes embedded in a conductive layer on top of conventional pavement is used to heat the top layer of pavement and melt snow and ice. The ability of the pavement to melt snow and ice depends on the resistivity of the conductive materials. Values required for deicing are typically less than 1000 ohm-cm (Abdualla et al. 2016). Electrode types reported in the literature include steel, perforated steel, perforated stainless steel, and galvanized iron. A good bond between the pavement and the electrode is also necessary for effective heating.

Abdualla et al. (2016) investigated requirements needed for electrically conductive concrete to be a cost-effective deicer. The underlying conventional pavement layer was 5 cm thick and had grooves on top to promote a good bond with the overlying conductive pavement layer. A 5 cm thick conductive layer with 0.75% (by volume) of 6 mm long carbon fibers provided a resistivity of 50 ohm-cm. There was also an insulating layer underneath the pavement. Tests investigated the ability of the pavement to melt 2.5 cm of snow on the surface. An AC power source of 80 volts and 11 amps was used. Abdualla et al. (2016) recommended using AC power as it enables electrons to find different pathways into the conductive materials, which more evenly distributes heat throughout the conductive layer. The power required to melt the 2.5 cm of snow was 0.54 kW-hour/m² and cost \$0.065/m², which Abdualla et al. (2016) claimed were the lowest values reported in the literature thus far. The low power requirement and associated cost were attributed to the low resistivity of the conductive layer. The authors concluded that the keys to having a well performing, cost-effective electrically conductive layer are low resistivity, electrodes that are bonded well with the conductive layer, and cost-effective thermal insulation. Additional studies investigating electrically conductive pavement are discussed below.

Li et al. (2013) investigated adding carbon nano-fiber polymer as a thermal source (powered by solar energy), a carbon nanotube cement-based thermal conduction layer, and insulating layers to a Portland cement pavement in order to remove snow and ice from the pavement surface. Laboratory and field tests were performed and the system did melt snow and ice on the surface. Based on laboratory test results, the maximum cost of deicing with the system was estimated to be \$0.29/m². With carbon nano-fiber polymer being a relatively new material at

the time of publication, Li et al. (2013) suggested that material costs will likely decrease in the future.

Galao (2014) also investigated carbon nano-fibers in cement but did not incorporate solar power. In these studies, cement paste with carbon nano-fibers ranging from zero to five percent by weight and voltages of 50, 100, and 150 volts were applied. Specimens with 1 or 2% carbon fibers could achieve high temperatures but required 150 volts. Specimens with 5% nano-fibers, casted as shotcrete, could increase temperatures by about 20 °C (36 °F) with only 65 volts. Heating rates were up to 10 °C (18 °F) per minute. Specimen sizes were 0.10 m by 0.10 m and power consumption to raise the middle of the most effective 5% carbon nano-fiber specimens from 20 °C to 30 °C (68 °F to 86 °F) ranged from about 0.0005 kW-hr to 0.0007 kW-hr. With an average cost of \$0.20/kW-hr, the cost to increase the center temperature of the 5% carbon nano-fiber specimens from 20 °C to 30 °C (68 °F to 86 °F) would range from approximately \$0.01 to \$0.014/m². No other information on power consumption was given.

For use at airports, Lai et al. (2014) investigated cement concrete with a steel mesh and carbon fiber heating wires 5 cm below the surface and spaced 10 cm apart. With a power supply of 350 W/m², the design could melt 2.7 cm thick layer of snow in two hours with air temperatures of -3 to -1 °C (26.6 to 30.2 °F). At \$0.20/kW-hr and 350 W/m² for two hours, the estimated cost is \$0.07/m².

Pan et al. (2014) investigated the impact of insulating layers between the bottom of asphalt pavement and the conductive (i.e. heated) layer. In a heated pavement system, the insulating layer causes more heat to transfer to the top of the pavement and melt more snow and ice than without the insulating layer. Three materials were tested to determine which one performed the best as an insulating layer. Those materials were slurry seal, expanded shale, and an unnamed waterproofing material. The waterproofing material had a lower thermal conductivity (0.3081 W/m-°C) than the expanded shale (0.6518 W/m-°C) and slurry seal (1.592 W/m-°C) with increased snow and ice removal.

Wu et al. (2015) investigated using steel fibers, carbon fibers, and steel fiber-graphite together in a concrete mix to increase the conductivity of the concrete for deicing purposes. The optimum mix used 1% steel fiber, 0.4% carbon fiber, and 4% graphite (all by volume). The mix demonstrated low resistivity (322 ohm-cm) and high power density. The temperature increased

8.7 °C (15.7 °F) after 2.5 hours when subject to 27 volts and 21.8 °C (39.2 °F) after two hours when subject to 44 volts. Wu et al. (2015) concluded that this design showed potential for snow melting and/or deicing applications.

Lai et al. (2015) also investigated heating pavement to melt snow and ice but used heating cables installed in the structural layer of the road. The cables were placed on a coarse gravel asphalt in a zig-zag fashion with a fine gravel asphalt layer placed on top. The design is intended for use on bridges and in tunnels and mountain roads and research included laboratory tests, field tests, and a numerical simulation. Results indicated that the design can melt snow and ice with a power input of 200 to 400 W/m² when the air temperature is between -20 and 0 °C (-4 °F and 32 °F). With an average cost of \$0.20/kW-hr, the cost to melt snow in this air temperature range would be \$0.04/m² to \$0.08/m² for every hour of heating. In the study with air temperatures ranging from -7 °C to -11.3 °C (19.4 °F to 11.7 °F), up to five hours were required to raise the pavement surface temperature to values above freezing. A total power cost estimate for the five hours of heating is from \$0.20/m² to \$0.40/m².

In a laboratory setting, Galao et al. (2016) investigated the feasibility of highly conductive carbon fibers in concrete as a self-heating material for ice prevention and melting. It was concluded that with an applied voltage difference of 20 volts, pavements in the field could increase their temperature to above 0 °C (32 °F) when they were initially at -15 °C (5 °F). Power required in the laboratory experiments was 300-500 W/m². Using the \$0.20/kW-hr estimate and assuming heating occurs for five hours (laboratory tests in this study ranged from 3.6 to 8.3 hours of heating), the total power cost would range from \$0.30/m² to \$0.50/m².

Bai et al. (2017) investigated the use of two parallel and horizontal layers of stainless steel fibers within concrete for heating purposes. The concrete mix included graphite, silica fume, and the stainless steel fibers. The following four concrete specimens were tested:

1. Plain concrete,
2. Same as 1 but with a double layer of stainless steel fibers,
3. Same as 2 but with steel fibers in concrete mix, and
4. Same as 2 but with graphite in concrete mix.

The resistivity of the specimens with the double layer of steel fibers was less than 30,000 ohm-cm and was still increasing with time after 56 days. Graphite and steel fibers added to the concrete mix further reduced resistivity to less than 200 ohm-cm and, after three weeks of increasing resistivity, the resistivity began to decrease with time. With this design, a 6 mm layer of ice was melted in 100 minutes with a power input of 800 W/m² at -20 °C (-4 °F). Most of the energy consumed was due to the heating of the concrete, not melting the ice. Also, it was determined that the ambient temperature is the most important factor in determining the time required for deicing.

Another method of heating pavement involves adding particles that absorb microwaves to the pavement mix design. This allows the pavement to be heated by a microwave unit on a passing vehicle that is also equipped to remove snow and ice as discussed below. In this process the ice is not melted because it does not absorb microwaves (Lu et al. 2017) but the pavement is heated, and this weakens the bond between ice and pavement. The weakened bond allows the vehicle, which is equipped with a crusher, to more easily grind and/or crush the ice layer so that it can be removed by a blade or shovel (also on the vehicle), all with less damage to the pavement. A schematic of this process from Gao et al. (2017) is shown in Figure 1 below.

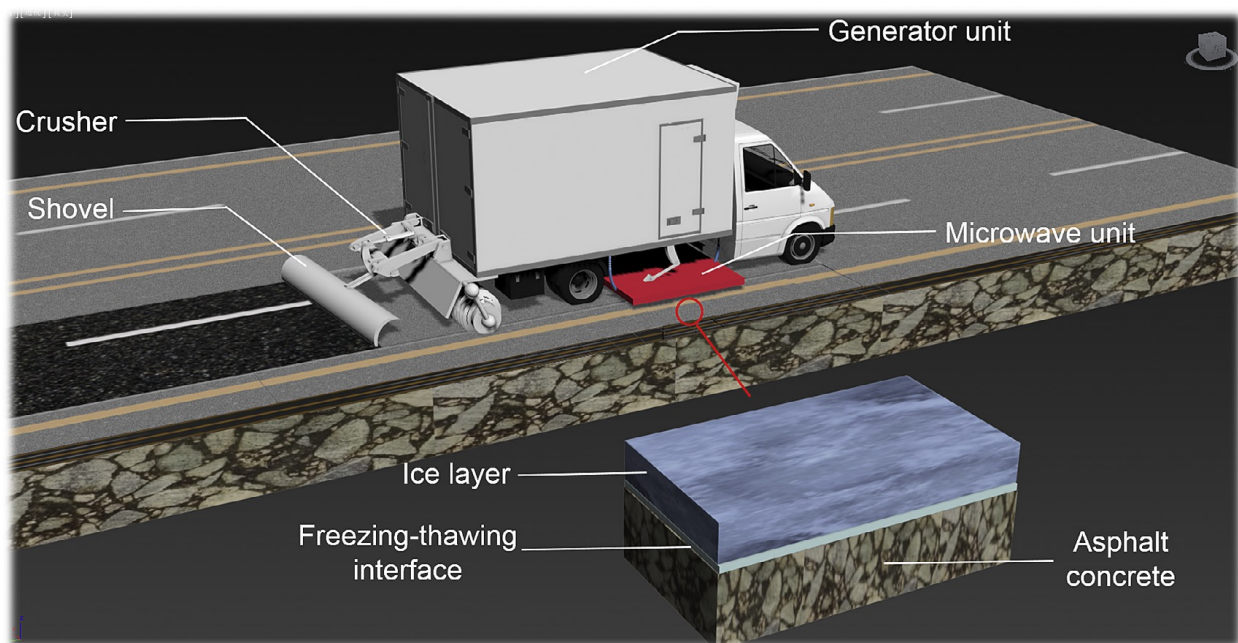


Figure 2. Schematic showing a microwave heating unit for ice removal from asphalt (from Gao et al. 2017).

In an investigation into the properties of an asphalt pavement for microwave ice removal, Wang et al. (2016) used magnetite as an aggregate in the asphalt due to its high microwave adsorption properties. The magnetite microwave heating efficiency was over 6 times that of conventional basalt aggregate. Properties of the asphalt with magnetite aggregate were examined and it was determined that it had adequate properties for use in roads. The actual ice melting ability of the pavement was not tested.

Lu et al. (2017) investigated ice removal from a concrete pavement after it was microwaved. Different microwave frequencies were tested and results showed that using 5.8 GHz as compared to 2.45 GHz decreased the microwave penetration depth from 118 mm to 53 mm and increased the deicing efficiency by more than five times. Adding 10% black iron oxide (by weight) to the pavement mix design increased the microwave efficiency by 1.8 times.

In an attempt to increase the microwave heating efficiency of pavements, Gao et al. (2017) investigated partially replacing conventional aggregate with steel slag. The microwave heating capacity of steel slag was found to be dependent on particle size with sizes of 0.6, 2.36, and 9.5 mm being the most effective. The heating uniformity and thermal conductivity of the pavement was found to decrease with an increase of steel slag content while the surface temperature increased with an increase in steel slag content. As a balance between heating uniformity/thermal conductivity and surface temperature, the authors recommended a steel slag content between 40 and 60% (by volume of total aggregate) for optimum performance. Tests were performed in a laboratory with a 850 W, 2.45 GHz microwave oven. Specimens were heated until a layer of ice that was initially adhered to the specimen surface fell off. No details were given regarding how long specimens had to be microwaved for this to occur, but graphs showing pavement surface temperature as a function of time in the microwave indicate it was less than 10 minutes. Figures in Gao et al. (2017) show specimens that appeared to be about 10 cm in diameter. Actual specimen size, however, was not given and, therefore, an estimate of the cost per pavement surface area is not possible.

Deicers in the Pavement Mix Design

Another innovation in pavement anti-icing and deicing has been the incorporation of anti-icing and/or deicing agents in the pavement itself. These agents help prevent ice formation or aid

in the melting of snow and ice on the pavement surface. After the agents at the pavement surface dissolve into water or are otherwise transported away from the surface, agents from below the surface move to the surface through diffusion (and/or other processes discussed below) and help in the anti-icing, deicing process. Peng et al. (2015), however, showed that chloride anions added to a pavement as anti-icing agents can be retained in the pavement rather than released.

Giuliani et al. (2012) investigated the use of a sodium chloride-based anti-icing filler (at 5.7% by weight) in asphalt and compared results to pavement with conventional calcareous filler. The anti-icing filler caused a delay in frost formation and icing, an acceleration of melting, and it reduced the adhesion strength between the ice and asphalt. After about 20 days about 65% of the original salt content had been released. The authors claimed, however, that the overall durability is expected to be “high” due to diffusion that moves salt from the asphalt body to the surface.

Wright (2013) investigated how the addition of sodium formate and sodium silicate to asphalt mixes impacts asphalt properties such as compactibility, stiffness, fatigue, permanent deformation, and skid resistance as compared to conventional asphalt. Reductions in ice adhesion and freezing point were also investigated. Studies showed that these additives do not negatively impact asphalt properties when subject to standard tests but that they may increase susceptibility to deterioration in the presence of water, which may reduce service life. The additives also reduced the freezing point and the ice adhesion strength. The study also investigated the transfer of the additives to the surface and found that the transfer is dependent on the ambient relative humidity and the number and arrangement of surface voids (chemical transfer is greatest in surface voids). Transfer to the surface was found to typically occur when the relative humidity was greater than 70%, which is the point at which the chemicals absorb water from the atmosphere. With regards to freezing point reduction, at 3 and 5% (by weight) these additives reduced the freezing point to -1.6 and -2.1 °C, respectively.

Liu et al. (2014) studied properties of asphalt made with a commercially available Chinese anti-freeze product that contained chloride salts. The study, which mainly focused on the impact of the anti-freeze on asphalt properties, did find that the anti-snow and ice performance of the pavement increased with the addition, but details were limited.

Wang et al. (2017) also studied asphalt properties but of asphalt containing salt storage aggregate at zero, 5, 10, 15, and 20% (by weight). The salt storage aggregate was made from 90% pure sodium chloride, glass powder, and maifanite powder. To make the aggregate the materials were mixed and milled, heated to 750 °C (1382 °F), crushed, cooled and formed. It was determined that all the asphalt mixes tested could meet standard asphalt specification requirements and that salt migrates to the surface due to osmotic and capillary pressures where it can gradually melt snow and ice.

Liu et al. (2015) studied the salt releasing characteristics of asphalt made with a salt product subject to static and dynamic loading. The salt product was provided by a Chinese company and contained SiO₂, NaCl, CaCl₂, Al₂O₃, CaO, and other unspecified substances. The release of salt depended on the loading cycle. Under static loading salt release plateaued but if dynamic loading was then applied, the salt release rate increased.

A high elastic asphalt pavement (created by adding a high elastic modifier to conventional asphalt) that contained the deicing agent Mafilon (which replaced 70% of the mineral fillers) was investigated by Luo and Yang (2015) for rutting performance, low temperature performance, moisture damage resistance, snowmelt performance, and deicing performance. The high elastic asphalt with deicer performed better than conventional asphalt with regards to rutting and low temperature performance but was slightly weaker in moisture damage resistance. The high elastic asphalt with deicer also had a higher snowmelt speed and a weaker ice bond on the surface. Four hours after snowfall, snow thickness on the elastic pavement was 5 mm while on conventional asphalt it was 22 mm. Also, after the snowfall stopped, an ice layer formed on only half of the Mafilon pavement surface area but it formed over the entire conventional pavement surface area. Finally, at an ambient temperature of -5 °C (23 °F), a saturated sponge did not freeze to the surface of the modified asphalt, which indicates that the deicer prevented the surface from freezing.

Another study by Ma et al. (2016) also investigated the effect of commercial chloride-based, anti-icing additives on pavement properties. Contrary to Luo and Wang (2015), the additives were found to be detrimental to rutting stability, thermal cracking resistance, and moisture susceptibility of the pavement. Polyester fibers, when added to the mix, however, reduced this negative impact to a level such that the pavement performed in a satisfactory

manner. The mix with anti-icing additives and polyester fibers provided some snowmelt and weakened the bond between ice and pavement.

Farnam et al. (2015) investigated the use of two products with high enthalpies of fusion (~130-170 J/g) and freezing temperatures of 2 to 3 °C (35.6 to 37.4 °F) when placed in concrete cement. The objective of the design was to improve snowmelt and anti-icing properties of the pavement. The high enthalpy of fusion materials store heat which reduces ice and snow on the surface. The two products, paraffin oil (a petroleum product) and methyl laurate (a vegetable product) were tested in two configurations. In the first configuration, the material was placed in lightweight aggregate which was placed in the mortar and, in the second configuration, the material was placed in tubes that were embedded in the mortar. The paraffin oil in the mortar did melt snow and ice and it worked well. The methyl laurate, however, damaged the mortar and didn't release heat due to a reaction with the mortar. When placed in the embedded tubes, both materials worked well. Heat releases were enough to melt 22 to 36 kg of pure ice per cubic meter of mortar on the surface of the pavement at temperatures ranging from approximately -1 °C to -3 °C.

