Environmental Impacts of Potassium Acetate as a Road Salt Alternative (University of Minnesota evaluation)

John Gulliver, Principal Investigator
St. Anthony Falls Laboratory
University of Minnesota

JULY 2022

Research Report
Final Report 2022-27A

To request this document in an alternative format, such as braille or large print, call 651-366-4718 or 1-800-657-3774 (Greater Minnesota) or email your request to ADArequest.dot@state.mn.us. Please request at least one week in advance.

Technical Report Documentation Page

1. Report No. MN 2022-27A	2.	3. Recipients Accession No.
4. Title and Subtitle Environmental Impacts of Potassium Acetate as a Road Salt Alternative (University of Minnesota evaluation)		5. Report Date July 2022
		6.
7. Author(s) John S. Gulliver, Chan Lan Chun, Peter T. Weiss, Andrew J. Erickson, William Herb, Jerry Henneck, Kathryn Cassidy		8. Performing Organization Report No.
9. Performing Organization Name and Address St. Anthony Falls Laboratory, University of Minnesota Minneapolis, MN Natural Resources Research Institute, University of Minnesota Duluth, MN Valparaiso University, Valparaiso, IN		10. Project/Task/Work Unit No. CTS #2020019
		11. Contract (C) or Grant (G) No. (c) 1034767
12. Sponsoring Organization Name and Address Minnesota Department of Transportation Office of Research & Innovation 395 John Ireland Boulevard, MS 330 St. Paul, Minnesota 55155-1899		13. Type of Report and Period Covered Final Report
		14. Sponsoring Agency Code

15. Supplementary Notes

https://www.mndot.gov/research/reports/2022/202227A.pdf

See related report "Environmental Impacts of Potassium Acetate as a Road Salt Alternative (Iowa State University evaluation)" by C. Rehmann at https://www.mndot.gov/research/reports/2022/202227B.pdf.

16. Abstract (Limit: 250 words)

Road salt (NaCl) is used predominantly across the state for winter road anti-icing (as brine) and de-icing (as a solid) operations. Road salt is used because it is inexpensive and effective, but the thousands of tons used annually have resulted in increasing chloride concentrations of surface water bodies throughout Minnesota. In many cases, chloride concentrations are above regulatory limits, which results in the loss of aquatic biota and the water body being labeled as impaired. Thus, there is a need for one or more road salt alternatives (RSAs) that are effective, relatively inexpensive, and environmentally friendly. This report investigates the environmental impacts of potassium acetate (Kac), which is effective at lower temperatures than most other potential RSAs and is also less corrosive to steel than conventional road salt. Field measurements indicate that current applications of KAc do not have a substantial influence on biochemical oxygen demand (BOD) and microbiological water quality in Lake Superior. However, KAc concentrations due to application to 25% of the roads in the Miller Creek watershed are predicted to be above the toxic limit for water fleas. 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.

17. Document Analysis/Descriptors Sodium chloride, Potassium, Acetates, Deicing chemicals, Environmental impacts, Toxicity, Calcium magnesium acetate	18. Availability Statement No restrictions. Document available from: National Technical Information Services, Alexandria, Virginia 22312

19. Security Class (this report) Unclassified	20. Security Class (this page) Unclassified	21. No. of Pages 164	22. Price

Environmental Impacts of Potassium Acetate as a Road Salt Alternative (University of Minnesota evaluation)

Final Report

Prepared by:

John S. Gulliver[1]
Chan Lan Chun[2]
Peter T. Weiss[3]
Andrew J. Erickson[1]
William Herb[1]
Jerry Henneck[2]
Kathryn Cassidy[2]

[1]St. Anthony Falls Laboratory, University of Minnesota
[2]Natural Resources Research Institute, University of Minnesota Duluth
[3]Valparaiso University

July 2022

ACKNOWLEDGEMENTS

Table of Contents

List of Figures

List of Tables

Executive Summary

Road salt (NaCl) is used predominantly across the state for winter road anti-icing (as brine) and de-icing (as a solid) operations. Road salt is used because it is inexpensive and effective, but the thousands of tons that are used annually have resulted in increasing chloride concentrations of surface water bodies throughout Minnesota. In many cases, chloride concentrations are above regulatory limits, which results in the loss of aquatic biota and the water body being labeled as impaired. Thus, there is a need for one or more road salt alternatives (RSAs) that are effective, relatively inexpensive, and environmentally friendly.

Research has led to the identification of various RSAs, most of which are organic compounds. One such group of RSAs are acetate-based, and this group includes potassium acetate. Potassium acetate (KAc) is effective at lower temperatures compared to most other potential RSAs (See Table 1.7) and is also less corrosive to steel than conventional road salt. KAc is, however, more expensive than road salt and, as an organic compound, exerts biochemical oxygen demand (BOD) when it is degraded by microorganisms in water or soil. Thus, there is concern that extensive use of KAc will result in the depletion of dissolved oxygen in water bodies near roads that receive KAc. There is also a concern regarding the toxicity toward fauna and flora of the potassium ion within KAc.

No literature was found that investigated the impact of KAc on dissolved oxygen levels of nearby water bodies, but field investigations and model studies have been performed on such impacts related to calcium magnesium acetate. All such studies have indicated that dissolved oxygen depletion will likely not rise to levels of concern at KAc concentrations that are expected to result from winter road applications if water bodies are not located close to the road and are not small ponds or slow-moving streams. Potassium acetate may, however, be more toxic toward fauna and flora than other RSAs, including other acetate-based RSAs.

When applied to winter roads, some KAc will be transported into the soil where it can be degraded by microorganisms. Potassium is a necessary plant nutrient, but at high concentrations it could be detrimental to the health of vegetation. Very little literature, however, was found on this topic. When in soil, the potassium ion can be adsorbed to soil particles through ion exchange processes. This process can release metal ions, thus KAc use can increase the mobility of metals in soils.

Potassium acetate can damage concrete pavements through alkali-silica reactions (ASR) or similar reactions, and it can damage asphalt pavements through ASR, binder softening, stripping, moisture damage, and the loosening of aggregates. Some studies have questioned the correlation between KAc use and concrete pavement damage and the exact processes are not fully understood, but it is clear that KAc can cause damage to pavements in laboratory settings.

Finally, although KAc is not as corrosive to steel as road salt, it is corrosive to galvanized steel, and this could be of concern near guard rails and other structures or vehicles containing galvanized steel parts. More research is needed to fully understand the processes involved in pavement degradation caused by

KAc and the exact relationship between its use in the field and concrete and asphalt pavement damage. More research is also needed to fully understand the toxicity of KAc and the potassium ion in soil and water environments toward the many organisms that it could impact.

0.2 TOXICITY ASSESSMENT

The toxicity of CF7, a KAc-based alternative anti-icer and deicer, to terrestrial and aquatic fauna and flora was assessed to understand if the chemicals in receiving water bodies and on the roadside after CF7 application affect vegetation and aquatic life in proximity to roads. This study reports the toxicological endpoints of CF7 and its relevant salts for roadside grasses and water fleas. Germination experiments of roadside grasses, sheep fescue (*Festuca ovina*) and switchgrass (*Panicum virgatum),* were designed for the toxicity test for terrestrial flora. To assess aquatic toxicity of CF7, water fleas (*cladocerans*) were selected as sensitive indicators for acute toxicity tests. In addition to determination of toxicological endpoints, the toxicity experiments were designed to inform us which ionic species (K^+, Ac^-, the combination or CF7 additives) is responsible for toxicological effects in each case.

Overall, both CF7 and pure KAc have lower toxicological endpoints (EC_{50} and LC_{50}) for both roadside grasses and water fleas in comparison to NaCl, indicating the organisms were more sensitive to KAc at lower concentration than NaCl. Based on toxicological endpoints, there is no statistical difference between CF7 and KAc, suggesting the contribution of additives in CF7 to overall toxicity was minimal. The acetate anion (Ac^-) of KAc was found to be responsible for sensitivity of grass seed germination while potassium ion (K^+) was attributed to acute toxicity for water fleas.

The seed germination experiment revealed that the effects on seed germination begin between 20 and 50 mM. Even though seed germination is affected by CF7 at lower concentrations than NaCl, the concentration at which germination is impaired is rarely reached in the field. The concentration of 20 mM CF7 at which deleterious effects occur is equivalent to 2 g/L CF7 as KAc. Soil concentrations of NaCl have been reported to reach 1.5 g/L (Pederson et al., 2000) and are unlikely to reach the EC_{50} of 5 g/L CF7 due to dilution from roadside snowmelt.

However, for aquatic toxicity, the LC_{50} endpoints could be surpassed if CF7 is applied to roads draining into a smaller water body than Lake Superior. The field evaluation (Chapter 3) of CF 7 application to Blatnik bridge and I-35 indicate K^+ concentration did not reach concentrations causing acute toxicity to aquatic life in Lake Superior except for one location. It was observed that the concentration of K^+ may briefly surpass the LC_{50} endpoint in the protected bay site (Rice's Point) during spring melt but is likely to be diluted quickly. However, if CF7 application is expanded to other roadways that have runoff draining into smaller waterbodies, the probability of surpassing the LC_{50} in waterbodies with less dilution is greater. The LC_{50} endpoints for *C. dubia and D. magna* are valuable in determining if the runoff carrying CF7 will result in toxic effects in receiving waterbodies.

Future work in vegetative toxicity could expand the roadside species tested and move beyond petri dishes to a field study. Salinity causes toxicity by osmotic potentials preventing water uptake or direct ion toxicity, but in the field, the soil texture and chemistry would be additional factors that can impact vegetation. Likewise, growth of seeds in soil rather than salt solutions would also take cation exchange

capacity into consideration, as high inputs of a cation from the anti-icer and deicer have been shown to replace other cations such as calcium and magnesium on exchange sites, removing them from potential uptake by the plant (Hartl and Erhart, 2002).