Farnam et al. (2017) followed up their previous work with a second study that used paraffin oil in two ways. One was placing the oil in lightweight aggregate that was used to make concrete and the second was by placing the oil in metal pipes that were embedded in the pavement slab during casting. Both methods showed the ability to melt snow and ice on the pavement surface, but the pipe method released heat more rapidly than the aggregate method and, thus, melted snow and ice more quickly. The authors claimed that results indicated that both methods could reduce or eliminate the need for deicing salts or chemicals, especially in weather conditions that have recently dropped below freezing.

Peng et al. (2015) investigated making Mg-AlCl layered double hydroxide (LDH) from Mg-AlCO₃ and investigated its performance related to deicing. Mg-AlCl(LDH) was more effective than Mg-AlCO₃ (LDH) in decreasing the freezing point of water. At temperatures below the freezing point it can weaken the adhesion forces between the ice and asphalt. As was previously mentioned, tests also showed that chloride anions can be retained in the asphalt and not released into the environment.

Chen et al. (2018a) investigated the performance of anti-freezing asphalt with regards to the adhesion strength between ice and asphalt. In this asphalt mix design, mineral fillers were replaced with anti-freezing fillers that released salt after a snowfall or, more specifically as shown by Wright et al. (2016), under high relative humidity conditions (greater than 60-70%). The anti-freezing filler used consisted of CaO, Al₂O₃, SiO₂, Na₂O, K₂O, Fe₂O₃, and other substances and was used in different specimens to replace 33%, 67%, and 100% of the conventional aggregate (it is not clear if this was by weight or volume). The asphalt was also modified with a styrene butadiene styrene block polymer to improve rheological properties. The released salt helped to melt ice and snow. The technique did not melt all of the snow and ice but it did lower the adhesion strength between ice and pavement by up to 80%. Long-term ice adhesion (simulated by washing and drying cycles), however, greatly increased in strength, indicating that the effective life of the deicing ability of the pavement may be limited.

In a study of railway asphalt, Fang et al. (2017) also added anti-freeze additives to asphalt mix designs and tested asphalt properties. Additives tested included hydrated lime, fly ash, red clay brick powder, Portland cement, and an expansive water sealing agent. In tested mix designs the additives replaced 50% of the conventional fillers. The study found that the expansive agent was not an appropriate filler because moisture damage resistance was considerably reduced. A filler mix of hydrated lime (40%), fly ash (20%), red clay brick powder (20%), and Portland cement (20%) was found to be satisfactory, however, and this mix improved water damage resistance and, the authors claimed, enhanced asphalt anti-freeze ability, although no anti-freezing performance data was provided.

Hydronic Pavements

Another way to provide heat to a pavement in order to melt snow or ice is to embed pipes or tubes in the pavement and heat the pipes either by electricity or by circulating warm liquid through the pipes. Liquids used include brine, oils, and glycol-water, among others (Adl-Zarrabi et al. 2016). With either heating method, heat is transferred to the pavement surface where it can melt snow and ice or prevent the formation of ice. Pavements with such pipes or tubes are, by definition, called hydronic pavements. This section reviews publications regarding research into hydronic pavements.

Wang et al. (2010) investigated variables such as fluid temperature, pavement slope, and idling (or preheating) time on the design and performance of hydronic pavements. Slopes of 9 or 18° allowed melted slurry to drain out of the snow. This weakened the capillary effect in the snow and increased the total snow melt time. Compared to horizontal pavement, slopes of 9 and 18° and increased the time required to melt 27 mm of snow by 25.9% and 53.7%, respectively. These results corresponded to tests in which the pavement was preheated to 11.2 °C (52.2 °F). The authors noted that the impact of slope may be greater without preheating.

Chen et al. (2011) investigated the use of fluids in the pipes of hydronic asphalt pavement. In this investigation, heat was collected in the summer and stored for use in the winter to melt ice. In addition to melting ice in the winter time, the design can help prolong asphalt life because it moderates the temperature of the asphalt and reduces the extreme temperature swings experienced by conventional asphalt. In this study, graphite powder was added to the asphalt mix design to increase the thermal conductivity of the asphalt. Numerical simulations suggested placing the pipes between asphalt layers at a depth of 4 or 10 cm with a spacing between pipes of 18 to 40 cm. In experimental runs, snow melt times were longer than expected – 200 or more minutes to achieve completely bare pavement – but it was demonstrated that 25 °C (77 °F) water in the pipes of a hydronic pavement application can be used to melt snow on the surface of an asphalt pavement.

Adl-Zarrabi et al. (2016) also investigated the impact of hydronic pavement design parameters on pavement snow and ice melting performance. Modeling results showed that if pipe spacing is greater than 20 cm, the time required to melt increases rapidly. Thus, the authors recommended a pipe spacing of less than 20 cm. Also, if the embedded pipe depth is less than 10 cm, the impact of embedded depth is negligible. Pipe spacing had a larger impact on melt performance than pipe depth. In their model, the cost-effectiveness of using solar panels to heat stored fluid was investigated. It was determined that this is not justifiable due to added costs and complexity. Other important design parameters that were not investigated as part of the study included liquid flow rate, size of pipes, and the available amount of solar energy that can be harvested.

Mirzananamadi et al. (2018) also investigated hydronic pavement that used a heating fluid along with the practice of storing summer heat for winter use. Results of a numerical model were

compared to data from a field installation for model validation. Numerical model results indicated that the performance of the system will improve as pipe spacing is decreased, embedded depth of pipe in the pavement is decreased, when larger pipes are used, and when the pavement has lower emissivity. As others have found, the distance between the pipes had the largest impact on snow melt performance.

Through simulation, Liu et al. (2017a) also investigated optimum design of hydronic concrete cement pavement but with electrically heated pipes. Optimum values of pipe spacing and embedded depth were 10 cm and 6 cm, respectively. It was also suggested that power input could be varied depending on if the time required to heat the pavement was important (i.e. high power, short heating time) or if efficiency was important (i.e. low power, longer heating time, but higher efficiency). Liu et al. (2017b) used simulation and laboratory experiments to show that the method could be effective with a power consumption of 100 to 400 W/m as long as the heating pipe spacing is between 10 and 25 cm, the pipe depth is between 6 and 12 cm, and the wind velocity is less than 15 m/s.

Hydrophobic Pavements

Some researchers have investigated the effectiveness of hydrophobic materials used as coatings on asphalt or concrete pavements as a means to reduce ice adhesion strength. For example, Ceylan et al. (2016) sprayed polytetrafluoroethylene (PTFE) in layers on asphalt pavement and found that the ice-repelling performance (as measured by water contact angles) was impacted by the spray time and PTFE dose. The authors concluded that spraying PTFE on asphalt has potential as an ice-repellent surface.

Sobolev et al. (2013) applied superhydrophobic siloxane admixtures to concrete surfaces in order to repel ice. The best water repellent materials (measured by the contact angle) were obtained using polymethyl-hydrogen-siloxane with a small amount of fibers (such as silica fume). The fibers and the extent of the dilution of the emulsion were found to be parameters that greatly influenced the level of hydrophobicity. Diluted emulsions (5% active material) allowed the fiber to produce a hierarchical surface of fibers and aggregates so the material had superhydrophobic properties. When tested, coated mortar specimens had ice shear strengths of about 30 kPa, which was about 10% of value corresponding to uncoated specimens.

Others have, however, found that the ice-repellent performance of hydrophobic surfaces is not long-lasting. Ahlborn and Poehlmann (1976) found that a traffic paint with silicone rubber and a weather proofing material with the same silicone rubber were effective in reducing ice adhesion strengths. They also found, however, that the material was worn off the road surface after 150,000 to 300,000 vehicles drove over the surface. Kulinich et al. (2010) found that the hydrophobic surfaces on pavements are gradually damaged through icing/deicing cycles and that the ice-repellent properties deteriorate over time. It was also determined that the hydrophobic surfaces were less effective during humid conditions due to the condensation of water on the surface, which resulted in much stronger ice adhesion strengths. In a literature review, Chen et al. (2018c) made similar conclusions mostly due to the fact that ice-repelling surfaces are worn off over time due to tire abrasion and that the micro-structure of hydrophobic surfaces are also vulnerable and consumable. Chen et al. (2018c) concluded that hydrophobic surfaces for pavements must still be researched and improved. Thus, although hydrophobic surfaces may have potential as an anti-icing method, the technology appears to still be in the research and development stage and not ready for implementation.

Other Pavement Innovations

The performance of a pavement made with aggregate and polyurethane binder (in place of traditional asphalt binder) with regards to anti-icing and deicing was investigated by Chen et al. (2018b). The polyurethane pavement was compared to the traditional asphalt pavement made with the same aggregate and particle size distribution. The two pavements had similar thermal conductivity values, but the polyurethane pavement had a much higher specific heat capacity. Results indicated the polyurethane pavement can significantly retard the formation of ice on the pavement surface. The pull-off strength and the shear strength at the ice/pavement interface in the polyurethane pavement was about 50 to 55% of that in the conventional asphalt pavement. The authors suggested that polyurethane pavement can provide better anti-icing and deicing performance and increase winter safety as compared to conventional asphalt. No mention, however, was made of the cost.

Observations and Recommendations

The use of road salt in Minnesota has caused chloride concentrations in many lakes, streams, and shallow groundwater bodies to increase to levels that have caused impairment. Similar trends have been observed in other locations within the United States and the world. In an effort to reduce chloride concentrations, research has been performed on road salt alternatives and pavement innovations with the objective of preventing the formation of road ice or melting snow and ice once it is on a roadway. This report is a review of literature associated with such research and is Task 1 of a Legislative-Citizens Committee on Minnesota Resources (LCCMR) 2018 funded project entitled “Investigation of Road Salt Alternatives and Pavement Innovations.” This project seeks to reduce or eliminate the transport of chloride into Minnesota’s lakes, streams, and groundwater. The report reviews previous published research that has investigated the topics of road salt alternatives (RSAs) and pavement innovations, and their environmental impact, with respect to anti-icing and deicing, and pavement friction.

Most potential RSAs are organic based products. Of all the RSAs investigated, the most heavily investigated and reviewed is calcium magnesium acetate (CMA). CMA, however, is not effective at lower temperatures than road salt, and therefore does not offer intrinsic advantages over road salt. Other commonly reported RSAs include other forms of acetate, formate-based products, glycol and glycerol, and succinate-based products. The current trend is to move to potassium acetate, which is effective at lower temperatures than road salt. In general, all of these products have higher monetary costs than road salt, are less corrosive to steel, and have a relatively high BOD. Other RSAs have been investigated and most of those are also organic based. They mostly consist of agricultural byproducts such as molasses, beet juice, corn processing products, and urea, which typically are applied with a chloride-based salt, although at reduced application rates.

Studies that have investigated the performance of RSAs with respect to anti-icing, deicing, or road friction have been reviewed. In general, RSAs are less effective in terms of quantity required than conventional road salts and, if equal performance (as compared to road salt) is desired, a greater amount of RSA must be used. Some studies, however, have found that using RSAs in combination with road salt (as an anti-icer or deicer) can increase salt effectiveness and, therefore, can reduce chloride use.

Due to their organic nature and eventual degradation, a common environmental concern of RSAs is BOD. In fact, some authors state it is the main concern with respect to RSAs. The many studies that have investigated the BOD of RSAs have generally concluded that the depletion of dissolved oxygen caused by RSAs will typically be small unless relatively large amounts of RSAs are transported to a small water body close to the roadway. Warmer temperatures or ice cover on the receiving water body can increase the impact due to faster degradation rates and the prevention of surface reaeration, respectively. Also, the conclusion that there will typically be a relatively small impact on dissolved oxygen has been supported for calcium magnesium acetate by at least two model studies.

Other studies have investigated the toxicological effect of RSAs on specific species of plants, invertebrates, or animals. Although toxicological impact has generally been found to be minimal and most investigators have concluded that organic RSAs have low toxicity, some have found direct negative effects on certain species and have recommended additional research. In particular, Pilgrim (2013) reports that a commercial potassium acetate product (CF-7) is more toxic to fathead minnows and an invertebrate than a number of chloride-based de-icing and anti-icing compounds.

The use of abrasives, such as sand and grit, to increase winter road friction was also reviewed. Although abrasives can cause negative environmental impacts ranging from increased water turbidity, lack of oxygenation, and decreased fish reproduction rates to air pollution, abrasives are still used for winter road maintenance. Small particles, which are the most difficult size to remove from stormwater runoff, likely cause most of the environmental impact but have also been shown to contribute minimally to increased road friction. Sweden uses larger particles (up to 4 and 8 mm diameter), which are easier to remove from stormwater runoff through settling and/or filtration processes. Also, simply placing abrasives on the road surface has been shown to be ineffective due to the fact that most of the abrasive particles either bounce off or are blown off the road relatively quickly. Pretreating the sand with hot water and/or by heating it just prior to road application, however, has been shown to cause an increase in road friction that can last for several days. An improved application of abrasives may be sufficient where speeds are low, such as residential streets and parking lots. This would reduce chloride use substantially.

Most pavement innovations designed with the intention of reducing the need for road salt can be grouped into one of the following four categories: 1. Adding conductive elements to the pavement mix design so the pavement surface can be more efficiently heated, 2. Adding anti-icing or deicing agents to the pavement mix design that are released at the pavement surface over time, 3. Hydronic pavements, which incorporate heating pipes into the cross-section of the pavement, and 4. Hydrophobic pavement coatings to reduce ice adhesion strengths. All have shown potential as a method to reduce dependence on road salts, but no full-scale applications have been documented. One pavement innovation with potential for future research is hydrophobic pavements, which require more research, including an assessment of how well they would work in field applications.

Overall, whether by RSA or pavement innovations, much research has been performed with the intention of ultimately reducing or eliminating the use of road salt. Although many studies have shown potential, further research is needed to fully optimize the implementation of pavement innovations in full-scale, practical applications. RSAs are more expensive and require more mass per road mile than chloride-based products, have high BOD, exhibit some toxicity, and can alter ecosystems. However, they result in clear roads during the winter months, similar to road salt, and they will likely not have long-term impacts as opposed to chloride-based salts. In addition, potassium acetate is currently being deployed for anti-icing at low temperatures, so some RSAs also can improve the level of service provided. Thus, it is our recommendation that the environmental impact and friction enhancement of RSAs, in particular potassium acetate, be further explored.

Although abrasives have been shown to have negative environmental impacts, those impacts can likely be reduced by selecting particles of larger size, which can be removed more easily than smaller particles. Because small particles do nothing to increase road friction, there will likely be no drop in effectiveness. Furthermore, the increase in road friction with pre-treated abrasives (either wetted or heated) has been shown to last for several days. Unlike chemical based RSAs, the abrasives will have little or no impact on BOD, little or no toxicity on aquatic life, and may be able to be collected after the winter and used again the following year. If the use of abrasives and corresponding pre-treatment methods are optimized for use on low speed

locations, effective winter road maintenance on these locations with minimal chemical and biological impact, including the reduction of chloride in the environment, may be possible.

There is no one treatment that will reduce chloride load to our lakes, rivers and groundwater. Some countries in northern climates have successfully reduced their chloride load through the use of road salt alternatives, in improvements across design of pavements and design and placement of roads, bridges, and sidewalks, in optimizing the physical form (liquid or granular) of the material applied, the timing of the material applied, the amount of material applied, the spread pattern of material applied and the chemical make up of the material applied, and finally in improvements in mechanical snow/ice removal equipment. Such efforts would create a more efficient and effective winter maintenance industry.

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ROAD SALT ALTERNATIVES AND PAVEMENT INNOVATIONS

A Literature Review

Project: Investigation of Road Salt Alternatives and
Pavement Innovations

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Introduction

This report is Activity 1 of the Legislative-Citizens Committee on Minnesota Resources (LCCMR) 2018 funded project entitled “Investigation of Road Salt Alternatives and Pavement Innovations.” The objective of the project is to investigate road salt alternatives (RSAs) and pavement innovations to reduce or eliminate the transport of chlorides into Minnesota’s lakes, streams, and groundwater. According to the project work plan, Activity 1 is a review of previous research on road salt alternatives, pavement innovations, and pavement friction.

Previous studies have investigated the performance of RSAs with regards to the prevention of ice formation on the pavement surface (anti-icing), the reduction or elimination of ice or snow cover on the pavement surface (deicing), their environmental impact, their cost, production processes, and various other related topics. To maintain alignment with the focus of the funded project with respect to RSAs, this report focuses on their performance, environmental impact, and cost. With regards to pavement innovations, this report focuses on concrete and asphalt pavement innovations that are intended to enhance anti-icing, deicing, and road friction.

The organization of this report is such that it first introduces and discusses RSAs investigated and reported in the literature. Studies that specifically investigated the performance of RSA with respect to anti-icing, deicing, or road friction follow. Although the previously mentioned sections on RSAs include a general discussion of their environmental impacts such as biochemical oxygen demand (BOD) and corrosivity, some studies focused specifically on the impact of RSAs on specific environmental aspects (e.g. toxicology). These studies are reviewed in a separate section on environmental impact, which also includes a review of studies that have modeled the fate, transport, or impact of RSAs, mainly the BOD of calcium magnesium acetate (CMA) in streams and lakes.

Lastly, previous research on pavement innovations are discussed. This discussion includes a description of the pavement innovation technique and, depending on the study, covers issues such as anti-icing, deicing, road friction, energy requirements, and cost.

Road Salt Alternatives

To minimize the environmental impact of salts, many RSAs have been investigated over the past several decades on the basis of water solubility, their ability to lower the freezing point

of water, corrosiveness, toxicity, cost, environmental impact, and flammability (Boice 1986). This section introduces and discusses these materials, most of which are organic compounds, and covers such issues as their cost, effectiveness, and general environmental impacts. Please note that there is a subsequent section devoted solely to studies that investigated a specific environmental impact of RSAs and that the current section presents a general overview of environmental concerns and findings for each of the RSAs presented.

Before beginning the discussion of RSAs that are intended to melt snow and ice, it is worthwhile to note that research has determined that abrasives (i.e. sand and grit) can be more effective at increasing road friction (Perchanok 2010) and provide longer lasting road friction if the abrasives are pre-wetted as they are placed on the road, heated to ~82 °C (~180 °F) just prior to placement, or mixed with hot water just prior to placement (Nixon 2001). These techniques help more abrasive stay on the road upon placement (i.e. not bounce off) and it helps abrasives stay on the road for a longer period of time because, upon placement without such treatment, a large fraction of the abrasives bounce off the road surface, are blown off by natural winds (D'Itri 1992), or are swept off in 10 to 100 vehicle passages (Nixon 2001).

Concerning the organic RSAs discussed in the literature, much focus has been on acetates-based products, formate-based products, glycol and glycerol, and succinate-based products. A discussion of these RSAs begins immediately below.

Acetate-Based Alternatives

As previously mentioned, one organic RSA is acetate (Boice 1986, Baltrenas and Kazlauskiene 2009), which includes potassium acetate, sodium acetate, and calcium magnesium acetate (CMA) (Fay and Muthumani 2017). Although most of the research has been completed on CMA, potassium acetate is currently favored in cold climates because of its improved level of service, i.e., it will melt snow and ice at lower temperatures than road salt and most other RSAs. The main advantage of acetate-based alternatives is that they are not as corrosive to most metals as salts (Ihs and Gustafson 1996, MDOT and Tetra Tech 2006, Fay and Muthumani 2017) and Ihs and Gustafson (1996) have stated that CMA also causes less freeze/thaw damage to pavements. Acetates are, however, corrosive to galvanized steel and they can cause damage to concrete and asphalt through alkali-silica reactions on aggregates and emulsification of asphalt

binder (Fay and Muthumani 2017). With regards to steel, Baltrenas and Kazlauskiene (2009) found that magnesium acetate was three times less corrosive than calcium chloride and two times less corrosive than magnesium chloride. Boice (1986) found that the corrosiveness (and ice melting ability) of CMA depends on the ratio of calcium to magnesium, with optimum values from three to seven. In one study investigating aluminum corrosion, the potassium acetate corrosion rate was equal to that for chloride, although the corrosion rate for CMA was lower (Levelton Consultants 2008). Levelton Consultants (2008) also pointed out that many studies that have investigated the corrosivity of CMA were done on steel bars submersed in CMA, not of steel bars embedded in concrete exposed to CMA, which would more accurately represent the true exposure process. They also noted that concrete scaling is more dependent on the quality of concrete than on the deicer used.

With regards to cost, acetates are significantly more expensive than chloride-based deicers and, therefore, are mostly used at airports and where steel corrosion is a concern, such as at bridges. In fact, only 10-15% of department of transportations that responded to a survey indicated they use acetate in some way (Fay and Muthumani 2017). Acetates can be up to 20 times more expensive than chloride-based deicers (Boice 1986, Fay and Muthumani 2017) and Albright (2009) found that CMA is still more expensive than salts even when factoring in the cost of corrosion damage caused by salts. The lack of an economic and reliable production method of CMA contributes to the high cost (Boice 1986). Albright (2009) noted, however, that future advances in CMA production could result in a price drop of 20%. In one such method, Jin et al. (2010) converted a vegetable waste product into acetic acid and CMA. Electrodialysis was used to condense CMA from the acetic acid with 22% of the total organic carbon in the vegetable waste being converted to CMA.

In a study that investigated methods with the potential to reduce the total negative impact of deicing by considering the total life-cycle impact, Fitch et al. (2013) showed that CMA has higher total life-cycle environmental impacts than conventional rock salt and preemptive treatment of roads with salt brine and/or CMA. Most of the total life-cycle environmental cost of CMA was due to CMA production, which uses more energy and water and produces more greenhouse gases than chloride-based methods. As previously discussed, it also has a higher BOD.

Another drawback of acetates is that they are less effective than chloride-based deicers (Bang and Johnston 1998). For example, Boice (1986) found that it took 1.65 times the CMA to obtain an equivalent melting power of salt. Others have found or estimated different amounts of CMA are required to equal the effectiveness of chloride-based deicers, but every study has found more CMA (or acetate) is needed. For example, MDOT and Tetra Tech (2006) found that up to two times the amount of CMA was required for equal effectiveness and Fay and Muthumani (2017) stated values ranging from 1.3 to 1.5 times are typical when the temperature is below - 6.7 °C (20° F).

Acetates also work more slowly compared to salts such as sodium chloride, they are less effective in freezing rain, dry snow, and light traffic and they also don't work well when applied to thick accumulations of snow or ice (Fay and Muthumani (2017). Ihs and Gustafson (1996), however, found that, in some cases, the effectiveness of CMA lasted longer than that of sodium chloride.

D'Itri (1992) noted that, in practical applications, powdered CMA was blown off the road surface due to winds (either natural or vehicle induced) and Boice (1986) noted that because CMA is lightweight it cannot penetrate snow and ice. CMA also absorbs moisture and can form sticky conglomerations (Boice 1986). The use of CMA in pellet form prevented winds from blowing the material off the surface of the road (D'Itri 1992) and allowed the Michigan Department of Transportation to more optimally use CMA. In a different application, acetates can also be used to pre-wet salts, which increases the effectiveness of the salt (MDOT and Tetra Tech 2006).

A summary of acetate-based deicers is shown in Table 1 below.

Table 1. Summary of information on acetates (modified from Fay et al. 2015).

Form	Application Rate	Cost*	Effectiveness
Sodium Acetate	Near 32° F (thin ice): 190-320 lbs/lane-mile. 10° F (1" ice): 600-1500 lbs/lane-mile	\$1000-\$1500 per ton or \$95-\$240 per lane mile	Excellent at melting. Works more quickly and at lower temperatures than NaCl
CMA	250-400 lbs/lane-mile	\$600-\$2000 per ton or \$75-\$400 per lane-mile	Similar to NaCl but requires more CMA to achieve similar results. Works more slowly. Not as effective in freezing rain and light traffic
Potassium Acetate	Deicing: 60-80 gal/lane-mile. Anti-icing: 25-60 gal/lane-mile.	\$600-\$1200 per ton or \$192-\$512 per lane-mile**	Activates quickly. Works more quickly than glycol and is less slippery

* Product cost only (does not include labor or other application related costs)

**Assumes density of 10.7 lbs per gallon

Environmental concerns regarding the use of acetates as RSAs include impact to soils, vegetation, aquatic life, and water bodies. Most studies have found or estimated minimal or no environmental impact of acetates when they are used as an anti-icing or deicing agent. For example, Albright (2009) concluded that CMA would cause negligible changes to soil permeability and fertility even at concentrations much higher than those expected in road runoff and there would be no negative impact on vegetation on land or on aquatic organisms. The only environmental threat, according to Albright (2009), would be BOD in “poorly flushed” waters in which CMA accumulates. Similarly, Baltrenas and Kazlauskiene (2009) stated that calcium acetate and magnesium acetate do not affect water bodies and do not build up over time and that the calcium and magnesium can improve both soil structure and fertility. The Transportation Research Board (1991) stated that CMA is likely to have no adverse effect on humans and few negative environmental impacts. CMA produced from alternative sources, such as municipal solid waste, however, could cause contamination and introduce other problems.

Other studies have found, however, that there could be some environmental impacts. For example, at high concentrations, CMA could affect certain kinds of algae and it could free

aluminum and iron ions from the soil. The calcium and magnesium ions, however, when released through microbial degradation, could help neutralize acid rain (Boice 1986). The Minnesota Stormwater Manual (2018) also states that acetates would characteristically be absorbed by the soil but if they made it to the groundwater, they would be mobile, and they could impact surface waters. Small ponds and slow moving waters are the most likely water bodies to be impacted by acetates, especially from sodium acetate and potassium acetate, which are more mobile. Bang and Johnston (1998) noted that CMA may increase water hardness but that these ions tend to precipitate, which reduces the risk of groundwater contamination. Others, however, have reached different conclusions. For example, Ihs and Gustafson (1996) stated that CMA infiltration to groundwater can be significant and these substances should not be placed near groundwater. D'Itri (1992) found that CMA did not mobilize metal ions in the soil. In fact, it decreased the mobility of some.

Fay and Muthumani (2017) stated that the biggest environmental concern of acetates is BOD. Also, the Western Transportation Institute (2017) found that, in general, non-chloride deicers can temporarily impact BOD but will have limited or no long-term impact on water quality and aquatic species. If an acetate-based product were to have a high BOD and it was used frequently it could, however, have a greater environmental impact for an extended period. Ihs and Gustafson (1996) stated that the oxygen demand and decomposition of CMA is strongly dependent on temperature and, at low temperatures, CMA may last long enough to be carried to receiving water bodies. D'Itri (1992) found that CMA biodegradation in a soil was complete when temperatures were between 10 and 20°C (50 and 68 °F) but results were variable when temperatures were near 2 °C (35 °F). BOD due to acetate road application may also impact wastewater treatment plants (WWTP). Rabideau et al. (1987) found that if CMA were to replace chloride deicers in whole or in part, it would have significant impacts on WWTPs in Buffalo, NY due to increased aeration requirements (caused by the increased in BOD) and increased sludge handling.

A table (in modified form) from McKenney (2015) that summarizes negative environmental impacts of CMA (and, for comparison, sodium, calcium, and magnesium chlorides) on surface water, groundwater, soil, vegetation, and other aspects is shown in Table 2.

For studies that have investigated specific environmental impacts of BOD and other issues, see the “Environmental Impact” section later in this report.

Table 2. Negative environmental impact of CMA compared to conventional deicers (modified from McKenney 2015).

Deicer Environmental Impact on:	Calcium Magnesium Acetate (CMA)	Sodium Chloride	Calcium Chloride	Magnesium Chloride
Soils	Ca and Mg ions may exchange with metals in soil, which may release metals. Ca and Mg improve soil structure	Na ions can bind to soil, break down soil, and decrease permeability. Cl may form complexes with metals, increasing metal mobility	Cl may form complexes with metals, increasing metal mobility. Ca improves soil structure	Cl may form complexes with metals, increasing metal mobility. Mg improves soil structure.
Groundwater	Metals have potential to contaminate groundwater	Elevated chloride levels in groundwater	Metals have potential to contaminate groundwater	Metals have potential to contaminate groundwater
Surface Water	BOD can decrease oxygen levels in water, especially in lower waters of stratified bodies.	Elevated chloride levels, especially in small water bodies with high residence times near heavily salted areas. Can cause stratification and anoxia in bottom waters.	Elevated chloride levels, especially in small water bodies with high residence times near heavily salted areas. Can cause stratification and anoxia in bottom waters.	Elevated chloride levels, especially in small water bodies with high residence times near heavily salted areas. Can cause stratification and anoxia in bottom waters.
Vegetation	Little impact. Osmotic stress can occur at high concentrations.	Negative impact through traffic spray, osmotic stress, and nutrient imbalance. May influence spread of salt-tolerant non-native species	Osmotic stress and leaf scorch	Osmotic stress and leaf scorch
Wildlife	Little or no impact	Linked to salt poisoning in birds	Little or no impact	Little or no impact
Vehicles and Highway Structures	Increases conductivity which can increase corrosion. Less impact than chlorides	Initiates and accelerates corrosion of exposed metals. Exacerbates scaling	Similar to sodium chloride	Similar to sodium chloride. Cement paste deterioration due to reactions with Mg

Formate-Based Alternatives

Formates, like acetates, are a potential non-chloride based organic alternative to road salt. They have been researched much less than acetates and, therefore, there is much less available literature corresponding to the use of formates as an RSA. Like acetates, their main advantage is

that they are not as corrosive as road salts (Baltrenas and Kazlauskiene 2009) and they can help reduce dependence on chloride-based products.

Common forms are sodium formate and potassium formate, which are commonly used at airports for deicing airplanes. Formates are also corrosive to galvanized steel and damage concrete and asphalt but their main disadvantage is high cost.

With regards to environmental impacts, sodium formate can have some of the same negative environmental impacts as sodium chloride due to the release of the sodium ion (D'Itri 1992). Formate, like acetate, can increase water turbidity, hardness, and alkalinity. Formates will breakdown in topsoil, which can have a positive impact on plants at low concentrations but would be harmful at high concentrations.

Formates degrade in water and have a high BOD, which is more of a concern during spring runoff and warm weather (Fay and Muthumani 2017). BOD may be temporarily impacted but if the BOD and application rates are high, it could have a longer impact (Western Transportation Institute 2017).

A summary of formate-based RSAs is shown in Table 3 below.

Table 3. Summary of formate-based road salt alternatives (Modified from Fay et al. 2015).

Form	Application Rate	Cost	Effectiveness
Sodium Formate	Near 32° F (thin ice): 125-250 lbs/lane-mile. 10°	\$200-\$350 per ton or \$12-\$44 per lane mile (near 32° F, thin ice) \$40-\$175 per lane mile (10 °F, 1" ice)	Excellent at melting. Works more quickly and at lower temperatures than NaCl
Potassium Formate	F (1" ice): 400-1000 lbs/lane-mile	\$1000-\$1600 per ton or \$62-\$200 per lane mile (near 32o F, thin ice) \$200-\$800 per lane mile (10 oF, 1" ice)	Similar to NaCl but requires more CMA to achieve similar results. Works more slowly. Not as effective in freezing rain and light traffic

Glycol and glycerol are other organic, non-chloride based deicers that deice well and are typically used at airports. Both glycol and glycerol, which is a byproduct of biodiesel production, are not corrosive to steel and exert BOD when they break down in the environment (Fay and Muthumani 2017, Fortin et al 2014, Western Transportation Institute 2017). These products may be a carcinogen to plants, although the corresponding observations may have been influenced by airport sites that experienced high concentrations and high frequency of use. They can also negatively impact asphalt and concrete.

Overall, glycerin is less toxic than chloride, but in some situations they may affect plant cell metabolism, the functioning of enzymes, and fish fertility among other environmental impacts (Fay and Muthumani 2017).

Like the previous organic deicers discussed, these products are more expensive than chloride-based deicers and exert BOD in aquatic environments. The impact of BOD is not expected to be long-term, however, if a product has a high BOD and is used a lot, the BOD impact could exist for longer periods.

A summary of glycol and glycerol deicers is shown in Table 4 below.

Table 4. Summary of glycol and glycerol deicers (Modified from Fay et al. 2015).

Form	Application Rate	Cost	Effectiveness
Ethylene Glycol	50-2000 gal/lane-mile	\$14-\$40 per gallon or \$700-\$80,000 per lane mile	Very effective at deicing
Propylene Glycol		\$10-\$20 per gallon or \$500-\$40,000 per lane mile	
Glycerin	Varies depending on blend ratio. Typically used as an additive	\$10-\$30 per gallon	Used as ice inhibiting additive. Also provides anti-caking effect. Less expensive than glycols.

Succinate-Based Alternatives

Succinate, or succinic acid, is a dicarboxylic acid that is used in the food and pharmaceutical industries. Succinate salts exist in nature and can be produced from fermentation,

corn processing, and other processes. With regards to deicing, the most effective deicer has been potassium succinate (Fay and Muthumani 2017). Like the other organic deicers previously discussed, succinate is not corrosive to steel. It also is not corrosive to aluminum and causes no (or minimal) spalling of concrete (Fay and Muthumani 2017). In fact, when mixed with salt brine at 2% it reduced the corrosivity of the brine by 40%. Succinate BOD values are similar to values for acetate and formate and, like those materials, dissolved oxygen in receiving water bodies may temporarily be affected. Long-term impact is not expected unless application rates are high (Western Transportation Institute 2017).

A company, BioAmber, is working on producing a commercial potassium succinate deicer (Fay and Muthumani 2017). Because product manufacturing is not full-scale, the price of commercial potassium succinate has not yet been determined but BioAmber estimated that it could be similar to the cost of formate based deicers (Western Transportation Institute 2017). Fortin et al. (2014) has estimated costs could be up to \$75 per lane-mile and \$2.50 per gallon.

A summary table of the above RSAs and, for comparison, chlorides, is shown below in Table 5. Table 6 lists more detailed environmental impacts of some RSAs. Other literature that contains information similar to that discussed in this section and is related to general environmental impacts of RSAs include Fritzsche (1992), Fischel (2001), Ramakrishna et al. (2005), Fay and Shi (2012), and Fortin et al. (2014), among others.

Table 5. Summary of deicers (modified from Western Transportation Institute 2017).

Deicer	Low Temperature Effectiveness (°F)	Relative Cost	Relative Toxicity	Environmental Impacts	Infrastructure Impacts
Chlorides	NaCl: 15 MgCl ₂ : -5 CaCl ₂ : -15	Low	High	Accumulates in the environment. Impacts water quality and aquatic flora and fauna	Pavements and metals
Acetates	Kac: -26 NaAc: 0 CMA: 0	Moderate	Moderate	Moderate BOD	Pavements and galvanized steel
Formates	NaFm: 0 KFm: -20	High	Moderate	Moderate BOD	Pavements and galvanized steel
Glycols	-20	Moderate	High	High BOD	Limited
Succinates	Unknown	Unknown	Moderate	Moderate BOD	None known

Table 6. Environmental impacts of some RSAs (modified from Fay and Shi 2012).