Lastly, it is important to conduct toxicity tests for several aquatic and terrestrial flora and fauna relevant to the application sites, as the previous studies have reported variable toxicological response to anti-icer and de-icer salts among different organisms. For example, Joutti et al. (2003) also found that KAc anti-icer and de-icer was much more toxic to onions and duckweed than NaCl was, similar to the results in this work, but potassium (K^+) was identified as an agent of toxicity, which differs from the findings of this study. Conversely, Gerasimov (2021) found that KAc and sodium formate were less harmful to wheat root growth and biomass than NaCl. Despite that, minimal variation between grass species was observed in our study, with the Vigor Index showing sheep fescue has increased growth at 10 mM, and the germination of sheep fescue was slightly more sensitive to salinity of acetate salts than switchgrass. While two grass species were studied among the many grasses, forbs, and wildflowers found along roadsides, the similarity in response of switchgrass and sheep fescue to salinity was promising in that these effects can be broadly applied to grass species.

0.3 FIELD INVESTIGATIONS

MnDOT selected KAc, a liquid anti-icer and de-icer, as a non-corrosive alterative to NaCl that can be effective down to -26°F (Fay et al., 2015) for Duluth winters. Potassium acetate anti-icer was applied on I-35, Blatnik Bridge, and Central Entrance in the winter of 2019-2020. The fate and transport of KAc-containing runoff in Duluth was analyzed in the winter of 2019-2020 by collecting and analyzing meltwater runoff and receiving water body samples. KAc levels were observed to be up to 1000 mg/L while NaCl levels were also high, surpassing 20,000 mg/L in the runoff. These high levels of chloride entering sensitive freshwater systems emphasized the potential impact of chloride-based anti-icers and de-icers. The results of the 2019-2020 study show that KAc application did not have a significant influence on BOD and microbiological water quality, as BOD and *E. coli* concentrations in stormwater from KAc application sites were comparable to those of upstream NaCl sites.

Winter stormwater sampling presented several challenges such as cold safety, low flow rate, sample volume and tall bridges. Lessons learned through the challenges in the winter of 2019-2020 informed our practices for a successful second field season. The winter of 2020-2021 used both automated and grab sampling, with an effort to take composite samples with autosamplers whenever possible. Adjustments to Blatnik Bridge such as extending the drainage pipe increased bridge runoff sample frequency. Further sample collection and analysis provided a larger dataset of water chemistry and microbiology to better understand KAc impacts. Improvements to the weir and adapter system yielded an improved quality of flow data.

The water chemistry and microbiological water quality of KAc-containing runoff in Duluth in the 2020-2021 winter was assessed by collecting and analyzing meltwater runoff and receiving water body samples. The study of the 2020-2021 winter focused on fate of KAc and other water constituents in runoff at KAc application sites and water body receiving their runoff while the study of the 2019-2020

winter evaluated upstream sites from KAc application (NaCl sites) in addition to stormwater drains of KAc application and receiving water bodies.

In the 2020-2021 winter, KAc levels in collected samples were observed to be up to 12,000 mg/L while NaCl levels were also high, surpassing 18,000 mg/L in the runoff. Potassium acetate concentrations were much greater than those in runoff samples collected in the 2019-2020 winter. This may be due to the improved sampling methods to capture initial melt water from roadways. As acetate is degradable in receiving water body, potassium level was a good indicator of KAc level in the runoff to evaluate long-term impacts of KAc application. In contrast to high concentration of KAc and NaCl in road runoff samples, the concentration of anions, cations, and BOD_5 in Lake Superior water receiving the runoff was low and relatively stable except for in shallow receiving water bodies with limited mixing in March when snowmelt occurred.

In contrast to the results of the 2019-2020 winter, KAc application appears to moderately increase the levels of BOD_5 and fecal indicator bacteria (FIB), an indicator for microbiological water quality. This is particularly true in certain areas of the lake with less mixing and volume. Currently, KAc is only applied to roadways discharging stormwater into Lake Superior where runoff is usually mixed with larger quantities of lake water by waves and currents. If KAc application were to be expanded, runoff from roadways draining into creeks or smaller lakes could result in a high oxygen demand and toxicity to fauna in the aquatic biota. Interestingly, the Lake Superior water was oxygenated on the sampling dates when BOD_5 and KAc were high in the water, indicating that oxygen transfer was sufficient to avoid deleterious effects of oxygen depletion on aquatic life. However, in cases of runoff with a high BOD_5 entering stagnant or small areas of water, oxygen transfer may not be sufficient to prevent a decrease in oxygen from the BOD of the stormwater.

In addition to field evaluation, the rate and extent of degradation of acetate in Lake Superior water under cold temperatures were determined as a function of CF7® concentration in the laboratory. The biodegradation of acetate in Lake Superior water occurred under a cold temperature (4°C) with lag time of 9-30 days. After the lag time, the half-life of the acetate in the Lake Superior water was 0.6-3 days at room temperature and 1.5-5 days at 4°C. The results also indicate that there may be additional reaction pathways to degrade acetate in addition to biological degradation. The experiments also provided acetate stability and storage time of filtered field samples for the analysis.

The results of field measurement and the laboratory KAc degradation experiment were useful for modeling the watershed impacts of KAc use as a road salt alternative as initial input parameters and boundary conditions. Particularly, the two-year field measurement data showed the spatial and temporal variation of KAc concentration and other water chemistry parameters in stormwater runoff and receiving water. This information can be used to develop various scenarios (e.g., receiving water body size, distance from the road, precipitation, KAc application) for watershed modeling to predict the impact of KAc on dissolved oxygen (DO) concentrations of road runoff and receiving water bodies by verifying with the field measurement data.

In summary, a field evaluation of the application of CF7 as an anti-icing or a de-icing agent has determined the fate and transport of KAc in Lake Superior after application. Understanding the range of

concentrations of K^+ and Ac^- found in the highway or bridge runoff will inform future modeling work on the watershed impacts of KAc use. While the scope of this evaluation was narrowed to the impact of stormwater on Lake Superior, watershed modeling can determine the potential impacts on lakes and streams if CF7 use were to be expanded.

0.4 MODELING ENVIRONMENTAL IMPACTS OF POTASSIUM ACETATE

The potassium concentrations due to KAc application as an anti-icer to 25% of the roads in the Miller Creek watershed were predicted to be above toxic limit for water fleas. Broader application of KAc (e.g., all roadways, and all roadways plus parking lots) exacerbated the amount of time the toxicity threshold was exceeded. Potassium, especially, is a chemical with a low LC_{50} for water fleas and is a concern for the broad application of KAc. 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 modeling effort focus on estimating concentrations of KAc 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 effort 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 (French et al. 2001). Thus, it is possible that some acetate could appear in baseflow. If, however, the acetate concentration were 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 report are based on an analysis of the Miller Creek watershed in Duluth, Minnesota. Other watersheds with similar climate conditions, watershed response to precipitation, and application rates of anti-icers/de-icers 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.

1 LITERATURE REVIEW

Prepared by:

Peter T. Weiss[3] and John S. Gulliver[1]

[1]St. Anthony Falls Laboratory, University of Minnesota
[3]Valparaiso University

December 2019

1.1 INTRODUCTION

To prevent or reduce snow and ice cover during the winter season, over 100,000 tons of road salt are applied to Minnesota's roads each year (MnDOT 2019). This salt, typically NaCl, has a negative impact on vehicles, pavement, and metal structures (e.g., bridges) due to corrosion and has led to increasing chloride concentrations in water bodies throughout the state. In some cases, chloride concentrations exceed regulatory limits, which requires action to reduce concentrations. Even in water bodies where chloride concentrations do not exceed regulatory limits, concentrations in some lakes will continue to rise if current road salt usage rates do not decline (Novotny and Stefan 2010). Similar patterns exist in many cold climate states throughout the country and in other countries where road salt is used. As a result, the identification and/or development of a cost-effective and environmentally safe road salt alternative (RSA) has been the focus of many studies. One such potential alternative is potassium acetate (KAc), with structure CH_3COOK, which is more effective at lower temperatures than other potential RSAs and less corrosive to steel than chloride-based products. It is, however, much more expensive than common road salt and has other associated concerns such as biochemical oxygen demand (BOD) and toxicity. Potassium acetate is already used in some locations in Minnesota (i.e., Duluth), and if its use is going to continue or increase, it is desirable to understand more about its performance, properties, and impact on the environment. The objective of the project is to investigate the performance, corrosiveness, environmental impact, and corresponding properties of KAc when used as a RSA.

This report first focuses on KAc and the above-mentioned corresponding aspects and issues with its use as a RSA. Following the discussion of KAc, for comparison, a summary of other RSAs including acetate-based products, glycol and glycerol, formate-based, and succinate-based products is presented. This summary covers such topics as cost, performance, corrosivity, and environmental impacts.

1.2 POTASSIUM ACETATE

Over the past several decades many potential RSAs have been investigated to determine their water solubility, ability to lower the freezing point of water, corrosiveness, toxicity, cost, environmental impact, and flammability (Boice 1986). Most RSAs are organics and one such compound is KAc, which is

one of three acetate-based products that have been identified as potential RSAs. The others are sodium acetate and calcium magnesium acetate (CMA). As mentioned below, KAc is often preferred because it has a lower effective temperature than many other RSAs.

1.2.1   Overview and Effectiveness

Although most published research has been completed on CMA, KAc 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. More specifically, KAc has an effective temperature range of 32 °F down to -26 °F, whereas most other RSAs are only effective down to 0 °F, at best (Fay et al. 2015).

The main advantage of KAc (and 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). 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). The KAc corrosion rate of aluminum was equal to the corrosion rate for chloride (Levelton Consultants 2008).

With regards to cost, acetates are significantly more expensive than chloride-based anti-icer and de-icers and, therefore, are mostly used at airports and where steel corrosion is a concern, such as on 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 anti-icer and de-icers (Boice 1986, Fay and Muthumani 2017). Potassium acetate is typically applied at 60-80 gallons per lane mile when used as a deicer and 25-60 gallons per lane mile when used as an anti-icing agent. The cost of KAc is $600-$1200 per ton or, with an assumed density of 10.7 lbs/gal, $192-$512 per lane mile. The current State of Minnesota contract is $3.93 - $4.28/gallon of 50% KAc. Assuming the same application rate, this corresponds to $197 - $526 per lane mile. Based on costs and application rates presented by Fay et al. (2015), this compares to less than $40 per lane mile for NaCl.

Acetates 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). Also, although they have potential to help reduce chloride loadings to surface waters in the state, acetates including KAc have other negative environmental impacts that will be discussed later.