Context Deicer	Soil	Flora	Fauna	Surface & Ground Water	Human
Chloride-based	Cl, Ca, & K can mobilize metals. Na can ↓ permeability & ↑ density. Ca can ↑ permeability & aeration. Mg can ↑ stability & permeability. NaCl can ↓ fertility (which can ↓ plant growth & ↑ erosion)	Can cause leaf singe, browning, senescence, & osmotic stress	Little or no impact when ingested unless at extremely high concentrations. Can cause behavior changes and toxicity in birds and mammals by direct ingestion. > 250 mg/L can cause changes in community structures	Can ↑ hardness. Can cause density stratifications which can cause low DO at depth. Ca & K can mobilize metals. K can cause eutrophication	Skin & eye irritant. Sodium in drinking water can lead to high blood pressure. Can ↑ Cl, Ca, K, and Na concentrations above recommendations. Anti-caking agents may contain cyanide, a known carcinogen
Acetates & Formates	Ca & Mg can mobilize metals, ↑ stability & permeability. CMA degradation can ↑ pH	At low concentrations, acts as fertilizer. High concentrations can cause low yield, leaf browning, & senescence	High BOD can cause anoxic conditions in water. Can promote bacteria and algae growth. Kac & NaAc appear more toxic than CMA	Can leach metals into water. High BOD can lead to low DO. Can ↑ hardness and turbidity	Skin & eye irritant. Ca & Mg can increase water hardness
Glycols	Propylene glycol degradation may ↓ hydraulic conductivity in anaerobic soil	Can inhibit plant growth	Disrupts endocrine. Ingestion of concentrated fluid can cause death	Higher BOD than other deicers.	Disrupts endocrine. Ingestion of concentrated fluid can cause death
Urea	Can ↑ nitrate concentrations	Little information available	Little information available	Can ↑ nitrate. Urea additives can be toxic	Can ↑ nitrate concentrations in water

Other Road Salt Alternatives

The previously discussed RSAs are the most commonly mentioned and researched materials in the literature. Other materials, however, have been suggested and studied. Information on products such as urea, molasses, agricultural byproducts such as beet extract, and various commercial products consisting of different materials or material blends is available in the literature and is summarized below.

Laurinavicius et al. (2011) investigated potential RSAs and listed urea as potentially viable. D'Itri (1992) and Fortin et al. (2014) also discuss urea as a possible RSA. Urea is not corrosive to steel. Urea breaks down in the environment and will not accumulate, although it has a higher BOD than the other organic RSAs and is a fertilizer that contains nitrogen (Fortin et al 2014). According to Fortin et al. (2014), urea is most effective at melting ice from -10 to -5 °C (15 to 23 °F). Urea, however, could be a significant source of nitrogen input to the environment (Findlay and Kelly 2011) and the nitrogen could act as a fertilizer. As a fertilizer, urea could cause algal blooms and other undesirable plant growth in water bodies (D'Itri 1992). Also, ammonia, which has relatively high toxicity to aquatic life, and nitrate formation from urea is of concern (D'Itri 1992) due to soil and water contamination. Laurinavicius et al. (2011) concluded that another material containing nitrate, calcium magnesium nitrate, is a potential RSA, but again, groundwater and soil contamination is a concern due to nitrate.

Molasses, an organic byproduct from sugar production, has also been used as a RSA. A patented molasses product called Geo-Melt in the United States and Safecote in Europe has been used in the United States, Great Britain, and Europe. Baltrenas and Kazlauskiene (2009) state that this product, when added to sodium chloride, helps the solution remain on the road seven times longer and can reduce salt use by 30-50%. It doesn't require any additional salt spreading or applicator equipment, which is convenient for road maintenance crews and municipalities. Adding 10% Geo-Melt to sodium chloride for road deicing increases the cost by 1.5 to two times. Geo-Melt should not be applied to low volume roads because, with low traffic volumes it can form a slippery layer before it mixes with the snow. No mention was made of environmental impact of Geo-Melt but the product does meet all British water quality standards (Baltrenas and Kazlauskiene 2009). McCullough (2010) investigated the use of Geo-Melt and found that users

of the product felt it didn't last long enough on the road surface and, therefore, always required salt application in addition to Geo-Melt.

Harris et al. (1965) investigated low corrosivity deicers for airports and determined that the prime candidate was a mix of 75% tri-potassium phosphate and 25% formamide. Field testing was recommended as was further investigation into the effect the mixture had on concrete spalling. No other information on this mix was found in the literature.

Johnston and Huft (1992) suggested that mixtures of sodium salts and fatty acids with low molecular weights could be attractive RSAs. Advantages include the materials being non-toxic, non or only mildly corrosive, and biodegradable. Listed disadvantages include the cost and the release of sodium ions.

Jungwirth et al. (2014) developed and tested locally sourced brine alternatives for anti-icing winter roads in Alaska. The most successful mixes contained 2% potassium succinate, potassium acetate, or urea and corrosion inhibitors (potassium gluconate and sodium metasilicate). While most mixes lost their effectiveness over time due to evaporation, two mixes that contained urea and an organic proprietary product called Boost, increased their effectiveness as time elapsed. The successful mixes were high-performing anti-icers with low corrosivity compared to conventional deicers and were made with byproducts from local distilleries or breweries.

In a report that summarized the experiences of the Michigan Department of Transportation's use of an agricultural (primarily from corn processing) byproduct based anti-icing agent in southwest lower Michigan from 1999 to 2002, Kahl (2002) noted that some drivers thought that, due to its black color, the product used was black ice that had formed on the road surface. The agricultural byproducts were used as anti-icers and were initially applied at a rate of 35 gallons per lane-mile (~\$30/lane-mile). Results showed these anti-icing practices maintained bare pavement longer, that salt use was reduced by 61%, and that the use of pure CMA with no salt would have cost \$120/lane-mile. The study recommended that liquid agricultural byproducts be used as anti-icing agents prior to snowfall and the onset of ice formation, not as deicers.

In another study that investigated the use of bio-based RSAs, Nazari et al. (2016) developed a product that was designed to be environmentally friendly, contained no metals, and

could be derived from an eco-friendly and cost-effective process. Locally sourced agricultural materials were mixed with 23% (by weight) salt brine and commercial additives that had little or no toxicity and the mixes were tested for their ice-melting capacity, ice-penetration rate, ability to protect asphalt and concrete, impact on friction coefficient of iced asphalt pavement, and anti-corrosion performance. A 23% by weight salt brine was used as the control. The main criteria for choosing the best performing anti-icer were the ice-melting capacity and the ability to increase the friction coefficient of iced asphalt pavement.

The top performing mix was a water-based solution made of 3% (by weight) of sugar beet extract, 0.67% sodium metasilicate, and 23% sodium chloride. This mix had a high ice-melting capacity and ability to increase the friction coefficient of iced asphalt at 25° F. This mix also had a decent ice-penetration rate and low impact on Portland cement mortar scaling. It also had little impact on asphalt binder.

In his literature review, Albright (2009) discussed another agricultural based product, Ice Ban (or Magic Minus Zero). According to Albright (2009), Ice Ban was found to be an effective prewetting agent. Compared to salt it melted ice more quickly, penetrated more deeply, and was effective at lower temperatures than salt alone. The product has high concentrations of phosphorus and, although this phosphorus initially did not appear to be bioavailable, it was subsequently released through microbial action.

McCullough (2010) gave a more thorough summary of Ice Ban and its performance as an anti-icer and deicer. That investigation reported that Ice Ban melted more ice than magnesium chloride at all temperatures tested and it also melted ice more quickly. Furthermore, as the temperature dropped, all products became less effective at melting ice, but this effect was less for Ice Ban. Ice Ban melted as much or more ice than magnesium chloride even when Ice Ban was applied at temperatures 5.5 °C (10 °F) colder than magnesium chloride. Findings from McCullough (2010) include:

1. Ice Ban penetrated ice more quickly and deeper than magnesium chloride,
2. Ice Ban did not appear to be corrosive to metals or asphalt,
3. Friction test results after Ice Ban application on asphalt and concrete pavements had results similar to wet pavement results,

4. Dried Ice Ban on pavement did not decrease the skid resistance of asphalt but with concrete pavement skid resistance decreased slightly but remained within acceptable safety limits,
5. Field tests showed Ice Ban provided equal or better performance in all applications except one. That application was in Nebraska when Ice Ban was sprayed in a freezing rain (no liquid application is recommended, however, during a freezing rain),
6. Field tests confirmed previous lab experimental results that showed Ice Ban melts more ice more quickly than magnesium chloride,
7. Field tests confirmed previous lab experimental results that showed Ice Ban is less corrosive than salt, and
8. Salt that is pre-wet with Ice Ban is more effective than salt alone.

ASCE (1999) is an extensive study that investigated the effectiveness, corrosivity, and ease of use of Ice Ban. This report also notes that Ice Ban provided equal or better performance than control materials in almost every case. The low corrosivity of Ice Ban was also noted as was the fact that, in some cases, Ice Ban lowered corrosion rates to values less than the corrosion rate of pure water. The impact on concrete scaling was similarly low and was much better than the other deicing agents tested (chlorides and acetates). ASCE (1999) does note, however, that users sometimes had difficulty in using and applying Ice Ban due to its high viscosity and presence of solids, both of which lead to clogged nozzles and applicators.

A study by Roosevelt and Fitch (2000) determined that the Virginia DOT should not use Ice Ban M50 as a pre-wetting agent for snow and ice control because of the cost and operational problems associated with its use. The study found that Ice Ban M50 was more effective than a similar amount of magnesium chloride or sodium chloride and it was less stressful to roadside vegetation than any other chemical tested. There were problems, however, with consistency (product composition would change from batch to batch), mold, and product stability. Although the product was not recommended for use, it was recommended to conduct further tests on Ice Ban. McCullough (2010) found that users of Caliber, another commercial product, believed it was cleaner and much improved compared to Ice Ban. No further information on Caliber, however, was found in the literature.

Beet products and byproducts have also been investigated and used as RSAs. For example, in Arkansas, rock salt pretreated with BEET 55C ®, a natural beet product, has been used (McKenney 2015). Also, many states in the mid-west have used "Beet Heet", a sugar beet molasses-based commercial product that increases the ability of rock salt to melt ice (Rhodan and Sanburn 2014). It was estimated that about 175 municipalities in the mid-west were using "Beet Heet" in 2014.

Some RSA products investigated were a combination of previously discussed materials. For example, researchers at the South Dakota Department of Transportation developed Ice Shear TM which is a deicing mixture of equimolar sodium acetate and sodium formate (Bang and Johnston 1998). It has low corrosivity and is an effective deicer (Johnston and Huft 1992). The sodium ion in Ice Shear TM is more soluble than the calcium and magnesium in CMA and both acetate and formate promote bacterial growth. Drawbacks to this product include the fact that Ice Shear TM may deplete oxygen with its high BOD. Bang and Roseland (1989) found that Ice Shear TM decomposed quickly when temperatures were warm but decomposition rates were slow when temperatures were near freezing. Bang and Johnston (1998) evaluated the environmental effects of Ice Shear TM and investigated its behavior in soil and water. Their results indicated that Ice Shear TM chemical compounds are biologically oxidized and that biodegradation during transport is quick enough to dilute the concentrations of organic salts in highway runoff. Thus, concentrations reaching receiving waters were expected to be reduced. The tolerance of aquatic life to the product is high (overall it has a low toxicity) and it causes no harm to lab animals through skin contact or inhalation (Bang and Roseland 1989). Also, Bang and Johnston (1998) found that Ice Shear TM is relatively harmless to Rainbow Trout and roadside vegetation. At low concentrations in soils the product may act as a fertilizer for plants. Lettuce, however, is not tolerant of Ice Shear TM but other broadleaf vegetation is tolerant.

Finally, some reports suggested that methanol may have potential as an RSA (Dunn and Schenk 1980; D'Itri 1992) but methanol has limited effectiveness due to relatively rapid evaporation (D'Itri 1992).

Performance of Road Salt Alternatives

This section reviews literature in which the performance of RSAs has been directly evaluated. Performance with regards to anti-icing, deicing, road friction, corrosivity, and other

performance related issues have been investigated by various authors. Some of the investigations have been performed under controlled laboratory conditions while other studies have been conducted in the field. It is important to note that Muthumani et al. (2014) and Fay and Shi (2011) state that laboratory test results don't always accurately portray performance in the field due to varying temperatures, traffic, wind, differences in snow properties, pavement type, and pavement condition, etc. Because ice melting ability is a key performance issue of any RSA, a summary of the conditions that drive the ice melting process is given immediately below, just before the review of research that has investigated the performance of RSAs.

Wahlin and Klein-Paste (2017) investigated ice melting rates and the corresponding driving forces of deicers. The ability of a material to melt snow or ice is linked to the freezing point of the material. In general, a lower freezing point should mean a greater ability to melt snow and ice. There are, however, large differences in ice melting performance among materials with the same freezing point. These differences appear to be due to differences in the diffusivity of the material in water. The diffusive flux, which is a product of the driving force and diffusivity, correlated well with the rate of ice melt. This indicates that the chemical melting rate was rate-limited by mass diffusion. Fick's Law for diffusion, which is valid for very dilute solutions, however, could not be related to the rate of ice melting. The correlation between diffusive flux and ice melting rate existed only when using methods appropriate for non-ideal solutions in which the chemical potential, not the concentration gradient as used in Fick's Law, is the driving force. This indicates that properties such as chemical potential and activity are better descriptors of ice melting than concentration. With that background information, a review of the performance of RSAs follows.

Performance of Acetates, Formates, Glycol/Glycerol, and Succinates

Fay and Shi (2011) tested chloride-based products, a sodium acetate/sodium formate blend, CMA, and other RSAs for ice melting, ice penetration, ice undercutting, and their impact on freeze-thaw resistance of Portland cement concrete. Road friction following deicer application was also assessed as was corrosivity and thermal properties. Four deicers, all liquids, were identified as best performing. Two of the best performing were magnesium chloride based products, one was an agricultural product (containing magnesium and/or calcium chloride), and one was potassium acetate.

The magnesium chloride and CMA products had the least impact on Portland cement concrete and the potassium acetate product had the coldest effective temperature (followed by a magnesium chloride product). The agricultural product resulted in the lowest friction coefficient on both ice covered and deiced concrete. Acetates were not corrosive to steel but were corrosive to galvanized steel.

Based on the results of Western Transportation Institute (2017), Fay and Akin (2018) investigated the effectiveness of potassium succinate as a RSA. Results indicated that potassium succinate is similar to sodium chloride with regards to improving winter road friction. Potassium succinate, however, was found to be effective only down to -5°C (23°F), whereas salt brine was effective down to -10°C (15°F). This result is contrary to the value published by the Western Transportation Institute (2017) that lists the effective low temperature for succinates as -20°C (-4°F), although this result was based on results of just one test method. The Western Transportation Institute (2017), however, also states that the effective low temperature for succinates is “unknown” due to the uncertainty in the single value of -20°C (-4°F) obtained from just one test method. Also, the ice melting rate of potassium succinate was slightly less than that of salt brine. Based on these results, Fay and Akin (2018) suggest that potassium succinate can be a viable RSA at or above -5°C (23°F).

Fortin et al. (2014) stated that potassium acetate works at the lowest temperature of all acetates (-28.9 to 0°C ; -20 to 32°F) while formates and potassium succinate are also effective in this temperature range with formates having the lowest BOD of all the non-chloride deicers. Urea has one of the highest BODs of non-chloride deicers and is effective from -9.4 to 0°C (15 to 32°F).

Shi et al. (2009) evaluated the performance of potassium acetate, sodium acetate/formate-blends, and potassium formate as compared to sodium chloride, magnesium chloride, and sand-salt mixes. Lab tests were conducted for ice melting, penetration, and undercutting of ice. Like Fay and Shi (2011) found, the four best performers were liquids. The best performers from high to low rank were 1. A magnesium chloride blend, 2. Apex Meltdown (which is magnesium chloride based), 3. A blend of magnesium chloride and Ice Ban, and 4. CF7 (a commercial product that is potassium acetate based). CF7 had the coldest effective temperature (followed by

Apex Meltdown) but CF7, sodium chloride, and IceSlicer (another commercial product) were the most harmful to concrete.

Wahlin and Klein-Paste investigated the effect of deicing chemicals on the hardness of snow. Dendritic snow was mixed with six different solutions in equilibrium with ice and then compressed. After compression, hardness of the snow was measured. Snow mixed with potassium formate was 25% softer than snow mixed with sodium chloride whereas the urea/snow mix was 20% harder than the sodium chloride/snow mix. This could impact the required amount of chemicals needed to achieve the same hardness, which could impact chemical usage in practical applications.

Performance of Other RSAs

Some studies have investigated the performance of other RSAs such as molasses-based products or agricultural products. For example, Fu et al. (2012) compared two liquid molasses-based materials with salt brine for use as pre-wetting agents and, in separate tests, as anti-icing agents. Pre-wetting involved spraying salt with a solution of the molasses-based product before road application. Pre-wetting the salt helps the salt adhere to the road surface and provides moisture, which salt needs for effective deicing, on cold, dry days. When used as an anti-icing agent, the materials were sprayed directly on the road surface before a snowfall event. Results showed that, when used as pre-wetting agents, none of the materials performed better than the others for 85% of the tests. For the remaining 15% of the tests, results were mixed and there was no consistent material that outperformed the others. When used as anti-icing agents, the two molasses-based products resulted in higher friction values than salt brine. The molasses materials were applied at a lower rate yet outperformed the salt brine by up to 10% with regards to friction.

Muthumani, et al. (2015) compared agriculturally derived products and complex chloride minerals in a laboratory investigation by measuring the degree to which products lower the freezing point of water and improve the ice melting capacity, weaken the ice bond to pavement, improve product longevity on the road surface, prevent ice formation, influence absorbance of sunlight on performance, and reduce corrosion of carbon steel. A best practices manual was developed which included storage guidelines, material handling and loading, storage and mixing,

brine production equipment, application methods and guidelines, anti-icing and direct liquid application, and identified issues with agriculturally derived products.

Hosseini et al (2017) compared the road friction performance of RSAs with conventional brine (a 23% sodium chloride solution). The RSAs tested were Snowmelt (a fully bio-based product), Fusion (a mixture of a bio-based product and chloride salt), and Caliber M1000 (another mix of a bio-based product and chloride). Tests, which were performed in a parking lot in Ontario, Canada, were done at three different application rates (3, 6, and 9 liters per 1000 ft²). The application rate did not affect product performance and treated sections had from 10 to 40% increased friction as compared to untreated control sections. There was no statistical difference, however, in the performance of each of the three products.

Lee et al. (2017) investigated the performance of chloride-based and organic-based materials mixed with chlorides with respect to ice melting and their impact on steel and concrete. Hazardous components of the products were also compared. Field tests showed that most of the organic products met South Korea's corrosion, concrete freeze-thaw, and environmental requirements. Field tests also showed that chloride products were more effective than the organic products except when temperatures were below -17.2 °C (1 °F), at which point no product was effective. Lab test results agreed with field test results in that the organic-based materials were not as effective as chloride products. Liquid organic-based materials were effective deicers, however, but solid organic-based materials were not.

Specific Environmental Impact of RSAs

Although environmental impacts of RSAs were previously discussed, many studies investigated specific impacts of RSAs on water bodies, soil, or organisms. A thorough review of such studies was beyond the scope of the previous sections and would have cluttered the broad discussion in those sections. The work, however, is significant, relevant, and contributes much to the field of RSAs and, as such, is reviewed in this section. A sub-section at the end of this section covers studies that involve modeling the fate of RSAs (mainly CMA) in the environment.

In a general study that investigated three different deicing management techniques to determine possible methods to reduce phosphorus and sediment export to a lake, Albright (2009) investigated the impact of: 1. Abrasives with just enough salt to avoid clumping (the abrasives

were fines with high phosphorus content), 2. Reduced abrasives and increased salt use along with liquid Ice Ban applied in spot applications, and 3. Use of only pre-wetted salt and Ice Ban applied in spot applications. Each of the three strategies were implemented for a period of one to six years and phosphorus and sediment export to the lake was recorded. The third technique (only pre-wetted salt with some Ice Ban application) resulted in the lowest phosphorus and sediment loading. It was noted, however, that chloride concentrations in the lake were increasing and this strategy would likely increase this trend.

Horner (1988) investigated CMA in the environment and recommended that, to prevent DO depletion, CMA not be used in watersheds where road runoff can directly reach receiving water bodies that have less than 100:1 dilution available in the runoff season. Other recommendations and conclusions included:

1. Provide a vegetated drainage course between roads where CMA is applied and receiving water bodies (at least 25% of acetate and butyrate can be removed in five meters of overland flow in vegetation but cation removal cannot be assumed in three meters),
2. Avoid CMA use where coarse soils overlay sensitive aquifers,
3. Avoid CMA use where soils are contaminated with metals because CMA may mobilize metals,
4. Dilute CMA by at least 4-times in order to keep concentrations below water quality standards,
5. CMA can increase soil permeability by up to 20 times depending on the soil type and CMA concentration,
6. Complete CMA degradation occurs in soils within two weeks at 10 and 20 °C (50 to 68 °F) but it takes two to four weeks at 2 °C (35.6 °F),
7. A soil depth of 3 cm was enough to degrade CMA in lab experiments,
8. There can be a lag of up to one week before CMA degradation begins,
9. Plants can withstand 2500 mg/L of CMA in soil but this concentration may be deadly to seedlings if immediately exposed,
10. Spraying or flooding plants with water containing 3000 mg/L of CMA does not affect the plants, and
11. In water, the ultimate BOD is about 75% of the CMA added.

Brenner and Horner (1992) investigated the impact of CMA, with respect to DO, on terrestrial and water ecosystems. Specific goals were to determine the BOD of CMA, determine the effect of temperature on degradation rate, determine if there is any BOD from contaminants in corn-based CMA, compare lab results to field results, and predict impact of full-scale CMA application on the DO of receiving waters and recommend ways to minimize the impact. It was estimated that the high range of CMA in road runoff could be 100 mg/L. This concentration completely depleted DO within two days at 20 °C while 10 mg/L of CMA depleted 4.5 mg/L and 7.0 mg/L of DO for reagent grade CMA and corn-based CMA, respectively. This indicates a larger BOD in corn-based CMA, which could be attributed to butyrate that was present in the corn-based CMA (both CMA products had equal acetate concentrations).

The DO depletion rate was a strong function of temperature and seemingly followed an Arrhenius relationship. Tests were conducted at 2 °C, 6 °C, 10 °C and 20 °C (35.6 °F, 42.8 °F, 50.0 °F and 68.0 °F). The standard, first-order BOD equation did not fit well at low temperatures (2 °C and 6 °C) due to a lag, however, and an alternative log curve was proposed. DO depletion due to CMA was tested in microcosms and in ponds and, although DO depletion occurred, it did not occur to the same extent as in lab experiments. This was likely due to reaeration of the microcosm, which could occur in the field but did not occur in the laboratory. In support of this theory, one pond, when ice covered, experienced a much larger drop in DO with a relatively small inflow of CMA. Recommendations to limit the impact of CMA included no application in areas where receiving water bodies are close to the road, where or when water bodies are ice covered, where CMA will not be diluted, and where there are fish that are sensitive to low DO. No application was also recommended when there may be late spring storms because water temperatures would be higher and this would likely lead to increased degradation rates and greater DO depletion.

To assess for DO depletion, Brenner and Horner (1992) suggested obtaining information on typical winter snowfall, water content of snow, typical amounts of deicer applied, volumes of runoff and runoff patterns after a thaw, distance from roads to receiving water bodies, permeability of soil, volumes of lakes and flow rates of streams, types of fish and spawning habits in nearby water bodies, and knowledge of potential for under-ice DO depletion in water bodies.

Horner and Brenner (1992) focused on environmental impacts of CMA other than BOD and DO depletion and included such topics as CMA transport characteristics, CMA fate in the environment, and its impact on terrestrial and aquatic ecosystems. With respect to soil, the only significant impact found was that CMA increases soil permeability. Lab studies showed potential acetate mobility, but field studies showed only minor evidence of this. CMA can also, through ion exchange with calcium and magnesium, release certain metals from the soil. Field results showed less of a tendency to do so and less consistency than lab studies. Also, the amount of metals released would not cause environmental problems. The authors noted, however, that the actual behavior in roadside soils is not known. At concentrations in the soil that were much higher than those expected in road runoff, no adverse effects were observed except when the high concentration was in the root zone, which killed seedlings.

Through a literature review and limited laboratory studies, Winters et al. (1984) reviewed the toxicity of CMA and found that it is less toxic to rainbow trout and fathead minnows than sodium chloride. A concentration of 5000 mg/L of CMA was found to slightly delay the hatching of rainbow trout but it did not affect the number of eggs hatched. Water flea reproduction was significantly inhibited at 250 mg/L CMA and at 125 mg/L sodium chloride. CMA, however, was found to be more toxic to algae than sodium chloride, but at concentrations under 50 mg/L CMA there was no harmful impact to algae. Overall, sodium chloride did more damage to plants than CMA, although one plant (Russian Olive) was damaged less by sodium chloride. CMA transport through the soil resulted in some removal of iron, aluminum, and nutrients from the soil. At concentrations likely to be generated in deicing applications, CMA may have less of a negative impact on the environment than sodium chloride.

Buteau et al. (1992) performed toxicity tests on Chevron's Ice-B-Gone® Deicer, which was a pellet form of CMA. Acute oral toxicity, sub-chronic toxicity, acute inhalation toxicity, acute dermal toxicity, skin irritation, eye irritation, and skin sensitization tests were performed on rats and the latter two tests were also performed on human volunteers. All tests showed a low level of toxicity. CMA was found to be a slight eye irritant but not a skin irritant or skin sensitizer.

Goldman and Lubnow (1992) investigated the impact of CMA on 10 lakes in northern California with respect to microbial processes. Concentrations of 10 mg/L CMA appeared to

increase chlorophyll in one lake and a concentration of 1 mg/L resulted in statistically higher chlorophyll concentrations in another lake. During the summer, eight out of the ten lakes showed no response to CMA at doses of 0.1, 1.0, and 10 mg/L CMA but bioassays in the late spring and early winter showed slight responses to CMA. Temperature, weather, and the standing stock of microbial populations were the most important variables that influenced algae populations. The authors theorized that increases in water temperature likely increased microbial activity and bacterial mineralization, which, in turn, could have caused the increases in chlorophyll.

Tanner and Wood (1999) investigated the effect of CMA application by the Oregon Department of Transportation on Bear Creek, which is in the Cascade Mountains. The road on which CMA was applied and Bear Creek run parallel to each other for about one mile and the creek is close to the road. At the time of the study, the road received CMA applications several times a year. The creek is small with a flow rate of approximately 4 cfs and it receives runoff directly from the road and shoulder. CMA (96% pure) was mixed with water at a dilution factor of 0.33 by weight and applied at 35 gallons per mile. Streamflow, rainfall precipitation, stream DO, pH, specific conductance, and water temperature were monitored continuously through the winter of 1998-99. No effect was observed with respect to calcium concentration, BOD, or magnesium concentration. BOD was small in water samples taken before CMA application and also in those taken after CMA application. Five-day BOD was 0.1 to 1.5 mg/L and twenty-day BOD was 0.2 to 2.0 mg/L.

Some studies have investigated the impact of RSAs on groundwater quality. For example, Granato et al. (1995) took groundwater samples at test sites next to Route 25 in Massachusetts and analyzed them for major trace chemicals. Groundwater concentrations were higher down gradient from the road as compared to samples taken up gradient. This suggests that the road (and possibly deicing agents) are affecting groundwater quality. One site was particularly impacted by both CMA and road salt. Results suggest, but are not conclusive, that there is potential mobilization due to winter recharge, ion exchange, acidification from road salts, and mineral weathering caused by deicing chemicals. No chemical concentrations exceeded national primary drinking water standards, but chloride and manganese exceeded secondary standards and surface water recommendations were exceeded for chloride, cadmium, and copper.

Hellstén and Nystén (2003) investigated the migration of sodium chloride, calcium chloride, magnesium chloride, CMA, potassium acetate, and potassium formate in aquifers. Potassium formate caused fewer negative impacts to infiltrated water than chloride and acetate. For example, overall results showed more metals were leached from the soils by sodium chloride than by acetate or formate. CMA, however, leached more arsenic, lead, nickel, and zinc than formate and formate leached more molybdenum and chromium than acetate or chloride. Although metals were leached from the soil, only manganese and sodium exceeded European Union drinking water standards.

Jain (2018) used experimental mesocosm to investigate the impact chloride and acetate salts of sodium and calcium had on soil permeability and the retention of copper in the soil. Results showed that chloride-based salts reduced permeability and acetate-based salts had minimal impact on permeability. Acetate-based salts, however, increased organic removal in the soil (as measured by chemical oxygen demand), which may indicate microbial growth. Also, less copper was retained by the soil when salt was included in the runoff.

Hellstén et al. (2005) monitored groundwater chemistry in an aquifer to determine the fate of potassium formate on an aquifer scale. Formate did not enter the saturated zone through the vadose zone because of biodegradation in the topsoil. Thus, no undesirable changes in groundwater chemistry were observed.

Some studies have specifically investigated the impact of deicers on metal mobility in soils. For example, Amrhein et al. (1992) investigated the impact of deicers on metals leaching from roadside soils. Roadside soil samples were taken, placed in 50 mL syringes that acted as columns, and tested under laboratory conditions. Two sets of experiments were performed. In one set, 175 mL of a sodium chloride-CMA solution was run through the columns followed by 105 mL of distilled water (to represent snow melt water). In the second set of experiments, 90 mL of the sodium chloride-CMA solution was run through the soil columns followed by 90 mL of distilled water. Slightly more nickel, chromium, cadmium, lead, and iron were leached when high CMA concentrations were used. This suggests effects of ligand complexation (chloride versus acetate) and competitive ion exchange on metal mobilization. Solubilization of cadmium was mostly controlled by competitive cation exchange and complexation by chloride and acetate. High concentrations of CMA leached more cadmium than sodium chloride leached and more

than dilute salt solutions leached. Concentrations of lead, chromium, nickel, cadmium, and copper in leachate never exceeded drinking water regulations but copper, nickel, and iron concentrations often exceeded limits set to protect freshwater life. Sodium tends to destroy soil structure and increase organic matter mobility, thereby increasing chances of metal mobility. The calcium and magnesium in CMA increases soil permeability and soil structure and reduces the dispersion of organic matter and clays. Horner and Brenner (1992), however, found that there was less tendency and consistency for the release of metals through ion exchange due to CMA application in the field as compared to laboratory studies.

Burkett and Gurr (2004) followed up on a modeling study performed by Scarsbrook et al. (1996; discussed below) by performing field tests. Preliminary field tests indicated that, of the four streams modeled, the smallest stream (baseflow of 1.8 cfs; 0.05 m³/s) would need a CMA application of 110 g CMA/m² on a nearby road to result in a 20% reduction in DO from saturation. In full-scale field tests an average application rate of 30 g CMA/m² was applied to the road and the stream DO never dropped below 90% saturation. There was also no noticeable effect on benthic growth or aquatic invertebrates. No impact was noticed on a beech or tea tree forest or in fernland or grassland. No impact on soil chemistry was observed and increases in phosphorus and exchangeable calcium and magnesium were insignificant with decreases in values being as common as increases. Observed benefits of CMA application over sand/grit application were 1. A reduction in accidents, 2. A decrease in travel time during icy conditions, 3. A 24% increase in friction when CMA was used in place of sand, and 4. Less road closures.

Finally, Rasa et al. (2005) investigated the impact of sodium chloride and potassium formate on the mobility of cadmium in roadside soils. Formate elevated the soil pH, which increased the fraction of cadmium adsorbed onto oxide surfaces to up to 80%. Sodium chloride, however, increased the water soluble fraction of cadmium due to cation competition and the formation of cadmium-chloride complexes.

Deicer Impact on Specific Species

Other studies on the impact of RSAs have investigated their impact on a specific species of plant or organism. For example, Robidoux and Delisle (2001) investigated the environmental impact of sodium formate, CMA, sodium chloride, on three plants (barley, red fescue grass,

Kentucky bluegrass) and an earthworm (*Eisenia fetida*). It was concluded that, overall, the toxicological impact of sodium formate was approximately the same as sodium chloride with both having a larger impact than CMA. The authors noted, however, that due to the fact that more CMA is required for the same deicing effect as sodium chloride or sodium formate, the total impact of using any of the three deicers may be similar.

Joutti et al. (2003) tested sodium chloride, calcium chloride, magnesium chloride, potassium formate, potassium acetate, and CMA with different bioassays. Bioassays were an onion plant root elongation test, a duckweed growth inhibition test, an enzyme inhibition test, and a microbial test (luminescent bacteria, BioTox test). Overall, the organic chemicals were more toxic than the inorganic salts. The rank of toxicity, according to the root elongation and growth inhibition tests, were, from most toxic to least toxic: potassium formate, potassium acetate, CMA, calcium chloride, sodium chloride, and magnesium chloride. CMA could not be tested for the other two bioassays due to the turbidity of the samples.

Dougherty and Smith (2006) investigated the effect of sodium chloride, magnesium chloride, calcium acetate, magnesium acetate, sodium ferrocyanide, and sodium formate on tadpoles of two frog species and one toad species. Some salt compounds negatively affected some tadpoles but the acetates, sodium ferrocyanide, and sodium formate did not. All the concentrations tested were less than 170 mg/L and it was noted that higher concentrations may result in more of an impact.

Hanslin (2011) investigated the impact of CMA, potassium formate, and sodium chloride on the growth and stress responses of tree saplings. Tests were conducted in pots with five species of saplings and different concentrations of the deicers. Increasing concentrations (zero to 13.3 mmol/L soil) caused negative responses but results varied with species. Root growth decreased in two species and leaf biomass decreased in four of the five species. There was no impact on specific leaf area, relative chlorophyll content, height increase, or chlorophyll fluorescence. Overall, the organic deicers did not have less impact on saplings than sodium chloride did during active growth.

Harless et al. (2011) conducted 96 hour acute toxicity tests on larval wood frogs for urea, sodium chloride, magnesium chloride, potassium acetate, calcium chloride, and CMA. Larval were least sensitive to urea, sodium chloride, and magnesium chloride and were most sensitive to

CMA, potassium acetate, and calcium chloride. Toxicity varied greatly and the authors suggested more research be done to determine effects on other species.