Fay and Shi (2011) investigated several RSAs, including KAc, for ice melting ability, ice penetration, ice undercutting, freeze-thaw resistance of portland cement concrete exposed to the anti-icer and de-icers, friction of deiced concrete surface, thermal properties of the anti-icer and de-icers, and their effect on the corrosion of metals. Four top performing RSAs were identified based on their ice melting, penetration, and undercutting ability. Three of the four were chloride-based products and the fourth was the commercial product, CF-7, which is 50% aqueous KAc solution, by weight, plus corrosion inhibitors. Thus, although there are some challenges to using KAc, it clearly has potential to help alleviate the chloride problem that is building in our surface waters.

After a review of literature focusing specifically on KAc as it relates to 1) environmental impacts and toxicity, and 2) corrosion and pavement damage, a general review of several of the most common RSAs follows. This general review compares acetate-based RSAs, formate-based RSAs, glycol and glycerol, succinate-based RSAs, and other RSAs in terms of performance, cost, corrosivity, and environmental impacts.

1.2.2 Environmental Impacts and Toxicity of Potassium Acetate

Potassium acetate is an organic salt that can have impacts on the environment in addition to helping reduce snow and ice on winter roads. As an organic compound, it can be degraded by organisms and this can cause a reduction in oxygen in soil and in water. It can also impact other organisms including flora and fauna and, if concentrations are high enough, it can be fatal. This section summarizes available literature that has investigated these issues.

1.2.2.1 BOD and COD

Several investigators have reported the biochemical oxygen demand (BOD) and/or the chemical oxygen demand (COD) of KAc. Mussato and Guthrie (2000) investigated the BOD of four acetate-based anti-icer and de-icers in the laboratory and found that all four had values over 100,000 mg/L. Values over 100,000 mg/L are considered high and likely to cause oxygen depletion of surface waters. In a review of pollution at airports, Sulej et al. (2012) found BOD_5 values for KAc to be 315,000 mg/kg. Corsi et al. (2012) found the COD of KAc to be 315,000 mg/kg (250,000 mg/L) and the BOD_5 to be 247,000 mg/kg (196,000 mg/L), which falls within the range of BOD_5 reported by the US EPA (2000) of 140,000 – 300,000 mg/kg. Corsi et al. (2012) also found that sodium formate anti-icer and de-icers had lower COD values than acetate-based anti-icers and de-icers but that the BOD and COD of KAc were lower than glycol-based anti-icers and de-icers used on airplanes. Corsi et al. (2012) determined the BOD of KAc at 5, 15, 28, and 40 days at both 68 and 41 °F (20 and 5 °C). Results are shown in Table 1.1 below.

Table 1.1. Values of BOD (mg/kg) at 68 and 41 °F (20 and 5 °C) by day as reported by Corsi et al. (2012).

Day	68 °F (20 °C)	41 °F (5 °C)
5	864,000	320,000
15	1,020,000	807,000
28	970,000	894,000
40	993,000	897,000

Nolan Davis (1994) found that acetate can be broken down by bacteria but it is more stable than formate. In their investigation, Nolan Davis (1994) found that KAc significantly increased BOD_5 but the cause was difficult to determine. Results suggested that acetate was diluted and dispersed while being flushed off the site rather than degraded. Acetate concentration correlated well with flow rate. As the flow rate dropped, so did the acetate concentration, indicating a decrease in physical flushing was

occurring, not degradation. Lab experiments also showed that acetate didn't degrade unless fertilized with phosphate and possibly ammonia.

In the airport conditions of the Nolan Davis (1994) investigation, KAc did not degrade in the normal residence time of the surface water system. One possible reason for the correlation between KAc application and increasing BOD was that there may have been extra caustic compounds in the commercial product that caused a temporary increase in pH that, in turn, caused an increase in biological activity. Whatever the cause, the BOD_5 levels were equivalent to a stream that had been polluted with raw sewage. Also, BOD_5 tests were done at 15 °C and the temperatures at the airport were much colder. The lower temperatures likely slowed biological activity in the field.

Although Horner and Brenner (1992) investigated CMA, they also observed the effect of temperature on BOD rates. In their study it took 5, 10, and 100 days to exert the BOD of CMA in water at 68, 50, and 35.6 °F (20, 10, and 2 °C), respectively. A similar trend with temperature would likely exist for KAc. Potassium acetate applied to a roadway would likely be diluted by the time it traveled to a water body. Fischel (2001), for example, stated that as anti-icers and de-icers travel from the roadway to nearby water bodies, dilution is estimated to be 100 to 500 times and, as a result, oxygen depletion is only likely to occur in slow moving streams or small ponds. McFarland and O'Reilly (1992) modeled CMA and found that most of the acetate applied in the winter would be degraded before reaching receiving water bodies.

The acetate ion can also be degraded in the soil by soil microorganisms and this may result in soil oxygen depletion, which, in turn, may have a negative effect on vegetation (Fischel 2001). Field evidence of this effect, however, is limited. Defourny (2000) found that the half-life of acetate in soil at 45 °F (7 °C) was less than two days. Hellstén and Nystén (2003) found that organic anti-icers and de-icers increased the pH of soils and reduced levels of nitrogen and phosphorus. They also observed that formate degraded more quickly than acetate at temperatures of 37 – 43 °F (3 – 6 °C). With regards to potassium, it is usually in high concentrations in soil (20000 ppm) but only 100 ppm is available as a plant nutrient (Schulte and Kelling 2004). Too much potassium, however, can cause problems, such as calcium inhibition and the interference with the uptake of other substances.

1.2.2.2 Degradation Rates and Transport

As stated, KAc has been found to biodegrade in water and soil. However, Nolan Davis (1994) found that potassium and acetate concentrations at monitoring stations increased after storm events. They concluded that KAc is stable and primarily removed from the application site by flushing, dispersion, and dilution. Any degradation that does happen will occur as KAc moves overland (or as shallow groundwater flow) from the pavement surface to a water body. Thus, not only are degradation rates important when considering how much KAc will be biodegraded before it reaches a water body, but transport processes are important as well. This section summarizes the limited number of studies that have reported on these processes.

Stevenson and Katznelson (1958) found that acetate degradation follows first-order reaction kinetics. French et al. (2001) performed field experiments in Norway that investigated the transport and degradation of propylene glycol and KAc with non-reactive tracers using a lysimeter trench and natural

snowmelt conditions. Samples of infiltrated water containing anti-icer or deicer, which were taken 0.4 to 2.4 meters below the surface, were analyzed and the results used to estimate rate constants and retardation factors. The soil degradation rate constant for acetate was found to be 0.02 1/day during snowmelt conditions. Retardation factors of 1.34 and 1.24 were determined for potassium and acetate, respectively. The KAc was initially transported quickly into the soil during the melt season but experienced no movement during the summer.

Revitt and Worrall (2003) investigated the biodegradability of aircraft de-icers between 32 and 50 °F (0 and 10 °C) including one product, Clearway, which is KAc-based. The Clearway degradation rate constants measured at 34, 39, and 46 °F (1, 4, and 8 °C) were 0.048, 0.033, and 0.036 /day, respectively. The uncertainty in these measurements were not quantified, but must be substantial, because the 0.048 degradation constant at 1° C does not make sense compared to the other values. The other two compounds tested were glycol-based and both exhibited more biodegradation than Clearway.

Hellstén et al. (2005) used lysimeters to investigate the fate of potassium formate in winter and spring. It was determined that 99% of the potassium was retained in the soil via ion exchange processes but, as a result, the soil released barium, calcium, magnesium, and sodium. It was concluded that if potassium formate was applied for several years, potassium may leach into the groundwater. Davis et al. (1993), however, reported that KAc did not penetrate groundwater aquifers and did not affect water chemistry.

1.2.2.3 Toxicity

Several studies have investigated the toxicity of KAc to plants, animals, or microorganisms. This section summarizes such studies. In one such study, field tests were conducted on KAc to evaluate its effects on vegetation (Nolan Davis 1994). It was determined that, if used at concentrations below 500 mg/L, as is typically done during anti-icing operations, there was little or no inhibition of surface vegetation. At concentrations of 1000 mg/L, however, plant growth was inhibited by almost 50%. Concentrations this high would only be observed if pure reagent was spilled on the ground. Nolan Davis (1994) in a limited investigation also found no effects of KAc on phytoplankton, periphyton, or macroinvertebrate abundance. They did note that small changes may have not been detected, however, due to the high variability in the data. Also, KAc did not affect in-situ concentrations of bacteria (anaerobic, aerobic, psychrophilic, or mesophyllic) or psychrophilic or mesophyllic fungi. There was also no change in soil respiration characteristics. In summary, Nolan Davis (1994) found that KAc had no detectable impact on groundwater, vegetation, and other soil and stream life. The only impact it did have on surface water was the increase in BOD.

With regards to potassium, there is not much information in the literature, but potassium is a plant nutrient and is typically part of fertilizers. Plants are tolerant of high levels of potassium but at high application rates it can increase osmotic pressure of the soil. As discussed above, potassium does have the potential for cation exchange and, through this process, can increase the mobility of metals. Overall, potassium has low potential for air quality impairment, low to moderate potential for soil impairment (it improves soil structure and increases permeability) and has low potential for vegetation and animal impairment (Levelton Consultants 2008).

Ellis et al. (1997) reported that the airplane deicer, *Clearway 1*, which is KAc-based, was being investigated as a non-toxic deicer due to alleged lack of death of rainbow trout when they were exposed to 100 mg/L for over 48 hours. It was not clear if the reported concentration was 100 mg KAc per liter or 100 mg of *Clearway 1* per liter.

Joutti et al. (2003) investigated six different anti-icers and de-icers for toxicity including KAc, CMA, potassium formate, and three chloride salts. Tests performed were a root elongation test on onion (*Allium cepa*), a growth inhibition test on duckweed (*Lemna*), and a microbial test on luminescent bacteria (*Vibrio fischeri*). Overall, the organic anti-icers and de-icers were more toxic than the chloride salts with potassium formate being most toxic and KAc ranking second in toxicity. These two top toxic anti-icers and de-icers were substantially more toxic (up to one or two orders of magnitude) than the others as measured by a toxicity classification system (Bulich 1982) and, according to that same rating system, were "very toxic" to onion and duckweed. It was noted that the anti-icers/de-icers used in the study may have contained anti-caking substances such as iron cyanide that may have affected results. Fischel (2001), however, in a review of different RSAs including products containing KAc (CF-7 ®), sodium acetate (NAAC ®), and a mixture of CMA and KAc (CMAK™), stated that KAc is not harmful to terrestrial vegetation at concentrations typically used on roads.

Harless et al. (2011) conducted 96-hour acute toxicity tests on larval wood frogs for urea, sodium chloride, magnesium chloride, KAc, calcium chloride, and CMA. Larval were least sensitive to urea, sodium chloride, and magnesium chloride and were most sensitive to CMA, KAc, and calcium chloride. Toxicity varied greatly and the authors suggested more research be done to determine effects on other species.

Cheng and Guthrie (1998) reported that KAc has a LD_{50} (i.e., the dose that is lethal to 50% of the population) of greater than 5000 mg/kg in rabbits and an acute oral toxicity in rats of 3250 mg/kg. The authors stated that there are no serious human health effects associated with KAc and it is not a carcinogen. Potential minor health effects include skin, eye, respiratory, and GI tract irritation (Cheng and Guthrie 1998). According to the material safety data sheet (MSDS), in young children or adults with kidney or heart disease, KAc can cause inflammation or irritation of their stomach lining, weakness in muscles, a slower or irregular heartbeat, reduced blood pressure, or burning, tingling, and numbness in their hands and feet. These effects have been attributed to the potassium.

Levelton Consultants (2008) also investigated the toxicity of KAc. Their results are in Table 1.2 below.

11

Table 1.2. Toxicity endpoints from Levelton Consultants (2008).

Endpoint Concentrations (mg/L) for Fathead minnows:
96 hr LC$_{50}$: 1033
7-day LC$_{50}$: 907
7-day IC$_{25}$: >788
7-day IC$_{50}$: >788
Selenastrum capricornutum toxicity testing endpoints (mg/L)
96-hr IC$_{25}$: 2373
96-hr IC$_{50}$: 3535
Ceriodaphnia dubia toxicity testing endpoints (mg/L)
3 Brood LC$_{50}$: 1994
3 Brood IC$_{25}$: <25
3 Brood IC$_{50}$: <25

LC$_{50}$ = concentration that is lethal to 50% of the population
IC$_{25}$ = concentration which would cause a 25% inhibition in reproduction or growth
IC$_{50}$ = concentration which would cause a 50% inhibition in reproduction or growth

Pilgrim (2013) reviewed results from other studies that have investigated the toxicological acute and chronic endpoints of anti-icing/de-icing compounds are summarized. Those summaries, which are reproduced in Tables 1.3 and 1.4, show that, while there is variability, the ranked order of toxicity from high to low is potassium chloride, magnesium chloride, and then sodium and/or calcium chloride. It also appears that acetate, when combined with potassium, is more toxic than when sulfate or chloride is the anion.

Table 1.3. Acute and chronic toxicological endpoints for chemicals (Pilgrim 2013).

Chemical	Species	Test Endpoint	Test Duration	Concentration (mg/l)	Reference
NaCl	Ceriodaphnia dubia	EC50	7 Days	2340	Evans and Frick 2001
		IC25	7 Days	1010	Sanders 1993
				910	Stark 1999
		LC50	2 Days	2308	Cowgill and Milazzo 1990
				1590	Harmon et al. 2003
				790	Hoke et al. 1992
				2132	Mount et al. 1992
				1042	Mount et al. 1992
				1956	Mount et al. 1992
		LC50	7 Days	1794	Cowgill and Milazzo 1990
				1510	DeGraeve et al. 1992
		NOEC	7 Days	250	Aragao and Pereira 2003
				1800	Cooney et al. 1992
				740	DeGraeve et al. 1992
				440	Harmon et al. 2003
				1250	Sanders 1993
				1000	Stark 1999
	Pimephales promelas	EC50	7 Days	7210	Evans and Frick 2001
		IC25	7 Days	3100	Geis et al. 2003
				1600	Sanders 1993
				1470	Stark 1999
		LC50	2 Days	7690	Adelman and Smith 1976
				6510	Mount et al. 1992
			4 Days	7600	Adelman and Smith 1976
				6570	Birge et al. 1985
				11400	Meyer et al. 1985
				6390	Mount et al. 1992
			7 Days	5740	Aquatic Toxicity Group 1998
				5490	Beak International Inc. 1999
		NOEC	7 Days	4000	Pickering et al. 1996
				2500	Sanders 1993
				500	Stark 1999
				500	Taylor et al. 1988
CaCl₂	Ceriodaphnia dubia	EC50	7 Days	1440	Evans and Frick 2001
		LC50	2 Days	1830	Mount et al. 1997
				1794	Mount et al. 1997
				1830	Ball et al. 2008
	Pimephales promelas	EC50	7 days	9520	Evans and Frick 2001
		LC50	4 Days	4630	Ball et al. 2008
				4630	Mount et al. 1997
	Selenastrum capricornutum	EC50	3 Days	2900	Ball et al. 2008
				2700	Ball et al. 2008
MgCl₂	Ceriodaphnia dubia	LC50	2 Days	880	Mount et al. 1997
				962	Mount et al. 1997
	Pimephales promelas	LC50	2 Days	2840	Mount et al. 1997
		LC50	4 Days	2120	Mount et al. 1997
K₂SO₄	Ceriodaphnia dubia	LC50	2 Days	680	Mount et al. 1997
	Pimephales promelas	LC50	2 Days	860	Mount et al. 1997
		LC50	4 Days	680	Mount et al. 1997
K-Acetate	Ceriodaphnia dubia	IC25	6-7 days	43	Corsi et al. 2009
		LC50	2 Days	313	Corsi et al. 2009
	Pimephales promelas	IC25	7 Days	324	Corsi et al. 2009
		LC50	4 Days	421	Corsi et al. 2009
	Selenastrum capricornutum	IC25	4 Days	28.8	Corsi et al. 2009
KCl	Ceriodaphnia dubia	LC50	2 Days	630	Mount et al. 1997
	Pimephales promelas	LC50	2 Days	910	Mount et al. 1997
		LC50	4 Days	880	Mount et al. 1997
		LOEC	7 Days	1000	Pickering et al. 1996
		NOEC	7 Days	500	Pickering et al. 1996

Table 1.4. Acute and chronic toxicological endpoints for anti-icing/de-icing products (Pilgrim 2013).

Deicing Chemical	Supplier	Species	Test Endpoint	Test Duration	Product Concentration (mg/L)	Chloride or Potassium in Product (% by Weight)	Reference
Potassium Acetate Deicer	not identified	*Ceriodaphnia dubia*	LC50	2 Days	421	not given	Corsi et al. 2009
		Ceriodaphnia dubia	IC25	6-7 Days	54.5		
		Pimephales promelas	LC50	4 Days	298		
		Pimephales promelas	IC25	7 Days	366		
		Selenastrum capricornutum	IC25	4 Days	19.9		
MgCl$_2$-Freezgard	Premium/IMC	*Ceriodaphnia dubia*	LC50	2 Days	4514	25	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	1634		
		Ceriodaphnia dubia	IC50	7 Days	2807		
		Selenastrum capricornutum	IC25	3 Days	1426		
		Selenastrum capricornutum	IC50	3 Days	3158		
IceBan	IceBan America	*Ceriodaphnia dubia*	LC50	2 Days	395	0.19	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	103		
		Ceriodaphnia dubia	IC50	7 Days	173		
		Selenastrum capricornutum	IC25	3 Days	186		
		Selenastrum capricornutum	IC50	3 Days	277		
CaCl$_2$-Liquidow	Dow	*Ceriodaphnia dubia*	LC50	2 Days	5454	23	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	2109		
		Ceriodaphnia dubia	IC50	7 Days	2971		
		Selenastrum capricornutum	IC25	3 Days	1039		
		Selenastrum capricornutum	IC50	3 Days	3424		
CaCl$_2$-Inhibited	Dow	*Ceriodaphnia dubia*	LC50	2 Days	3828	23	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	1841		
		Ceriodaphnia dubia	IC50	7 Days	2722		
		Selenastrum capricornutum	IC25	3 Days	1737		
		Selenastrum capricornutum	IC50	3 Days	2422		
MgCl$_2$ (80%) + IceBan (20%)	Premium	*Ceriodaphnia dubia*	LC50	2 Days	1530	18.6	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	644		
		Ceriodaphnia dubia	IC50	7 Days	1004		
		Selenastrum capricornutum	IC25	3 Days	1154		
		Selenastrum capricornutum	IC50	3 Days	4144		
NaCl (23%) + IceBan (20%)	Premium	*Ceriodaphnia dubia*	LC50	2 Days	2127	14.4	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	451		
		Ceriodaphnia dubia	IC50	7 Days	808		
		Selenastrum capricornutum	IC25	3 Days	1483		
		Selenastrum capricornutum	IC50	3 Days	4017		
MgCl$_2$ (50%) + IceBan (50%)	Premium	*Ceriodaphnia dubia*	LC50	2 Days	585	11.7	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	86		
		Ceriodaphnia dubia	IC50	7 Days	164		
		Selenastrum capricornutum	IC25	3 Days	298		
		Selenastrum capricornutum	IC50	3 Days	1090		
CaCl$_2$ (50%) + IceBan (50%)	America West	*Ceriodaphnia dubia*	LC50	2 Days	676	11.6	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	94		
		Ceriodaphnia dubia	IC50	7 Days	142		
		Selenastrum capricornutum	IC25	3 Days	556		
		Selenastrum capricornutum	IC50	3 Days	876		
K-Acetate	Cryotec	*Ceriodaphnia dubia*	LC50	2 Days	660	190,000 mg/L	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	158		
		Ceriodaphnia dubia	IC50	7 Days	240		
		Selenastrum capricornutum	IC25	3 Days	217		
		Selenastrum capricornutum	IC50	3 Days	318		
NaCl + Caliber (10%)	Minnesota Corn	*Ceriodaphnia dubia*	LC50	2 Days	3114	12.7	Insurance Corporation of British Columbia, July 2000, File 498-0954
		Ceriodaphnia dubia	IC25	7 Days	399		
		Ceriodaphnia dubia	IC50	7 Days	538		
		Selenastrum capricornutum	IC25	3 Days	1837		
		Selenastrum capricornutum	IC50	3 Days	2721		

Pilgrim (2013) also investigated the acute and chronic toxicity of several anti-icers and de-icers on an invertebrate (*Ceriodaphnia dubia*), fathead minnows, and phytoplankton (*Selenastrum capricornutum*) in a controlled laboratory setting. He performed tests to determine the toxicity of eight commercial anti-icers and de-icers that included either sodium chloride, calcium chloride, magnesium chloride, KAc, and glycerol. The anti-icer and deicer containing KAc was CF-7 by Cryotec, which contains 50% KAc. Results for CF-7 are summarized in Table 1.4 and Figure 1.1.