Schuler et al. (2017) investigated the effect sodium chloride, magnesium chloride, ClearLane TM and two salts mixed with GeoMelt TM (a proprietary blend containing beet juice) and Magic Salt TM (a proprietary blend of magnesium chloride mixed with a distillation byproduct) had on food webs in experimental aquatic communities. Sodium chloride had little effect but the organic additives reduced DO and, after microbial breakdown, transformed phosphorus to a usable form that resulted in an increase in algae. More algae lead to more zooplankton. Magnesium chloride reduced compositional differences of zooplankton and, at low concentrations, increased the number of amphipods. The authors concluded that RSAs can alter ecosystems.

A summary of the studies that investigated specific environmental impacts of RSAs is given in alphabetical order in Table 7 below.

Table 7. Major conclusions from studies investigating specific environmental impacts of RSAs.

Study Citation	Major Conclusions	Comments
Albright 2009	Pre-wetted salt with Ice Ban was best of three methods to reduce phosphorus export to a lake.	Increase in Cl^- in lake would be accelerated.
Amrhein et al. 1992	CMA can leach metals from soil.	
Brenner & Horner 1992	Should not use CMA where water bodies are close to road, are ice covered, are not diluted, and where fish are sensitive to low DO.	Suggest obtaining additional watershed info such as typical snowfall, water content of snow, soil permeability, etc.
Burkett & Gurr 2004	Field tests showed that road application of 30 g CMA/m ² did not drop BOD of 1.8 cfs stream below 90% saturation. Also had limited or no other environmental impacts.	
Buteau et al. 1992	Ice-B-Gone form of CMA has low level of toxicity.	
Dougherty & Smith 2006	Salts negatively impacted tadpoles but acetates and sodium formate did not.	
Goldman & Lubnow 1992	CMA did not affect 8 of 10 lakes in summer but CMA impacted algae populations in late spring & early winter.	
Granato et al. 1995	Groundwater adjacent to road can be impacted by CMA and road salt.	
Hanslin 2011	During active growth, organic deicers did not have less impact on saplings than sodium chloride.	
Harless et al. 2011	Larval wood frogs were most sensitive to CMA, potassium acetate, CaCl_2 , and were least sensitive to urea, NaCl , and MgCl_2 .	Recommended additional tests on other species.
Hellstén & Nystén 2003	In soil, acetate and formate leach less metals than sodium chloride. Potassium formate causes less negative environmental impact on infiltrated water quality than chloride and acetate.	
Hellstén 2005	Potassium formate was degraded in soil and did not impact groundwater.	
Horner 1988	Should not use CMA where road runoff directly enters water body with dilution factor < 100.	See body of this report for additional conclusions.
Horner and Brenner 1992	CMA increases soil permeability and can release metals.	
Joutti et al. 2003	Organic deicing chemicals are more toxic than non-organic salts	
Rasa et al. 2005	Formate application to soil increased pH, which increased the fraction of cadmium bound to the soil.	
Robidoux & Delisle 2001	Toxicological impact of sodium formate is about equal to sodium chloride and both have larger impact than CMA.	More CMA is needed to get the same deicing effect.
Schuler et al. 2017	Organic deicers can alter ecosystems.	
Tanner & Wood 1999	CMA road application had no impact on a small creek (~4 cfs) that ran parallel to the road.	Investigated impact on BOD and calcium and magnesium concentrations.
Winters et al. 1984	CMA is less toxic to rainbow trout and fathead minnows than NaCl . CMA is more toxic to algae than NaCl but, overall, NaCl is more toxic to plants.	

Environmental Modeling Studies

Some documents reported on model studies to determine the fate and/or impact of roadway deicers in the environment. For example, Lindstrom (2006), who modeled the fate of chloride using a model for the unsaturated groundwater zone and a different model for the

saturated zone, showed that aquifer chloride concentrations will increase and take several decades to decrease even if all chloride use is stopped. The only model studies found in the literature that investigated RSA fate, transport, and/or impact focused on CMA. Since Task 2 of this project involves such a model, a discussion of those studies is included below.

D'Itri (1992) modeled the effect of CMA road applications on surface waters by using rate and empirical coefficients from other studies and assuming that CMA applied to a road surface is either: 1) Transported by runoff to adjacent soil where it begins to degrade, or 2) Stored in a snow bank until it is released into the ground via snowmelt. Direct runoff from the road to receiving water bodies was not considered. The loss of acetate in the soil was modeled using the non-point source model *Simulator for Water Resources in Rural Basins-WQ* (SWRRBWQ). CMA degradation in receiving water bodies was modeled using first order equations for CMA and DO, again with rate constants from previous studies. Model results showed a 70% loss of CMA per 10 feet of runoff distance if CMA is applied directly to the soil or 50% if it is added to the snow pack. D'Itri (1992) plotted percent CMA remaining versus distance from the edge of a two-lane road with shoulder assuming the road runoff is delivered to a 10 foot wide buffer zone. This plot, which is reproduced as Figure 2, shows that CMA is totally degraded after 40 feet. D'Itri (1992) concluded that CMA input to a water body is not likely to be significant unless the water body is close to the road.

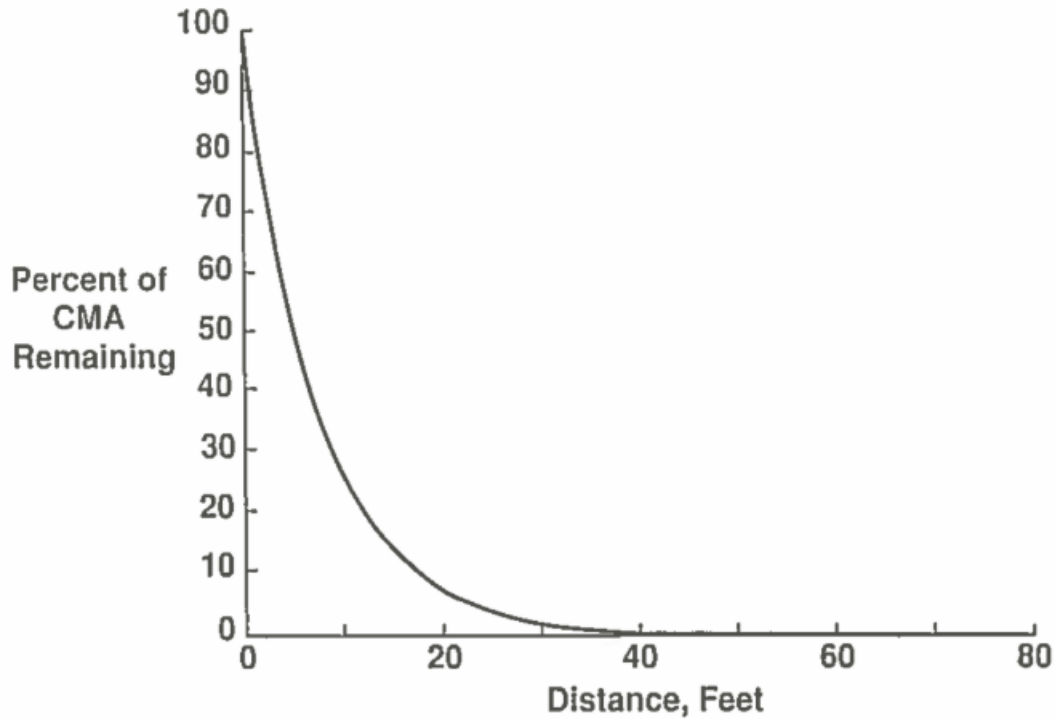


Figure 1. CMA remaining from distance of roadway assuming a two-lane road with shoulder delivers runoff and CMA to a 10 foot wide buffer (D'Itri 1992).

Additionally, the D'Itri (1992) model was conservative in that it ignored flow through the receiving water body, which could bring in more oxygen and, thus, help replenish some of the depleted DO. Model runs were conducted for receiving ponds from 1 to 14 hectares in size and from 2 to 8 meters in depth. Biodegradation was simulated by adjusting the biodegradation rate for a temperature of 20 °C (68 °F) with temperature dependence functions from other studies. Results showed that a 1 acre pond with a depth of 2 m (i.e. the worse case scenario) with an annual loading of 60 g BOD/m² would have a maximum DO deficit of about 2 mg/L. This deficit would occur during the winter when other DO sinks would not be present and the results would not be compounded. D'Itri (1992) also found there would be no significant impact of CMA on lake phytoplankton. This research indicates that, once CMA or other organic alternatives enters the soil, it will have a limited influence upon DO concentration in receiving water bodies.

Scarsbrook et al. (1996) modeled the impact of CMA road application in a national park area in New Zealand. The model, which implemented a Streeter-Phelps DO model for CMA impact on four streams, was used to test six scenarios. Four scenarios used estimates of BOD delivery rates (directly to the streams) and BOD values based on data from two rain events in

1995 to model CMA impact on stream DO levels. The two other scenarios estimated the mass of CMA road application required to cause a 20% drop in stream DO (from saturation) under average flood conditions and under short duration floods.

Model results showed the two largest streams were not at any risk even for the worst case scenario of 100% CMA delivery to the stream in a 5 hour runoff event. But the critical CMA burden (i.e. causing a 20% drop in DO from saturation) for the smallest stream (baseflow of 0.05 m³/s; Burkett and Gurr, 2004) was only 35 g CMA/m². For larger streams, this value was 153 g CMA/m² or above. Also, of the first four scenarios, the smallest streams were significantly impacted under three of the four model scenarios. Scarsbrook et al. (1996) recommended that field investigations be performed in order to estimate the amount of CMA carried to the streams by runoff, the amount lost in the soil, and the resulting DO values in the streams (so that the model could be refined and critical CMA values be reassessed). As previously discussed, Burkett and Gurr (2004) did some additional field tests related to Scarsbrook et al. (1996).

These two modeling studies indicate that the most important impact upon DO concentration would be due to direct runoff into the receiving water body.

Abrasives

Historically, sand has been applied to road surfaces in an attempt to increase friction between the road surface and vehicle tires. Numerous studies, however, have found that any increase in friction caused by sand placed on the road surface is usually quickly diminished due to the particles bouncing off or being blown off the road due to winds induced by passing vehicles (e.g. Salimi et al 2014, Saltan et al. 2014). Dahlen and Vaa (2001), for example, found that sand removal from the road surface can occur after the passing of just 50 vehicles. Nixon (2001) stated that this can occur with “light” vehicle passage, especially in colder weather. Schlup and Ruess (2001) also found this to be true and added that abrasives visible on the road surface can give drivers a false sense of security and cause them to drive too fast for conditions. Finally, Keyser (1973) found that abrasives less than 300 microns in size do almost nothing to increase road friction.

Studies have also found abrasives cost more than salts and cause more negative environmental impacts. For example, Fay and Shi (2012) stated that, in order to attain a

reasonable level of service, the environmental impacts of abrasives are more detrimental than that of salt. Abrasives can exacerbate the stress on roadside vegetation and soil (Fay and Shi 2012) and they are a significant risk to water quality and can threaten aquatic species (Staples et al. 2004). They can also increase water turbidity, clog streams and drains, reduce water body oxygenation, affect food chains, and reduce fish reproduction (Staples et al. 2004). Abrasives less than 10 microns in size can contribute to air pollution (Fay and Shi 2012) and their use can be limited in air quality non-attainment regions (Chang et al. 2002). Schlup and Ruess (2001) concluded that salts have less overall negative impact on the environment than abrasives and that, in a study of three Swiss cities over two winters, the cost of abrasives was six to 10 times more than that of salts. These studies have not considered the long-term impact of chloride on toxicity in fresh water bodies. In the Minneapolis-St. Paul metropolitan area, for example, the U.S. Environmental Protection Agency's chronic (~long-term) chloride toxicity criteria are frequently surpassed, and some water bodies have also surpassed the acute (~short term) toxicity criteria (MPCA, 2014).

Although many studies have found that sand, when applied using conventional methods, does not last long on the road surface, other studies have determined that alternative placement methods can increase the longevity of the impact of abrasives on road surfaces. For example, Nixon (2001) stated that prewetting sand at the tailgate of the truck just prior to placement can help the sand stay on the road and that heating the sand just prior to placement can have the same effect. When the sand is prewet the water, upon freezing, can freeze the particles to the road surface and when abrasives are heated it will cause a small portion of ice to melt, which, upon refreezing, will help adhere the sand to the surface. Ihs (2002) also noted this effect when spraying sand with hot water just prior to distribution.

FinnRA (1991) found that heating the sand to 80 °C (176 °F) prior to placing it in a truck for distribution did not make a statistical difference in friction. They also found that heated abrasives of up to 250 °C (482 °F) increased the coefficient of road friction from 0.22 to 0.37 but the value dropped back to 0.22 in less than 24 hours. Hallberg and Henrysson (1999) found that an application method called Hottstone®, which applied 2 to 5 mm aggregate at greater than 180 °C (356 °F) could increase friction for several days. Another method called Friction Maker™ applied 0 to 8 mm sand with hot water at 90 °C (194 °F) and also increased friction for

several days. The Friction Maker TM was cheaper than applying a salt/sand mix on a per application basis and the Hottstone [®] method was about 30% more expensive than applying a salt/sand mix on a per application basis. Nixon (2001) recommended that field trials be performed in Iowa to test application of abrasives using three different methods. The methods were 1. Pre-wetting the abrasives at the back of the spreader, 2. Heating abrasives to ~180 °C (356 °F) prior to placement, and 3. Mixing abrasives with hot water at ~90 °C (194 °F).

Dahlen and Vaa (2001) found that using heated abrasives or adding warm water to sand can allow the sand to stay on the road even after more than 2000 vehicles pass by and that using warm-wetted sand can reduce overall sand use by 40% to 50%. The most extensive report on using warm and/or wet sand was Perchanok et al. (2010) who reported on the Hot Water Sander, a material spreader developed in Sweden that prewets sand with water at 95 °C (203 °F) as it's being spread on the road. Tests in Scandanavia demonstrated that the sand could stay on the road for more than 10 hours whereas conventionally applied cold and dry sand would be blown away within minutes. Based on tests in Norway, this method is expected to increase the coefficient of friction values by 0.1 and this increase is expected to last two times longer than conventionally applied sand. Overall O&M costs and environmental footprints are also expected to be lower, although the authors also estimated the capital and operating cost over the equipment life span to be 1.5 times conventional equipment.

Perchanok et al. (2010), however, did note that the method has several practical concerns. The listed concerns were:

1. While in operation, a fog cloud formed around the spinner, severely reducing visibility behind the spreader. This is a safety concern.
2. The operational speed is 15 mph (24 km/hr), which is lower than conventional spreaders. This is another safety concern.
3. Sand is discharged at the rear end of the spreader, which means the vehicle could be on an unsanded road.
4. The operating range of the spreader is reduced by 40 % compared to conventional spreaders of the same load capacity, due to the load of water.
5. In order to prevent sand from freezing in unheated stockpiles, conventional sand with approximately 3% added salt was used.

Abrasives can still be an effective means of winter road maintenance. For example, Ihs (2002) stated that Sweden uses crushed stone aggregate (0-5 mm) in urban areas and they also

use sand (0-8 mm) with ~3% salt by weight. On roads with speed limits above 43.5 mph (70 km/hr), the maximum size of abrasive used is 4 mm. Norem (2009) studied traffic accident data from Sweden to determine the effectiveness of winter maintenance options. The study found that salted roads were more accessible than sanded roads, but no conclusions could be drawn nationwide regarding a safety comparison between salted and sanded roads. That is because roads were safer on salted roads in central and southern Sweden but in the cold winters of northern Sweden, the number of accidents was higher on salted roads. Norem (2009) recommended that salting should be avoided in areas and in periods when the frequency of road surface temperatures below -8°C (18°F) exceeds 20%. In these climates, the warm-wetted sand method, Norem (2009) concludes, is likely better for improved friction. Norem (2009) also stated that warm-wetted sand is favorable on roads with traffic volumes less than 2,000 average annual daily traffic and in periods with stable winter conditions.

In an investigation into the impact of sand spreading rates, Salimi et al. (2014) found that sand spread at a low rate (354 lb/lane-mile; 100 kg/lane-km) did not improve friction but sand spread at a medium rate (886 lb/lane-mile; 250 kg/lane-km) and a high rate (1428 lb/lane-mile; 420 kg/lane-km) did improve friction by 23% and 43%, respectively.

Wang et al. (2015) investigated the wear of asphalt pavement due to the application of winter sand and winter salt. By simulating applications and wear, it was determined that sand removed bitumen from the pavement and polished the aggregate, which reduced road friction of the bare pavement over the long-term. Salt only impacted the bitumen on the surface of aggregate and the aggregates were only minimally polished. Thus, the salt treated specimens had a higher friction coefficient than the sand treated specimens.

Finally, Saltan et al. (2014) evaluated a new machine, the Ice Melter Experiment Mechanism (IMEM), that evaluated the impact abrasives have on snow or ice surfaces. The IMEM measures the amount of ice melted as the pressure from an experimental wheel is rotated over abrasives on the ice surface. As the wheel rolls over abrasive particles, it pushes them into the ice, which can melt a portion of the ice. The IMEM was used to evaluate a conventional limestone sand and, for comparison, a new abrasive, which was a pumice waste from the Isparta-Karakaya region of Turkey. The limestone sand performed better in that it melted more ice. At wheel loads of 3, 4, 5, and 6 kg, the sand melted 93%, 105%, 59%, and 48% more ice,

respectively. The sand, however, was removed from the ice surface by the simulated traffic. Although the pumice melted less ice, once broken into small pieces by the wheel, it remained on the ice surface where it had a longer impact on road friction. Saltan et al. (2014) suggested that, since pumice is used as a fertilizer, rain runoff containing pumice may be beneficial to roadside vegetation. It should be noted, however, that it would also likely add to nutrient loads, which are a main target of most stormwater management plans.