Fathead minnows exhibited a decrease in acute and chronic survival and less growth with an increase in the KAc dose (Table 1.4 and Figure 1.1). For *Ceriodaphnia dubia*, acute and chronic survival effects were variable between doses of 0.0025 to 1.0 g/L of diluent. Reproduction declined at low doses (e.g., 0.0025 grams of product per liter of diluent) compared to controls and remained low between 0.0075 to 1.0 grams of product per liter of diluent. No reproduction occurred at 2.0 grams of product per liter of diluent. Based on trends shown in Figure 1.1, CF-7 had no stimulatory effect on *Selenastrum capricornutum* growth at low concentrations but there was a decrease in growth as product concentration increased.

Table 1.5. Dosing, chemistry, and toxicology results for CF-7 by Cryotec (Pilgrim 2013).

Test Species	Dose	Dosing Product Dose (g/L)	Dosing Product Dose (mL of Stock in 1 L)	Chemistry K (mg/L)	Chemistry Specific Conductance (us/cm)	Percent Survival or Mean # of Cells[1] 48 or 96 Hours	Percent Survival or Mean # of Cells[1] 7 Day	Chronic Endpoint[2] 7 Day
Fathead Minnow	Control	0	0	2	307	97.5	97.5	0.352
Fathead Minnow	Dose 1	0.020	0.016	6	337	95	95	0.355
Fathead Minnow	Dose 2	0.050	0.039	11	301	87.5	80	0.389
Fathead Minnow	Dose 3	0.100	0.078	19	328	87.5	72.5	0.368
Fathead Minnow	Dose 4	0.200	0.156	36	373	95	87.5	0.335
Fathead Minnow	Dose 5	0.500	0.391	88	525	80	77.5	0.3830
Fathead Minnow	Dose 6	1.000	0.781	174	777	90	70	0.3465
Fathead Minnow	Dose 7	2.000	1.56	346	1218	70	12.5	0.2833
Fathead Minnow	Dose 8	4.000	3.13	690	2180	0	0	0.0000
Ceriodaphnia dubia	Control	0	0	2	306	100	100	17.9
Ceriodaphnia dubia	Dose 1	0.0025	0.002	3	275	100	100	11.6
Ceriodaphnia dubia	Dose 2	0.0075	0.006	3	281	100	90	5.1
Ceriodaphnia dubia	Dose 3	0.010	0.008	4	281	100	80	1.8
Ceriodaphnia dubia	Dose 4	0.050	0.039	11	301	100	80	2.8
Ceriodaphnia dubia	Dose 5	0.200	0.156	36	373	90	80	1.9
Ceriodaphnia dubia	Dose 6	0.500	0.391	88	526	100	70	4.1
Ceriodaphnia dubia	Dose 7	1.000	0.781	174	768	100	100	4.3
Ceriodaphnia dubia	Dose 8	2.000	1.56	346	1240	0	0	0
Selenastrum capricornutum	Control	0	0	3	519	3.985	---	---
Selenastrum capricornutum	Dose 1	0.0025	0.0020	3	530	3.556	---	---
Selenastrum capricornutum	Dose 2	0.0075	0.0059	4	507	3.425	---	---
Selenastrum capricornutum	Dose 3	0.0100	0.0078	4	509	3.188	---	---
Selenastrum capricornutum	Dose 4	0.0500	0.0391	11	524	2.669	---	---
Selenastrum capricornutum	Dose 5	0.2000	0.1563	37	599	2.908	---	---
Selenastrum capricornutum	Dose 6	0.5000	0.3906	88	746	2.249	---	---
Selenastrum capricornutum	Dose 7	1.0000	0.7813	174	986	0.123	---	---
Selenastrum capricornutum	Dose 8	2.0000	1.56	346	1449	0.020	---	---

(1) Endpoint is percent survival for fathead minnows and *Ceriodaphnia dubia* and mean number of cells (shown as millions of cells) for *Selenastrum capricornutum*.

(2) Chronic endpoint for fathead minnows is weight (mg) and for *Ceriodaphnia dubia* it is mean young production per adult female.
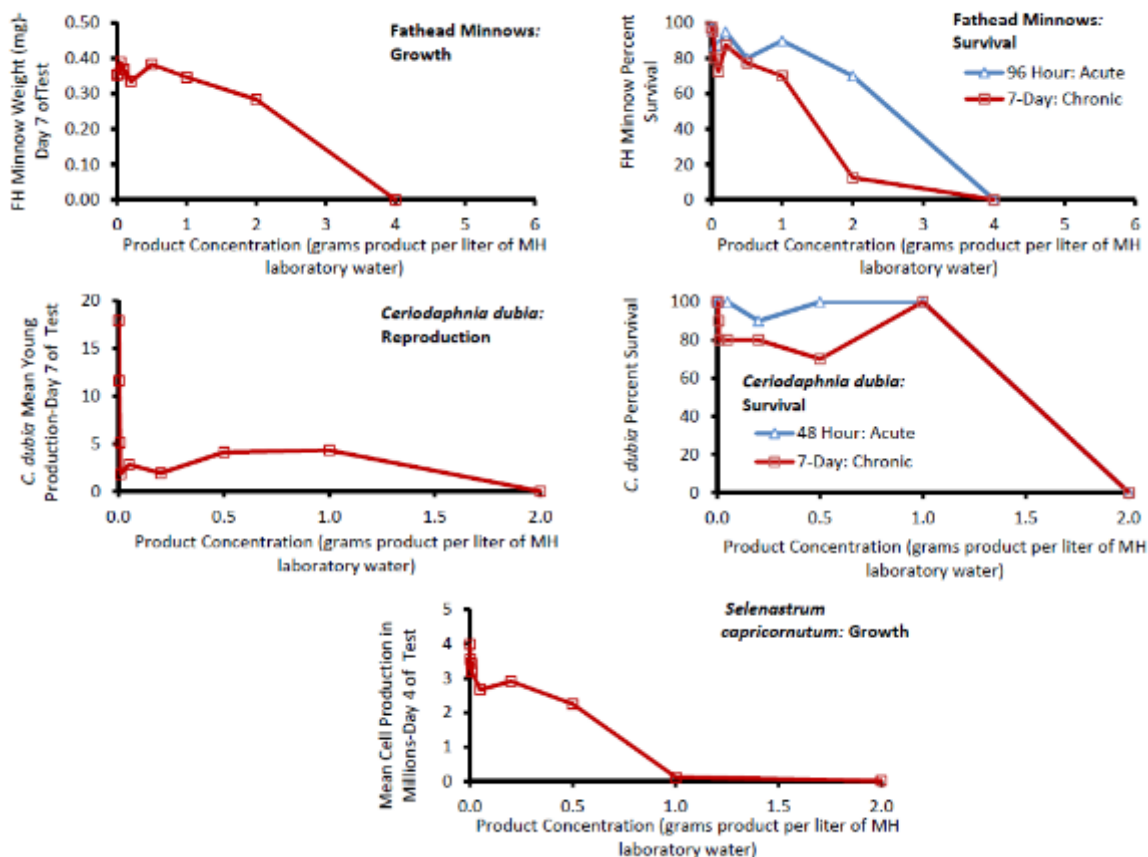
Figure 1.1. Results of chronic toxicology tests with CF-7 from Cryotec (Pilgrim 2013).

1.2.3 Corrosivity and Pavement Damage of Potassium Acetate

Unlike chloride salts, KAc is not very corrosive to steel. It is, however, very corrosive to galvanized steel and can be just as corrosive to galvanized steel as chloride-based salts. Also, KAc can damage asphalt and concrete pavements. Shi and Fu (2018) reported that when salt concentrations are below 3% physical damage is the main source of pavement damage whereas chemical reactions are the main source of damage at concentrations above 3%. Some researchers have reported that concrete damage by KAc was caused by alkali-silica reactions (ASR) (Rangaraju et al. 2007, Shi et al. 2009a) but others have suggested that the damage is caused through other, or additional and perhaps similar, processes.

ASR is a concrete damaging process that results from reactions between alkalis in cement paste and reactive silica in portland concrete cement aggregate. The reaction, which occurs between the hydroxyl ion and reactive silica, produces a gel that can expand with moisture. This expansion can cause large internal stresses that can crack the concrete. Damage is usually in the form of cracking, expansion, and popouts (i.e., small cone-shaped holes in the surface of concrete that occur when small pieces of the mortar break off).

Rangaraju et al. (2007) attributed concrete damage to ASR. In their study, concrete specimens containing reactive aggregate were exposed to either a 1 N solution of sodium hydroxide or a 50% solution of KAc. Expansion of the specimens and the pH of the solutions were monitored as were changes in the dynamic modulus of elasticity. For identical specimens, more damage was caused by KAc than by sodium hydroxide and the damage was attributed to ASR. Rangaraju et al. (2007) concluded that KAc is capable of causing ASR in concrete that contains reactive aggregates and that more damage will occur as the reactivity of the aggregates increases. It was noted that the damage mechanism appeared to be due to an increase in the pH of the soak solution that resulted from an interaction between the cement paste and the solution. A secondary reaction product, however, consisting of mostly potassium sulfate was also found in the cracks and voids of the concrete specimens. For the State of Minnesota, reactive aggregates are not used or available so ASR has not presented a local concern. Most of the Minnesota concern is with expansion joint galvanizing and corrosion, although limited effect of KAc on the galvanized components of joints and metal railings on bridges has been observed. The thickness of galvanizing and low concentration of KAc are attributed to this limited effect.

Shi et al. (2009b) and Xie et al. (2017) found that potassium and sodium acetates had significant potential to trigger and accelerate ASR in concrete specimens with reactive aggregates and increasing the temperature and anti-icer/deicer concentration accelerated degradation. Shi et al. 2009b and Xie et al. 2015 also observed that concrete exposed to KAc develops byproducts from other, perhaps secondary, reactions. Lee et al. (2000) reported that KAc exposure can significantly reduce mechanical properties of concrete.

Potassium acetate also has been found to cause damage to asphalt pavements and this damage may be KAc induced ASR in asphalt containing reactive aggregate and calcium hydroxide (Apeagyei et al. 2008). Also, anti-icer and deicer solutions can penetrate bitumen and cause stripping and emulsification of asphalt binder due to the low surface tension between the anti-icer or deicer and the asphalt (Shi and Fu 2018), which leads to asphalt degradation. Asphalt degradation is due to binder softening, loose aggregate, stripping, and/or moisture damage (Alatyppö and Valtonen 2007, Pan et al., 2008, Mallela et al. 2010). The emulsification may change the chemical composition of asphalt binder which results in loose binder, loose aggregate, and bleeding and stripping of binder.

Hassan et al. (2002) compared the damage done to aggregates and asphalt pavement specimens containing either quartzite or limestone aggregate when subjected to freeze-thaw cycles while submerged in solutions of varying concentrations of KAc, sodium formate, urea, and conventional road salts. Damage to aggregates was quantified as the percent of weight loss observed and damage to asphalt pavement was quantified as weight loss, density loss, change in mechanical properties, penetration, and variation in the gradation of recovered aggregates. The greatest damage for each anti-icer/deicer solution was caused at a concentration of $1 - 2\%$, regardless of the anti-icer/deicer. Also, for all anti-icers and de-icers, the quartzite aggregate was damaged more than the limestone aggregate. Road salts caused comparable quartzite aggregate damage and much less damage to limestone aggregate as compared to the damage caused by organic anti-icers/de-icers. Conclusions from Hassan et al. (2002) were:

- When solutions of distilled water were used as a control, damage (measured as weight loss) was always less than when an anti-icer/deicer was used,

- Urea caused the most damage to aggregates and to asphalt pavement,

- Mechanical properties were lower for asphalt pavement specimens subjected to freeze-thaw cycles while in solution (as compared to dry specimens) even when the solution was distilled water,

- The deterioration of mechanical properties of specimens subjected to KAc, sodium formate, and road salt was not greater than those of specimens submerged in distilled water,

- Freeze-thaw cycling while submerged in a anti-icer/deicer appeared to soften the asphalt cement.

Tsang et al. (2016) observed the mass loss of a concrete specimens exposed to KAc when they investigated the development of a test method to quantify the resistance of pervious concrete to anti-icers/de-icers. In this study calcium chloride, magnesium chloride, CMA, sodium acetate, and KAc were investigated. Pervious concrete samples were prepared by either 1) submerging in a anti-icer/deicer and then draining, 2) partially submerging in a anti-icer/deicer (and not draining), or 3) fully submerging in a anti-icer/deicer (and not draining). After preparation the specimens were subject to freeze-thaw cycling. Results were, again, quantified as percent mass loss of each specimen.

All anti-icers and de-icers caused more mass loss than when water was used as the solution. CMA had the least percent mass loss whereas KAc and sodium acetate had slightly more mass loss (but the difference was stated as likely being not statistically significant) (Tsang et al. 2016). The percent mass loss for the KAc sample was under 5% at 30 cycles and under 10% at 50 cycles.

In a study that investigated concrete damage caused by sodium chloride and KAc, Xie et al. (2017) used samples cored from two bridge decks. While in service the pavement cores were repeatedly subject to the application of a anti-icer/deicer. One bridge deck was repeatedly subject to KAc applications and the other subject to sodium chloride applications. The cores taken from the bridge that was subject to KAc had much more degradation in strength (compressive and splitting tensile) and microhardness compared to the sodium chloride exposed samples.

In a second part of the study, Xie et al. (2017) subject concrete specimens prepared in the laboratory to either the KAc or the sodium chloride solutions. Both groups showed calcium leaching along with the formation of precipitates in the concrete. The formation of the precipitate was attributed to chemical reactions between the cement paste and the anti-icers/de-icers and, it was stated, that this could lead to expansion of the pores in the concrete. In Xie et al. (2017), the mass loss of each lab specimen and the mechanical properties of compressive strength and split tensile strength were recorded in order to quantify damage. The lab specimens subject to KAc had lower compressive strength and similar splitting tensile strength compared to those specimens subject to sodium chloride.

Xie et al. (2017) also tested the ice melting capability of each anti-icer/deicer at -26 °F (-32 °C) by applying test methods SHRP H-205.1 and H-205.2 (Chappelow et al. 1992) and measuring how much of a 3.2 mm thick layer of ice each anti-icer/deicer could melt within 60 minutes. The KAc melted 1.4 ml whereas the sodium chloride melted 0.8 ml. These tests are conducted in a 22.86 cm diameter (410 cm^2)

Plexiglass dish. Thus, the KAc melted an equivalent of 0.034 mm and the sodium chloride melted 0.02 mm of ice.

Rangaraju and Desai (2009) reported that fly ash and ground granulated blast furnace slag was effective in reducing expansion caused by ASR in concrete subject to KAc. Fly ash at low, intermediate, and high lime content was investigated at 15, 25, and 35% by mass replacement of cement and slag at 40 and 50% by mass replacement. Changes in length, dynamic elastic modulus, and microstructure were recorded. Fly ash with low and intermediate lime content was effective at 25 and 35% replacement and the high lime fly ash was ineffective at all replacement percentages. Slag at 50% replacement was highly effective while at 40% replacement the effectiveness was determined to be inadequate. In general, over the range of values tested, as the lime content of fly ash decreased its effectiveness in reducing expansion increased.

Rangaraju and Desai (2009) concluded that Class F fly ash with a lime content of less than 15% was adequately effective in mitigating expansion in concrete subject to KAc anti-icer/deicer and that Class C fly ash with a lime content of more than 15% should not be used. Fly ash classes are designated by ASTM C 618 specification. Also, it was concluded that Grade 120 slag at a minimum of 50% replacement may be used to mitigate expansion of concrete subjected to KAc. No information on the slag grading system was given but the slag used in the study consisted of 38.17% silicon dioxide, 39.12% calcium oxide, 12.48% magnesium oxide, 7.31% aluminum oxide, 2.56% sulfur trioxide, and smaller amounts of a handful of other substances. The authors noted that their results should only be applied to the aggregates tested within their study, which were Spratt Limestone, New Mexico Rhyolite, North Caroline Argillite, and South Dakota Quartzite.

Rangaraju and Olek (2007) determined that small concrete specimens with reactive aggregate could have ASR induced when exposed to acetate anti-icers/de-icers but pore solutions in the specimens had hydroxyl ion concentrations lower than levels needed to trigger ASR. Rangaraju and Olek (2007) concluded that the ASR mechanism active in the specimens subject to acetate-based anti-icers/de-icers was different than the conventional ASR mechanism. Also, Bates et al. (2007) directly compared airport pavement subjected to KAc to specimens of the same concrete that had been subjected to KAc under controlled laboratory conditions and found no direct correlation between characteristics of the two groups of specimens. Also, Balachandran et al. (2011) noted that, in some cases at least, ASR related stresses existed uniformly over the entire depth of concrete specimens even though the anti-icer/deicer penetration was limited to near the surface of the concrete.

In addition, Balanchandran et al. (2011) investigated anti-icer/deicer penetration into pavement cores that were collected from a single airport where a KAc-based anti-icer/deicer (50% KAc by weight with corrosion inhibitors) was used repeatedly and they investigated the effects of KAc on laboratory prepared concrete specimens. In this work the maximum depth of KAc penetration in the airport pavement cores was found to be 0.8 inches (2 cm) and, though it was present, the KAc was found in negligible amounts. Thus, the authors could not conclude that KAc induced or enhanced ASR within the concrete. With regards to the laboratory prepared specimens, similar results were observed even though specimens were subject to several different exposure regimes over a six-month period. Observation of the laboratory prepared specimens revealed that KAc penetration was not significant

and the concentration of any KAc that did penetrate was low. Furthermore, any ASR damage that occurred in either the airport pavement cores or the laboratory specimens was uniform with depth even though KAc penetration was limited to near the surface. The authors stated that, although KAc can induce ASR under lab conditions it doesn't play a substantial role in field applications, and this is at least partially due to the limited penetration of KAc. It was noted, however, that the study investigated concrete from only one airport and KAc impacts could be different in other locations where pavements have cracked due to other causes.

Silva (2012) and Silva et al. (2014a, 2014b) investigated the interactions of natural microfines (i.e., smaller than 0.003 inches or 75 μm) associated with concrete aggregate and KAc to determine if these interactions can lead to ASR or other durability related issues in concrete. In their study, concrete specimens with and without microfines were prepared, some specimens contained reactive aggregate, and some contained non-reactive aggregate. A KAc anti-icer/deicer that was 50% KAc in water and included a corrosion inhibitor was used as the KAc source and the cement was Type I portland cement. Specimens were either placed in a high temperature atmosphere (100 °F, 38 °C) and subject to high humidity or placed in a high temperature atmosphere while submerged in the KAc solution. For all specimens, expansion and freeze-thaw durability were monitored as was corresponding damage.

The study found that microfines at less than 5% of the total aggregate weight and exposure to the KAc anti-icer/deicer caused significant deterioration of the concrete specimens and that specimens with microfines containing phylosilicates experienced the greatest degradation. Expansions in specimens with microfines ranged from 0.05 to 0.70% after one year and this expansion was dependent on the type of microfine (microfines containing a high amount of phylosilicates caused the greatest deterioration). Expansion in specimens with no microfines was negligible. Although expansions were greater in specimens with reactive aggregate, expansions of up to 0.50% were observed in specimens with non-reactive aggregate. Degradation and a drop in entrained air content also led to a substantial loss of freeze-thaw durability. Two indicators of ASR, ASR gel in the concrete and reaction rims around the aggregate, were not observed, however, thus the authors suggested that the deterioration was not caused by ASR.