Pavement Innovations

To prevent ice formation on roads and melt or otherwise remove snow and ice from road surfaces, researchers have looked beyond what can be applied to the road surface to what can be done to improve pavement designs to achieve this objective. Most of the research has focused on the following four innovations: 1. Adding materials to the pavement mix design so the pavement can be more effectively heated, 2. Adding deicing agents to the mix design, which are released over time and aid in deicing, 3. Adding pipes to the pavement cross-section so that the pipes can be heated, often by warm liquid moving through them, which can melt snow and ice on the pavement surface, and 4. Applying a hydrophobic coating to the surface of the pavement in order to reduce ice adhesion strengths. These, and one other study which investigated making asphalt with a polyurethane binder instead of conventional asphalt, are reviewed below.

Pavement Heating by Adding to the Mix Design

Yang et al. (2012) investigated placing manufactured carbon fiber tape in concrete sidewalks to heat the tape with electricity. The system was effective in melting snow and ice on the surface. With an electricity cost of \$0.20/kW-hr, the average cost of heating the pavement when the air temperature was -11 °C (11.5 °F) was \$0.0292/m²-cm. Units are per square meter of pavement area and per centimeter of accumulated snow depth. Costs would increase with colder temperatures and greater wind chill, but the authors concluded that the method could be viable for bridge decks, parking lots, and sections of road that are susceptible to icing.

A similar technique for heating pavement, called electrically conductive concrete, involves adding conductive materials to the pavement mix design. This allows the pavement to be more efficiently heated by an external power source. Typical conductive materials are steel fibers, graphite powder, or carbon particles (Abdualla et al. 2016), among others. Additional

required components include electrodes, a power supply, and temperature sensors. In this design, an electric current applied through electrodes embedded in a conductive layer on top of conventional pavement is used to heat the top layer of pavement and melt snow and ice. The ability of the pavement to melt snow and ice depends on the resistivity of the conductive materials. Values required for deicing are typically less than 1000 ohm-cm (Abdualla et al. 2016). Electrode types reported in the literature include steel, perforated steel, perforated stainless steel, and galvanized iron. A good bond between the pavement and the electrode is also necessary for effective heating.

Abdualla et al. (2016) investigated requirements needed for electrically conductive concrete to be a cost-effective deicer. The underlying conventional pavement layer was 5 cm thick and had grooves on top to promote a good bond with the overlying conductive pavement layer. A 5 cm thick conductive layer with 0.75% (by volume) of 6 mm long carbon fibers provided a resistivity of 50 ohm-cm. There was also an insulating layer underneath the pavement. Tests investigated the ability of the pavement to melt 2.5 cm of snow on the surface. An AC power source of 80 volts and 11 amps was used. Abdualla et al. (2016) recommended using AC power as it enables electrons to find different pathways into the conductive materials, which more evenly distributes heat throughout the conductive layer. The power required to melt the 2.5 cm of snow was 0.54 kW-hour/m² and cost \$0.065/m², which Abdualla et al. (2016) claimed were the lowest values reported in the literature thus far. The low power requirement and associated cost were attributed to the low resistivity of the conductive layer. The authors concluded that the keys to having a well performing, cost-effective electrically conductive layer are low resistivity, electrodes that are bonded well with the conductive layer, and cost-effective thermal insulation. Additional studies investigating electrically conductive pavement are discussed below.

Li et al. (2013) investigated adding carbon nano-fiber polymer as a thermal source (powered by solar energy), a carbon nanotube cement-based thermal conduction layer, and insulating layers to a Portland cement pavement in order to remove snow and ice from the pavement surface. Laboratory and field tests were performed and the system did melt snow and ice on the surface. Based on laboratory test results, the maximum cost of deicing with the system was estimated to be \$0.29/m². With carbon nano-fiber polymer being a relatively new material at

the time of publication, Li et al. (2013) suggested that material costs will likely decrease in the future.

Galao (2014) also investigated carbon nano-fibers in cement but did not incorporate solar power. In these studies, cement paste with carbon nano-fibers ranging from zero to five percent by weight and voltages of 50, 100, and 150 volts were applied. Specimens with 1 or 2% carbon fibers could achieve high temperatures but required 150 volts. Specimens with 5% nano-fibers, casted as shotcrete, could increase temperatures by about 20 °C (36 °F) with only 65 volts. Heating rates were up to 10 °C (18 °F) per minute. Specimen sizes were 0.10 m by 0.10 m and power consumption to raise the middle of the most effective 5% carbon nano-fiber specimens from 20 °C to 30 °C (68 °F to 86 °F) ranged from about 0.0005 kW-hr to 0.0007 kW-hr. With an average cost of \$0.20/kW-hr, the cost to increase the center temperature of the 5% carbon nano-fiber specimens from 20 °C to 30 °C (68 °F to 86 °F) would range from approximately \$0.01 to \$0.014/m². No other information on power consumption was given.

For use at airports, Lai et al. (2014) investigated cement concrete with a steel mesh and carbon fiber heating wires 5 cm below the surface and spaced 10 cm apart. With a power supply of 350 W/m², the design could melt 2.7 cm thick layer of snow in two hours with air temperatures of -3 to -1 °C (26.6 to 30.2 °F). At \$0.20/kW-hr and 350 W/m² for two hours, the estimated cost is \$0.07/m².

Pan et al. (2014) investigated the impact of insulating layers between the bottom of asphalt pavement and the conductive (i.e. heated) layer. In a heated pavement system, the insulating layer causes more heat to transfer to the top of the pavement and melt more snow and ice than without the insulating layer. Three materials were tested to determine which one performed the best as an insulating layer. Those materials were slurry seal, expanded shale, and an unnamed waterproofing material. The waterproofing material had a lower thermal conductivity (0.3081 W/m-°C) than the expanded shale (0.6518 W/m-°C) and slurry seal (1.592 W/m-°C) with increased snow and ice removal.

Wu et al. (2015) investigated using steel fibers, carbon fibers, and steel fiber-graphite together in a concrete mix to increase the conductivity of the concrete for deicing purposes. The optimum mix used 1% steel fiber, 0.4% carbon fiber, and 4% graphite (all by volume). The mix demonstrated low resistivity (322 ohm-cm) and high power density. The temperature increased

8.7 °C (15.7 °F) after 2.5 hours when subject to 27 volts and 21.8 °C (39.2 °F) after two hours when subject to 44 volts. Wu et al. (2015) concluded that this design showed potential for snow melting and/or deicing applications.

Lai et al. (2015) also investigated heating pavement to melt snow and ice but used heating cables installed in the structural layer of the road. The cables were placed on a coarse gravel asphalt in a zig-zag fashion with a fine gravel asphalt layer placed on top. The design is intended for use on bridges and in tunnels and mountain roads and research included laboratory tests, field tests, and a numerical simulation. Results indicated that the design can melt snow and ice with a power input of 200 to 400 W/m² when the air temperature is between -20 and 0 °C (-4 °F and 32 °F). With an average cost of \$0.20/kW-hr, the cost to melt snow in this air temperature range would be \$0.04/m² to \$0.08/m² for every hour of heating. In the study with air temperatures ranging from -7 °C to -11.3 °C (19.4 °F to 11.7 °F), up to five hours were required to raise the pavement surface temperature to values above freezing. A total power cost estimate for the five hours of heating is from \$0.20/m² to \$0.40/m².

In a laboratory setting, Galao et al. (2016) investigated the feasibility of highly conductive carbon fibers in concrete as a self-heating material for ice prevention and melting. It was concluded that with an applied voltage difference of 20 volts, pavements in the field could increase their temperature to above 0 °C (32 °F) when they were initially at -15 °C (5 °F). Power required in the laboratory experiments was 300-500 W/m². Using the \$0.20/kW-hr estimate and assuming heating occurs for five hours (laboratory tests in this study ranged from 3.6 to 8.3 hours of heating), the total power cost would range from \$0.30/m² to \$0.50/m².

Bai et al. (2017) investigated the use of two parallel and horizontal layers of stainless steel fibers within concrete for heating purposes. The concrete mix included graphite, silica fume, and the stainless steel fibers. The following four concrete specimens were tested:

1. Plain concrete,
2. Same as 1 but with a double layer of stainless steel fibers,
3. Same as 2 but with steel fibers in concrete mix, and
4. Same as 2 but with graphite in concrete mix.

The resistivity of the specimens with the double layer of steel fibers was less than 30,000 ohm-cm and was still increasing with time after 56 days. Graphite and steel fibers added to the concrete mix further reduced resistivity to less than 200 ohm-cm and, after three weeks of increasing resistivity, the resistivity began to decrease with time. With this design, a 6 mm layer of ice was melted in 100 minutes with a power input of 800 W/m² at -20 °C (-4 °F). Most of the energy consumed was due to the heating of the concrete, not melting the ice. Also, it was determined that the ambient temperature is the most important factor in determining the time required for deicing.

Another method of heating pavement involves adding particles that absorb microwaves to the pavement mix design. This allows the pavement to be heated by a microwave unit on a passing vehicle that is also equipped to remove snow and ice as discussed below. In this process the ice is not melted because it does not absorb microwaves (Lu et al. 2017) but the pavement is heated, and this weakens the bond between ice and pavement. The weakened bond allows the vehicle, which is equipped with a crusher, to more easily grind and/or crush the ice layer so that it can be removed by a blade or shovel (also on the vehicle), all with less damage to the pavement. A schematic of this process from Gao et al. (2017) is shown in Figure 1 below.

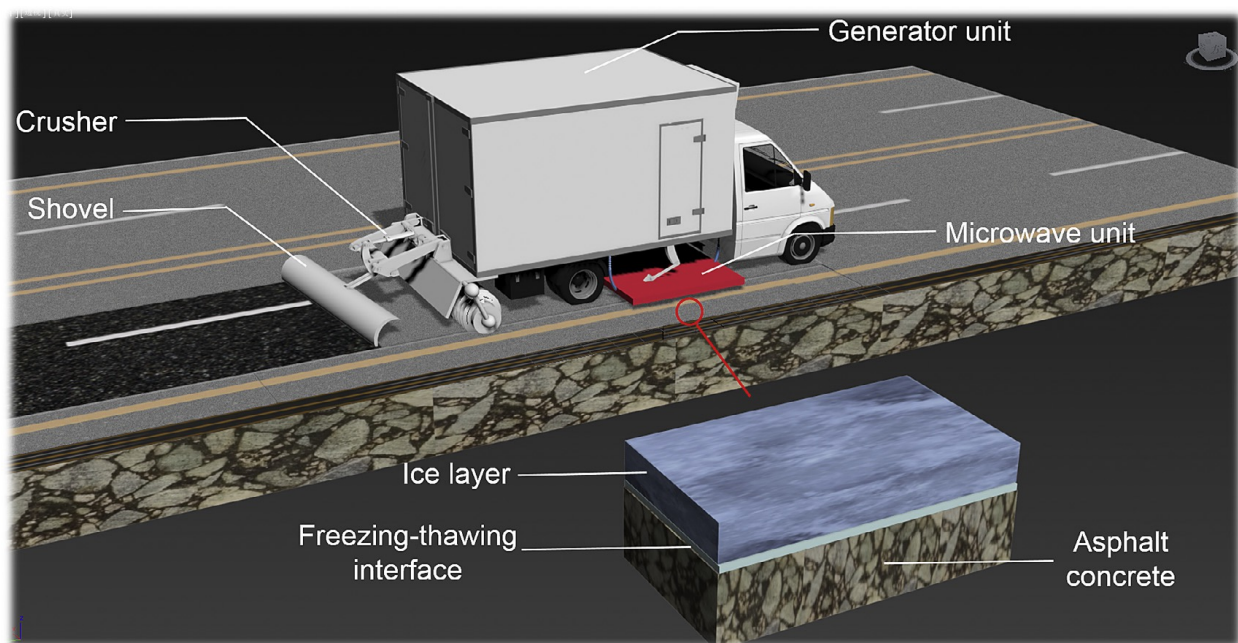


Figure 2. Schematic showing a microwave heating unit for ice removal from asphalt (from Gao et al. 2017).

In an investigation into the properties of an asphalt pavement for microwave ice removal, Wang et al. (2016) used magnetite as an aggregate in the asphalt due to its high microwave adsorption properties. The magnetite microwave heating efficiency was over 6 times that of conventional basalt aggregate. Properties of the asphalt with magnetite aggregate were examined and it was determined that it had adequate properties for use in roads. The actual ice melting ability of the pavement was not tested.

Lu et al. (2017) investigated ice removal from a concrete pavement after it was microwaved. Different microwave frequencies were tested and results showed that using 5.8 GHz as compared to 2.45 GHz decreased the microwave penetration depth from 118 mm to 53 mm and increased the deicing efficiency by more than five times. Adding 10% black iron oxide (by weight) to the pavement mix design increased the microwave efficiency by 1.8 times.

In an attempt to increase the microwave heating efficiency of pavements, Gao et al. (2017) investigated partially replacing conventional aggregate with steel slag. The microwave heating capacity of steel slag was found to be dependent on particle size with sizes of 0.6, 2.36, and 9.5 mm being the most effective. The heating uniformity and thermal conductivity of the pavement was found to decrease with an increase of steel slag content while the surface temperature increased with an increase in steel slag content. As a balance between heating uniformity/thermal conductivity and surface temperature, the authors recommended a steel slag content between 40 and 60% (by volume of total aggregate) for optimum performance. Tests were performed in a laboratory with a 850 W, 2.45 GHz microwave oven. Specimens were heated until a layer of ice that was initially adhered to the specimen surface fell off. No details were given regarding how long specimens had to be microwaved for this to occur, but graphs showing pavement surface temperature as a function of time in the microwave indicate it was less than 10 minutes. Figures in Gao et al. (2017) show specimens that appeared to be about 10 cm in diameter. Actual specimen size, however, was not given and, therefore, an estimate of the cost per pavement surface area is not possible.

Deicers in the Pavement Mix Design

Another innovation in pavement anti-icing and deicing has been the incorporation of anti-icing and/or deicing agents in the pavement itself. These agents help prevent ice formation or aid

in the melting of snow and ice on the pavement surface. After the agents at the pavement surface dissolve into water or are otherwise transported away from the surface, agents from below the surface move to the surface through diffusion (and/or other processes discussed below) and help in the anti-icing, deicing process. Peng et al. (2015), however, showed that chloride anions added to a pavement as anti-icing agents can be retained in the pavement rather than released.

Giuliani et al. (2012) investigated the use of a sodium chloride-based anti-icing filler (at 5.7% by weight) in asphalt and compared results to pavement with conventional calcareous filler. The anti-icing filler caused a delay in frost formation and icing, an acceleration of melting, and it reduced the adhesion strength between the ice and asphalt. After about 20 days about 65% of the original salt content had been released. The authors claimed, however, that the overall durability is expected to be “high” due to diffusion that moves salt from the asphalt body to the surface.

Wright (2013) investigated how the addition of sodium formate and sodium silicate to asphalt mixes impacts asphalt properties such as compactibility, stiffness, fatigue, permanent deformation, and skid resistance as compared to conventional asphalt. Reductions in ice adhesion and freezing point were also investigated. Studies showed that these additives do not negatively impact asphalt properties when subject to standard tests but that they may increase susceptibility to deterioration in the presence of water, which may reduce service life. The additives also reduced the freezing point and the ice adhesion strength. The study also investigated the transfer of the additives to the surface and found that the transfer is dependent on the ambient relative humidity and the number and arrangement of surface voids (chemical transfer is greatest in surface voids). Transfer to the surface was found to typically occur when the relative humidity was greater than 70%, which is the point at which the chemicals absorb water from the atmosphere. With regards to freezing point reduction, at 3 and 5% (by weight) these additives reduced the freezing point to -1.6 and -2.1 °C, respectively.

Liu et al. (2014) studied properties of asphalt made with a commercially available Chinese anti-freeze product that contained chloride salts. The study, which mainly focused on the impact of the anti-freeze on asphalt properties, did find that the anti-snow and ice performance of the pavement increased with the addition, but details were limited.

Wang et al. (2017) also studied asphalt properties but of asphalt containing salt storage aggregate at zero, 5, 10, 15, and 20% (by weight). The salt storage aggregate was made from 90% pure sodium chloride, glass powder, and maifanite powder. To make the aggregate the materials were mixed and milled, heated to 750 °C (1382 °F), crushed, cooled and formed. It was determined that all the asphalt mixes tested could meet standard asphalt specification requirements and that salt migrates to the surface due to osmotic and capillary pressures where it can gradually melt snow and ice.

Liu et al. (2015) studied the salt releasing characteristics of asphalt made with a salt product subject to static and dynamic loading. The salt product was provided by a Chinese company and contained SiO₂, NaCl, CaCl₂, Al₂O₃, CaO, and other unspecified substances. The release of salt depended on the loading cycle. Under static loading salt release plateaued but if dynamic loading was then applied, the salt release rate increased.