It was also determined that distressed concrete specimens that were exposed to temperatures of 100 °F (38 °C) and the KAc anti-icer/deicer was present to the core. The authors concluded that the distress was directly associated with the KAc, derivative forms of potassium complexes, and transformations of the microfines. It was further concluded that KAc caused the structure of the cement paste to transform and release hydroxyl ions that raised the pH. The authors noted that the potassium ion appeared to transform to calcium/potassium compounds and eventually to potassium sulfate.

In summary, Silva (2012) concluded that the KAc anti-icer/deicer in the concrete pores reacted to form potassium sulfate and calcium-bearing potassium sulfate compounds. This dramatically increased the hydroxyl ion concentration, which can cause reformation of silica species that have been released by the microfines and aggregates. Although not classical ASR, these reactions appear to be similar and can cause deterioration of concrete.

1.3 COMPARING THE MOST COMMON ROAD SALT ALTERNATIVES

The previous discussion focused solely on KAc as a RSA. There are, however, many other potential RSAs that have been investigated in detail. This section is a broader discussion that covers publications that report on other potential RSAs, and also contains further discussion of KAc, for comparison of performance, cost, and environmental impact. Also, other acetate-based RSAs such as sodium acetate and calcium magnesium acetate, have been investigated. Thus, literature on all acetate-based RSAs may be relevant because of the common acetate compound. Acetate-based RSAs are covered first, followed by formate-based RSAs, glycol and glycerol, succinate-based RSAs, and other RSAs. After a general discussion on cost, corrosivity, and other factors, the performance of these RSAs are discussed in the same order. This section ends with a review of literature that has investigated the environmental impact of these RSAs, including modeling studies on the transport and degradation of RSAs in the environment.

1.3.1 Acetate-Based Alternatives

As previously mentioned, one group of potential RSAs are acetate-based (Boice 1986, Baltrenas and Kazlauskiene 2009), and include KAc, sodium acetate, and calcium magnesium acetate (CMA) (Fay and Muthumani 2017). Although most research has investigated CMA, KAc is often favored in cold climates because it will melt snow and ice at lower temperatures than road salt and most other RSAs. One 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). 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) as previously discussed. 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 KAc 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 anti-icer/deicer used.

With regards to cost, acetates are significantly more expensive than chloride-based anti-icers/de-icers and, therefore, are mostly used at airports and where steel corrosion is a concern, such as at bridges. 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 anti-icing/de-icing 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.

Another drawback of some acetates is that they are less effective than chloride-based anti-icers/de-icers (Bang and Johnston 1998). For example, Boice (1986) found that it took 1.65 times the CMA to obtain and equivalent melting power of salt. Others have found or estimated different amounts of CMA are required to equal the effectiveness of chloride-based anti-icers/de-icers, but every study has found more CMA 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 anti-icers/de-icers is shown in Table 1.6 below.

Table 1.6. 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 de-icing 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. Most research has focused on CMA and information specifically on KAc is sparse.

Other studies have found, however, that there could be some environmental impacts of acetates. 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 KAc, 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 anti-icers/de-icers 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 50 and 68 °F (10 and 20°C) but results were variable when temperatures were near 35 °F (2 °C). 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 anti-icers/de-icers 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 1.7. For studies that have investigated specific environmental impacts of BOD and other issues, see the "Environmental Impact" section later in this report.

Table 1.7. Negative environmental impact of CMA compared to conventional anti-icers/de-icers (modified from McKenney 2015).

Deicer / Environ-mental 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

1.3.2 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, a 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 de-icing 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 can 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 1.8 below.

Table 1.8. 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° F (1" ice): 400-1000 lbs/lane-mile	$200-$350 per ton or $12-$44 per lane mile (near 32° F, thin ice) $40-$175 per lane mile (10 ^{o}F, 1" ice)	Excellent at melting. Works more quickly and at lower temperatures than NaCl
Potassium Formate		$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

1.3.3   Glycol and Glycerol

Glycol and glycerol are other organic, non-chloride based anti-icer and de-icers 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 anti-icers/de-icers discussed, these products are more expensive than chloride-based anti-icers/de-icers 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 anti-icers/de-icers is shown in Table 1.9 below.

Table 1.9. Summary of glycol and glycerol anti-icers/de-icers (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
Propylense 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 gylcols.

1.3.4 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. Of the succinate salts, the most effective anti-icer/de-icer has been potassium succinate (Fay and Muthumani 2017). Like the other organic anti-icer/de-icers 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 anti-icer/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 anti-icers/de-icers (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 1.10. Table 1.11 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 1.10. Summary of anti-icers/de-icers (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 1.11. 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	Distrupts endocrine. Ingestion of concentrated fluid can cause death	Higher BOD than other deicers.	Distrupts 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

1.3.5 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.

Laurinavičius 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 anti-icing or de-icing 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 anti-icers/de-icers 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 but 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, KAc, or urea and

corrosion inhibitors (potassium gluconate and sodium metalsilicate). 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 anti-icers/de-icers 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 de-icers.

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 agriculturally 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 10 °F (5.5 °C) 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 anti-icing/de-icing agents tested (i.e., 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 ™ which is a mixture of equimolar sodium acetate and sodium formate (Bang and Johnston 1998). It has low corrosivity and is an effective anti-icer/deicer (Johnston and Huft 1992). The sodium ion in Ice Shear ™ 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 ™ may deplete oxygen with its high BOD. Bang and Roseland (1989) found that Ice Shear ™ 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 ™ and investigated its behavior in soil and water. Their results indicated that Ice Shear ™ 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 ™ 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 ™ 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).

1.4   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, de-icing, 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.

Wåhlin and Klein-Paste (2017) investigated ice melting rates and the corresponding driving forces of anti-icers/de-icers. 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.

1.4.1   Performance of Acetates, Formates, Glycol/Glyercol, and Succinates

As was briefly mentioned previously, 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 anti-icer/deicer application was also assessed as was corrosivity and thermal properties. Four anti-icers/de-icers, 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 KAc.

The magnesium chloride and CMA products had the least impact on portland cement concrete and the KAc 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 where 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 23 °F (-5 °C), whereas salt brine was effective down to 15 °F (-10 °C). This result is contrary to the value published by the Western Transportation Institute (2017) that lists the effective low temperature for succinates as -4 °F (-20 °C), 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 -4 °F (-20 °C) 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 23 °F (-5 °C).

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

Shi et al. (2009) evaluated the performance of KAc, 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. As found by Fay and Shi (2011), 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. CF-7 (a commercial product that is KAc-based). CF-7 had the coldest effective temperature (followed by Apex Meltdown) but CF-7, sodium chloride, and IceSlicer (another commercial product) were the most harmful to concrete.

Wåhlin and Klein-Paste (2017) investigated the effect of anti-icing/de-icing 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.

1.4.2 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 de-icing, 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 for salt (i.e., materials applied to salt to prewet the salt prior to placement on the road), no material consistently outperformed the others. When used as anti-icing agents in a direct liquid application to the road surface, 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 solution that is 23% sodium chloride by weight). 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 ft^2). The application rate did not affect product performance and treated sections had from 10 to 40% increased friction on the pavement after accumulated, loose snow was removed 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 anti-icer/de-icers, however, but solid organic-based materials were not.

1.5   SPECIFIC ENVIRONMENTAL IMPACT OF RSAS

Although the broad environmental impacts of RSAs were previously discussed, many studies have investigated specific impacts of RSAs on water bodies, soil, or organisms. Such studies are 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 anti-icing/de-icing 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. In 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 course 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 50 to 68 °F (10 to 20 °C) 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 68 °F (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 were 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 anti-icer/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 anti-icing/de-icing 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 anti-icing/de-icing 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 anti-icing/de-icing 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, KAc, 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 mesocosms 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 anti-icers/de-icers on metal mobility in soils. For example, Amrhein et al. (1992) investigated the impact of anti-icers/de-icers 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 m^3/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.

1.5.1   Anti-icer/deicer Impact on Specific Species

Other RSA studies have investigated their impact on specific species of plants or organisms. 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 toxilogical 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 anti-icing/de-icing effect as sodium chloride or sodium formate, the total impact of using any of the three anti-icers/de-icers may be similar.

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 anti-icers/de-icers. 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 anti-icers/de-icers did not have less impact on saplings than sodium chloride did during active growth.

Schuler et al. (2017) investigated the effect sodium chloride, magnesium chloride, ClearLane ™ and two salts mixed with GeoMelt ™ (a proprietary blend containing beet juice) and Magic Salt ™ (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 1.12 below.

Table 1.12. 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/m² 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, and were least senstive to urea, NaCl, and MgCl$_s$.	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	Toxilogical 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.	

1.5.2 Environmental Modeling Studies

Some literature reported on model studies that investigated the fate and/or impact of roadway anti-icers/de-icers 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 Chapter 4 of this project involves such a model, but for KAc, 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 1.2, 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.
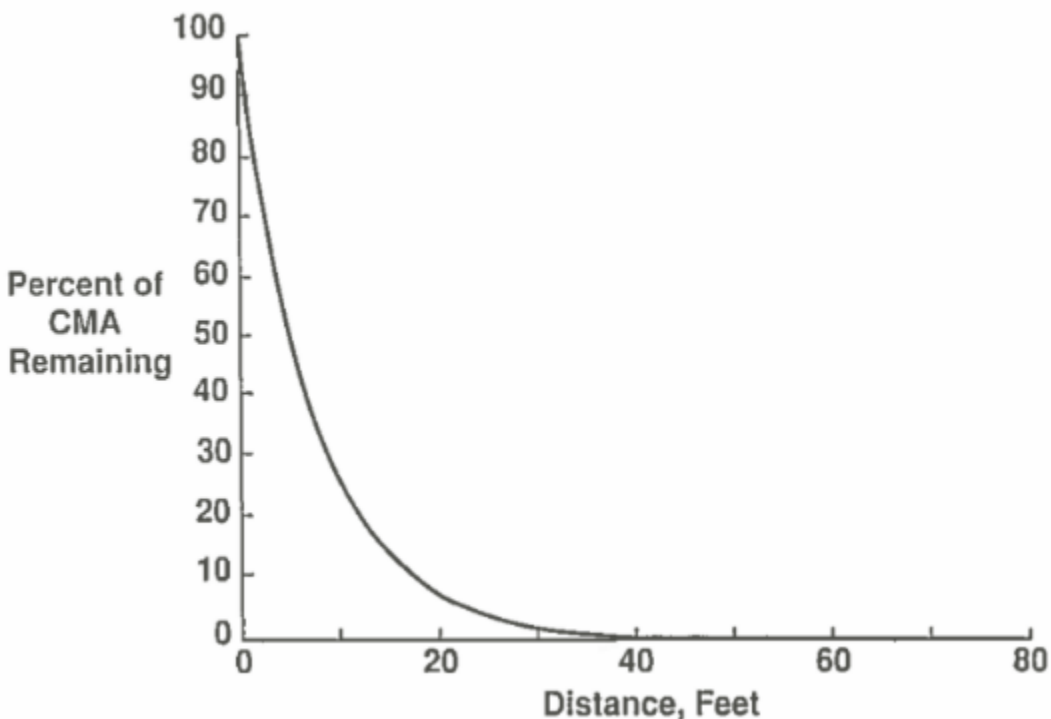
Figure 1.2. CMA remaining from distance of roadway assuming a two-lane road with shoulder delivers runoff and CMA to a 10-foot wide buffer (D'Itri 1992).