A high elastic asphalt pavement (created by adding a high elastic modifier to conventional asphalt) that contained the deicing agent Mafilon (which replaced 70% of the mineral fillers) was investigated by Luo and Yang (2015) for rutting performance, low temperature performance, moisture damage resistance, snowmelt performance, and deicing performance. The high elastic asphalt with deicer performed better than conventional asphalt with regards to rutting and low temperature performance but was slightly weaker in moisture damage resistance. The high elastic asphalt with deicer also had a higher snowmelt speed and a weaker ice bond on the surface. Four hours after snowfall, snow thickness on the elastic pavement was 5 mm while on conventional asphalt it was 22 mm. Also, after the snowfall stopped, an ice layer formed on only half of the Mafilon pavement surface area but it formed over the entire conventional pavement surface area. Finally, at an ambient temperature of -5 °C (23 °F), a saturated sponge did not freeze to the surface of the modified asphalt, which indicates that the deicer prevented the surface from freezing.

Another study by Ma et al. (2016) also investigated the effect of commercial chloride-based, anti-icing additives on pavement properties. Contrary to Luo and Wang (2015), the additives were found to be detrimental to rutting stability, thermal cracking resistance, and moisture susceptibility of the pavement. Polyester fibers, when added to the mix, however, reduced this negative impact to a level such that the pavement performed in a satisfactory

manner. The mix with anti-icing additives and polyester fibers provided some snowmelt and weakened the bond between ice and pavement.

Farnam et al. (2015) investigated the use of two products with high enthalpies of fusion (~130-170 J/g) and freezing temperatures of 2 to 3 °C (35.6 to 37.4 °F) when placed in concrete cement. The objective of the design was to improve snowmelt and anti-icing properties of the pavement. The high enthalpy of fusion materials store heat which reduces ice and snow on the surface. The two products, paraffin oil (a petroleum product) and methyl laurate (a vegetable product) were tested in two configurations. In the first configuration, the material was placed in lightweight aggregate which was placed in the mortar and, in the second configuration, the material was placed in tubes that were embedded in the mortar. The paraffin oil in the mortar did melt snow and ice and it worked well. The methyl laurate, however, damaged the mortar and didn't release heat due to a reaction with the mortar. When placed in the embedded tubes, both materials worked well. Heat releases were enough to melt 22 to 36 kg of pure ice per cubic meter of mortar on the surface of the pavement at temperatures ranging from approximately -1 °C to -3 °C.

Farnam et al. (2017) followed up their previous work with a second study that used paraffin oil in two ways. One was placing the oil in lightweight aggregate that was used to make concrete and the second was by placing the oil in metal pipes that were embedded in the pavement slab during casting. Both methods showed the ability to melt snow and ice on the pavement surface, but the pipe method released heat more rapidly than the aggregate method and, thus, melted snow and ice more quickly. The authors claimed that results indicated that both methods could reduce or eliminate the need for deicing salts or chemicals, especially in weather conditions that have recently dropped below freezing.

Peng et al. (2015) investigated making Mg-AlCl layered double hydroxide (LDH) from Mg-AlCO₃ and investigated its performance related to deicing. Mg-AlCl(LDH) was more effective than Mg-AlCO₃ (LDH) in decreasing the freezing point of water. At temperatures below the freezing point it can weaken the adhesion forces between the ice and asphalt. As was previously mentioned, tests also showed that chloride anions can be retained in the asphalt and not released into the environment.

Chen et al. (2018a) investigated the performance of anti-freezing asphalt with regards to the adhesion strength between ice and asphalt. In this asphalt mix design, mineral fillers were replaced with anti-freezing fillers that released salt after a snowfall or, more specifically as shown by Wright et al. (2016), under high relative humidity conditions (greater than 60-70%). The anti-freezing filler used consisted of CaO, Al₂O₃, SiO₂, Na₂O, K₂O, Fe₂O₃, and other substances and was used in different specimens to replace 33%, 67%, and 100% of the conventional aggregate (it is not clear if this was by weight or volume). The asphalt was also modified with a styrene butadiene styrene block polymer to improve rheological properties. The released salt helped to melt ice and snow. The technique did not melt all of the snow and ice but it did lower the adhesion strength between ice and pavement by up to 80%. Long-term ice adhesion (simulated by washing and drying cycles), however, greatly increased in strength, indicating that the effective life of the deicing ability of the pavement may be limited.

In a study of railway asphalt, Fang et al. (2017) also added anti-freeze additives to asphalt mix designs and tested asphalt properties. Additives tested included hydrated lime, fly ash, red clay brick powder, Portland cement, and an expansive water sealing agent. In tested mix designs the additives replaced 50% of the conventional fillers. The study found that the expansive agent was not an appropriate filler because moisture damage resistance was considerably reduced. A filler mix of hydrated lime (40%), fly ash (20%), red clay brick powder (20%), and Portland cement (20%) was found to be satisfactory, however, and this mix improved water damage resistance and, the authors claimed, enhanced asphalt anti-freeze ability, although no anti-freezing performance data was provided.

Hydronic Pavements

Another way to provide heat to a pavement in order to melt snow or ice is to embed pipes or tubes in the pavement and heat the pipes either by electricity or by circulating warm liquid through the pipes. Liquids used include brine, oils, and glycol-water, among others (Adl-Zarrabi et al. 2016). With either heating method, heat is transferred to the pavement surface where it can melt snow and ice or prevent the formation of ice. Pavements with such pipes or tubes are, by definition, called hydronic pavements. This section reviews publications regarding research into hydronic pavements.

Wang et al. (2010) investigated variables such as fluid temperature, pavement slope, and idling (or preheating) time on the design and performance of hydronic pavements. Slopes of 9 or 18° allowed melted slurry to drain out of the snow. This weakened the capillary effect in the snow and increased the total snow melt time. Compared to horizontal pavement, slopes of 9 and 18° and increased the time required to melt 27 mm of snow by 25.9% and 53.7%, respectively. These results corresponded to tests in which the pavement was preheated to 11.2 °C (52.2 °F). The authors noted that the impact of slope may be greater without preheating.

Chen et al. (2011) investigated the use of fluids in the pipes of hydronic asphalt pavement. In this investigation, heat was collected in the summer and stored for use in the winter to melt ice. In addition to melting ice in the winter time, the design can help prolong asphalt life because it moderates the temperature of the asphalt and reduces the extreme temperature swings experienced by conventional asphalt. In this study, graphite powder was added to the asphalt mix design to increase the thermal conductivity of the asphalt. Numerical simulations suggested placing the pipes between asphalt layers at a depth of 4 or 10 cm with a spacing between pipes of 18 to 40 cm. In experimental runs, snow melt times were longer than expected – 200 or more minutes to achieve completely bare pavement – but it was demonstrated that 25 °C (77 °F) water in the pipes of a hydronic pavement application can be used to melt snow on the surface of an asphalt pavement.

Adl-Zarrabi et al. (2016) also investigated the impact of hydronic pavement design parameters on pavement snow and ice melting performance. Modeling results showed that if pipe spacing is greater than 20 cm, the time required to melt increases rapidly. Thus, the authors recommended a pipe spacing of less than 20 cm. Also, if the embedded pipe depth is less than 10 cm, the impact of embedded depth is negligible. Pipe spacing had a larger impact on melt performance than pipe depth. In their model, the cost-effectiveness of using solar panels to heat stored fluid was investigated. It was determined that this is not justifiable due to added costs and complexity. Other important design parameters that were not investigated as part of the study included liquid flow rate, size of pipes, and the available amount of solar energy that can be harvested.

Mirzananamadi et al. (2018) also investigated hydronic pavement that used a heating fluid along with the practice of storing summer heat for winter use. Results of a numerical model were

compared to data from a field installation for model validation. Numerical model results indicated that the performance of the system will improve as pipe spacing is decreased, embedded depth of pipe in the pavement is decreased, when larger pipes are used, and when the pavement has lower emissivity. As others have found, the distance between the pipes had the largest impact on snow melt performance.

Through simulation, Liu et al. (2017a) also investigated optimum design of hydronic concrete cement pavement but with electrically heated pipes. Optimum values of pipe spacing and embedded depth were 10 cm and 6 cm, respectively. It was also suggested that power input could be varied depending on if the time required to heat the pavement was important (i.e. high power, short heating time) or if efficiency was important (i.e. low power, longer heating time, but higher efficiency). Liu et al. (2017b) used simulation and laboratory experiments to show that the method could be effective with a power consumption of 100 to 400 W/m as long as the heating pipe spacing is between 10 and 25 cm, the pipe depth is between 6 and 12 cm, and the wind velocity is less than 15 m/s.

Hydrophobic Pavements

Some researchers have investigated the effectiveness of hydrophobic materials used as coatings on asphalt or concrete pavements as a means to reduce ice adhesion strength. For example, Ceylan et al. (2016) sprayed polytetrafluoroethylene (PTFE) in layers on asphalt pavement and found that the ice-repelling performance (as measured by water contact angles) was impacted by the spray time and PTFE dose. The authors concluded that spraying PTFE on asphalt has potential as an ice-repellent surface.

Sobolev et al. (2013) applied superhydrophobic siloxane admixtures to concrete surfaces in order to repel ice. The best water repellent materials (measured by the contact angle) were obtained using polymethyl-hydrogen-siloxane with a small amount of fibers (such as silica fume). The fibers and the extent of the dilution of the emulsion were found to be parameters that greatly influenced the level of hydrophobicity. Diluted emulsions (5% active material) allowed the fiber to produce a hierarchical surface of fibers and aggregates so the material had superhydrophobic properties. When tested, coated mortar specimens had ice shear strengths of about 30 kPa, which was about 10% of value corresponding to uncoated specimens.

Others have, however, found that the ice-repellent performance of hydrophobic surfaces is not long-lasting. Ahlborn and Poehlmann (1976) found that a traffic paint with silicone rubber and a weather proofing material with the same silicone rubber were effective in reducing ice adhesion strengths. They also found, however, that the material was worn off the road surface after 150,000 to 300,000 vehicles drove over the surface. Kulinich et al. (2010) found that the hydrophobic surfaces on pavements are gradually damaged through icing/deicing cycles and that the ice-repellent properties deteriorate over time. It was also determined that the hydrophobic surfaces were less effective during humid conditions due to the condensation of water on the surface, which resulted in much stronger ice adhesion strengths. In a literature review, Chen et al. (2018c) made similar conclusions mostly due to the fact that ice-repelling surfaces are worn off over time due to tire abrasion and that the micro-structure of hydrophobic surfaces are also vulnerable and consumable. Chen et al. (2018c) concluded that hydrophobic surfaces for pavements must still be researched and improved. Thus, although hydrophobic surfaces may have potential as an anti-icing method, the technology appears to still be in the research and development stage and not ready for implementation.

Other Pavement Innovations

The performance of a pavement made with aggregate and polyurethane binder (in place of traditional asphalt binder) with regards to anti-icing and deicing was investigated by Chen et al. (2018b). The polyurethane pavement was compared to the traditional asphalt pavement made with the same aggregate and particle size distribution. The two pavements had similar thermal conductivity values, but the polyurethane pavement had a much higher specific heat capacity. Results indicated the polyurethane pavement can significantly retard the formation of ice on the pavement surface. The pull-off strength and the shear strength at the ice/pavement interface in the polyurethane pavement was about 50 to 55% of that in the conventional asphalt pavement. The authors suggested that polyurethane pavement can provide better anti-icing and deicing performance and increase winter safety as compared to conventional asphalt. No mention, however, was made of the cost.

Observations and Recommendations

The use of road salt in Minnesota has caused chloride concentrations in many lakes, streams, and shallow groundwater bodies to increase to levels that have caused impairment. Similar trends have been observed in other locations within the United States and the world. In an effort to reduce chloride concentrations, research has been performed on road salt alternatives and pavement innovations with the objective of preventing the formation of road ice or melting snow and ice once it is on a roadway. This report is a review of literature associated with such research and is Task 1 of a Legislative-Citizens Committee on Minnesota Resources (LCCMR) 2018 funded project entitled “Investigation of Road Salt Alternatives and Pavement Innovations.” This project seeks to reduce or eliminate the transport of chloride into Minnesota’s lakes, streams, and groundwater. The report reviews previous published research that has investigated the topics of road salt alternatives (RSAs) and pavement innovations, and their environmental impact, with respect to anti-icing and deicing, and pavement friction.

Most potential RSAs are organic based products. Of all the RSAs investigated, the most heavily investigated and reviewed is calcium magnesium acetate (CMA). CMA, however, is not effective at lower temperatures than road salt, and therefore does not offer intrinsic advantages over road salt. Other commonly reported RSAs include other forms of acetate, formate-based products, glycol and glycerol, and succinate-based products. The current trend is to move to potassium acetate, which is effective at lower temperatures than road salt. In general, all of these products have higher monetary costs than road salt, are less corrosive to steel, and have a relatively high BOD. Other RSAs have been investigated and most of those are also organic based. They mostly consist of agricultural byproducts such as molasses, beet juice, corn processing products, and urea, which typically are applied with a chloride-based salt, although at reduced application rates.

Studies that have investigated the performance of RSAs with respect to anti-icing, deicing, or road friction have been reviewed. In general, RSAs are less effective in terms of quantity required than conventional road salts and, if equal performance (as compared to road salt) is desired, a greater amount of RSA must be used. Some studies, however, have found that using RSAs in combination with road salt (as an anti-icer or deicer) can increase salt effectiveness and, therefore, can reduce chloride use.

Due to their organic nature and eventual degradation, a common environmental concern of RSAs is BOD. In fact, some authors state it is the main concern with respect to RSAs. The many studies that have investigated the BOD of RSAs have generally concluded that the depletion of dissolved oxygen caused by RSAs will typically be small unless relatively large amounts of RSAs are transported to a small water body close to the roadway. Warmer temperatures or ice cover on the receiving water body can increase the impact due to faster degradation rates and the prevention of surface reaeration, respectively. Also, the conclusion that there will typically be a relatively small impact on dissolved oxygen has been supported for calcium magnesium acetate by at least two model studies.

Other studies have investigated the toxicological effect of RSAs on specific species of plants, invertebrates, or animals. Although toxicological impact has generally been found to be minimal and most investigators have concluded that organic RSAs have low toxicity, some have found direct negative effects on certain species and have recommended additional research. In particular, Pilgrim (2013) reports that a commercial potassium acetate product (CF-7) is more toxic to fathead minnows and an invertebrate than a number of chloride-based de-icing and anti-icing compounds.

The use of abrasives, such as sand and grit, to increase winter road friction was also reviewed. Although abrasives can cause negative environmental impacts ranging from increased water turbidity, lack of oxygenation, and decreased fish reproduction rates to air pollution, abrasives are still used for winter road maintenance. Small particles, which are the most difficult size to remove from stormwater runoff, likely cause most of the environmental impact but have also been shown to contribute minimally to increased road friction. Sweden uses larger particles (up to 4 and 8 mm diameter), which are easier to remove from stormwater runoff through settling and/or filtration processes. Also, simply placing abrasives on the road surface has been shown to be ineffective due to the fact that most of the abrasive particles either bounce off or are blown off the road relatively quickly. Pretreating the sand with hot water and/or by heating it just prior to road application, however, has been shown to cause an increase in road friction that can last for several days. An improved application of abrasives may be sufficient where speeds are low, such as residential streets and parking lots. This would reduce chloride use substantially.

Most pavement innovations designed with the intention of reducing the need for road salt can be grouped into one of the following four categories: 1. Adding conductive elements to the pavement mix design so the pavement surface can be more efficiently heated, 2. Adding anti-icing or deicing agents to the pavement mix design that are released at the pavement surface over time, 3. Hydronic pavements, which incorporate heating pipes into the cross-section of the pavement, and 4. Hydrophobic pavement coatings to reduce ice adhesion strengths. All have shown potential as a method to reduce dependence on road salts, but no full-scale applications have been documented. One pavement innovation with potential for future research is hydrophobic pavements, which require more research, including an assessment of how well they would work in field applications.

Overall, whether by RSA or pavement innovations, much research has been performed with the intention of ultimately reducing or eliminating the use of road salt. Although many studies have shown potential, further research is needed to fully optimize the implementation of pavement innovations in full-scale, practical applications. RSAs are more expensive and require more mass per road mile than chloride-based products, have high BOD, exhibit some toxicity, and can alter ecosystems. However, they result in clear roads during the winter months, similar to road salt, and they will likely not have long-term impacts as opposed to chloride-based salts. In addition, potassium acetate is currently being deployed for anti-icing at low temperatures, so some RSAs also can improve the level of service provided. Thus, it is our recommendation that the environmental impact and friction enhancement of RSAs, in particular potassium acetate, be further explored.

Although abrasives have been shown to have negative environmental impacts, those impacts can likely be reduced by selecting particles of larger size, which can be removed more easily than smaller particles. Because small particles do nothing to increase road friction, there will likely be no drop in effectiveness. Furthermore, the increase in road friction with pre-treated abrasives (either wetted or heated) has been shown to last for several days. Unlike chemical based RSAs, the abrasives will have little or no impact on BOD, little or no toxicity on aquatic life, and may be able to be collected after the winter and used again the following year. If the use of abrasives and corresponding pre-treatment methods are optimized for use on low speed

locations, effective winter road maintenance on these locations with minimal chemical and biological impact, including the reduction of chloride in the environment, may be possible.

There is no one treatment that will reduce chloride load to our lakes, rivers and groundwater. Some countries in northern climates have successfully reduced their chloride load through the use of road salt alternatives, in improvements across design of pavements and design and placement of roads, bridges, and sidewalks, in optimizing the physical form (liquid or granular) of the material applied, the timing of the material applied, the amount of material applied, the spread pattern of material applied and the chemical make up of the material applied, and finally in improvements in mechanical snow/ice removal equipment. Such efforts would create a more efficient and effective winter maintenance industry.

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