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 worst-case scenario) with an annual loading of 60 g BOD/m^2 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 (and possibly other organic RSAs) enter 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 m^3/s; Burkett and Gurr, 2004) was only 35 g CMA/m^2. For larger streams, this value was 153 g CMA/m^2 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.

1.6   CHAPTER 1 SUMMARY AND CONCLUSIONS

Road salt is used predominantly across the state for winter road anti- and de-icing operations. Road salt is used because it is inexpensive and effective, but the thousands of tons that are used annually have resulted in increasing chloride concentrations of surface water bodies throughout the state. In many cases, chloride concentrations are above regulatory limits, which results in the water body being labeled as impaired. Thus, there is a need for one or more road salt alternatives (RSAs) that are effective, relatively inexpensive, and environmentally friendly.

Research has led to the identification of various RSAs, most of which are organic compounds. One such group of RSAs are acetate-based, and this group includes KAc. Potassium acetate is effective at lower temperatures than most other potential RSAs and is also less corrosive to steel than conventional road salt. Potassium acetate is, however, more expensive than road salt, and as an organic compound, exerts BOD when it is degraded by microorganisms in water or soil. Thus, there is concern that extensive use of KAc will result in the depletion of dissolved oxygen in water bodies near roads that receive KAc. There is also legitimate concern regarding the toxicity toward fauna and flora of KAc and the potassium ion.

No literature was found that investigated the impact of KAc on dissolved oxygen levels of nearby water bodies, but field investigations and model studies have been performed on such impacts related to calcium magnesium acetate (CMA). All such studies have indicated that dissolved oxygen depletion will likely not rise to levels of concern at KAc concentrations expected to result from winter road applications as long as water bodies are not located close to the road and are not small ponds or slow-moving streams. Potassium acetate may, however, be more toxic toward fauna and flora than other RSAs, including other acetate-based RSAs.

When applied to winter roads, some KAc will be transported into the soil where it can be degraded by microorganisms. Potassium is a necessary plant nutrient, but at high concentrations, it could be detrimental to the health of vegetation. Very little literature, however, was found on this topic. When in soil, the potassium ion can be adsorbed to soil particles through ion exchange processes. This process can release metal ions, thus KAc use can increase the mobility of metals in soils.

Finally, KAc can damage concrete pavements through alkali-silica reactions (ASR) or similar reactions and it can damage asphalt pavements through ASR, binder softening, stripping, moisture damage, and the loosening of aggregates. Some have questioned the correlation between KAc use and concrete pavement damage and the exact processes are not fully understood, but it is clear that KAc can cause damage to pavements, at least in laboratory settings.

Finally, although KAc is not as corrosive to steel as road salt, it is very corrosive to galvanized steel and this could be of concern near guard rails and other structures or vehicles containing galvanized steel parts. More research is needed to fully understand the processes involved in pavement degradation caused by KAc and the exact relationship between its use in the field and concrete and asphalt pavement damage. More research is also needed to fully understand the toxicity of KAc and the potassium ion in soil and water environments toward the many organisms it could impact.

2 Toxicity Assessment

Prepared by:

Chan Lan Chun[2]
Kathryn Cassidy[2]
John S. Gulliver[1]

[1]St. Anthony Falls Laboratory, University of Minnesota
[2]Natural Resources Research Institute, University of Minnesota Duluth

December 6, 2021

2.1 DESCRIPTION AND OBJECTIVE

A field evaluation (Chapter 3) investigated impacts of an alternative anti-icer and deicer, potassium acetate (KAc contained in a commercial product, CF7®), to water chemistry, oxygen depletion, and microbiological water quality in the receiving water body of Lake Superior. Here, the toxicity of KAc to aquatic and terrestrial fauna and flora was assessed first through the information gained by the Literature Review (Chapter 1). Based on the information, the toxicity experiments of CF7 to vegetation and aquatic life, specifically roadside grasses and water fleas (*cladocerans*) were conducted. The tests were performed to determine the toxicity of cation (K^+), acetate (Ac^-), KAc, sodium chloride (NaCl), and CF7. Toxicological endpoints were evaluated along with KAc concentrations found in the field evaluation to determine whether there would be adverse effects of this anti-icer/deicer on aquatic or vegetative life. Moreover, this study also identified which species (K^+, Ac^-, the combination or CF7 additives) is responsible for toxicological effects on water fleas and roadside grasses. The grass seed germination experiments upon exposure of salts were conducted at the Natural Resources Resource Institute and the aquatic toxicity tests with water fleas were performed at the Great Lakes Toxicology and Ecology Division of the Environmental Protection Agency (EPA).

2.2 TOXICITY OF SALTS ON VEGETATION

2.2.1 Background

As road salts, largely chloride-based, are applied on roadways, they are carried onto nearby soils by traffic spray, runoff and wind up to 50 m away from the road (Lundmark and Olofsson, 2007). Several studies have identified anti-icers/de-icers as responsible for death and damage to roadside vegetation (Bryson and Barker, 2002; Dudley et al., 2014; Hall et al., 1972), but little work has been done on the toxicity of non-chloride anti-icers/de-icers. Sodium and potassium are plant nutrients, but in excess amounts salinity will reduce germination and seedling growth. However, the threshold of salinity at which plants are affected is highly variable depending on species. In addition, most research on anti-

icers/de-icers has only reported toxicity results of sodium chloride. Some of the only work found on the toxicity of alternative anti-icers/de-icers to vegetation reported that a KAc anti-icer/deicer decreased the growth of onion and duckweed at a much lower concentration than chloride-based anti-icers/de-icers, with effects seen under 100 mg/L of the anti-icer/deicer (Joutti et al., 2003). Gerasimov et al. (2021) reported the opposite; they found that wheat grown in a KAc anti-icer/deicer solution was more resilient to changes in root length and biomass than other anti-icer/de-icers.

The infiltration of anti-icer and de-icers into the soil induces toxicity either through altering the osmotic balance which would decrease or prevent water uptake through roots, or by the uptake of the ions into the plant, where a high concentration of one ion can be toxic to the seedling (Bewley and Black, 1994). The accumulation of excess sodium inside plant cells has been demonstrated to alter key biochemical processes in protein synthesis and metabolism (Tester and Davenport, 2003), harden the cell wall (Neumann et al., 1994), and alter permeability of the cell membrane (Cramer et al., 1985).

As a part of the environmental impact evaluation of CF7, the objective of this research is to determine if CF7 accumulated in roadside soil from the application of anti-icer/deicer will affect germination of roadside grass as the concentration of anti-icers/de-icers would peak in snowmelt period. Seed germination experiments were performed to determine (a) the toxicological endpoints of CF7 and other salts in comparison to concentrations seen in the field and (b) the driver of toxicity in CF7 and other anti-icers/de-icers: is toxicity driven by the cation, anion, combination or additives to commercial products? To answer these questions, the germination experiments were designed and conducted with two roadside grasses used by MnDOT as a function of salt concentration (10-250 mM). The concentration range in the toxicity experiments includes the concentration of KAc and NaCl found in the field evaluation of 2019-2021 winter seasons.

2.2.2 Germination Experiment Methods

Panicum virgatum (switchgrass) was selected for the germination toxicity experiment due to its presence in a MnDOT seed mix applied in Duluth. *Festuca ovina (*sheep fescue) was also chosen as there is interest in the use of modified turfgrass along roadsides. Lake Superior water was chosen as the base matrix due its low concentration of ions that mimics the soil porewater environment in the field. Lake Superior water was collected near the mouth of Lester River and filtered to remove biomass in the laboratory. Stock solutions, 500 mM KAc, NaCl, sodium acetate (NaAc), potassium chloride (KCl), and CF7 as KAc were prepared with the filtered Lake Superior water and used to create target concentrations for seed germination experiments: 250 mM, 100 mM, 50 mM, 20 mM, and 10 mM.

The seeds were soaked in 8% sodium hypochlorite for 15 minutes to sterilize them and break the seed coat, then rinsed under distilled water. Sterilized seeds were placed in 9-cm petri dishes lined with Whatman filter paper. Seeds were cold stratified in 4°C for 6 days, then placed in an incubator at 25°C and kept from drying out with additions of deionized water every 2-3 days. Germination experiments were attempted at colder temperatures (< 25°C), which is more relevant to spring germination field temperatures. However, the percentage of germination in control was lower than 50% of the control, which is not suitable for toxicity experiment. Filter paper was wetted with 4 ml of Lake Superior water for the control, or 4 ml of each salt solution with target concentration. Three petri dishes of 20 seeds

each were used per treatment, for a total sample size of 60 seeds/treatment. The design is factorial, with two factors (salt solution and salinity) and 3 replicates; an example is shown in Figure 2.1. Seeds were monitored daily for germination for 15 days. Germination was recorded with the emergence of the radical or primary root which is the first part of embryo to break through the see coat. Toxicity endpoints, EC_{50}, Effective Concentration at which 50% of seeds are affected, were determined based on a monotonic relationship between the dose of salt and the germination response:

$$EC_{50} = c \left(\frac{a - 50\% \ response}{50\% \ response - d} \right)^{1/b}$$

a & d: lower and upper plateau (commonly referred to as the min and max) in a dose-response plot

b: the steepness of the linear portion of the curve (slope)

c: the concentration corresponding to the response midway between a and d
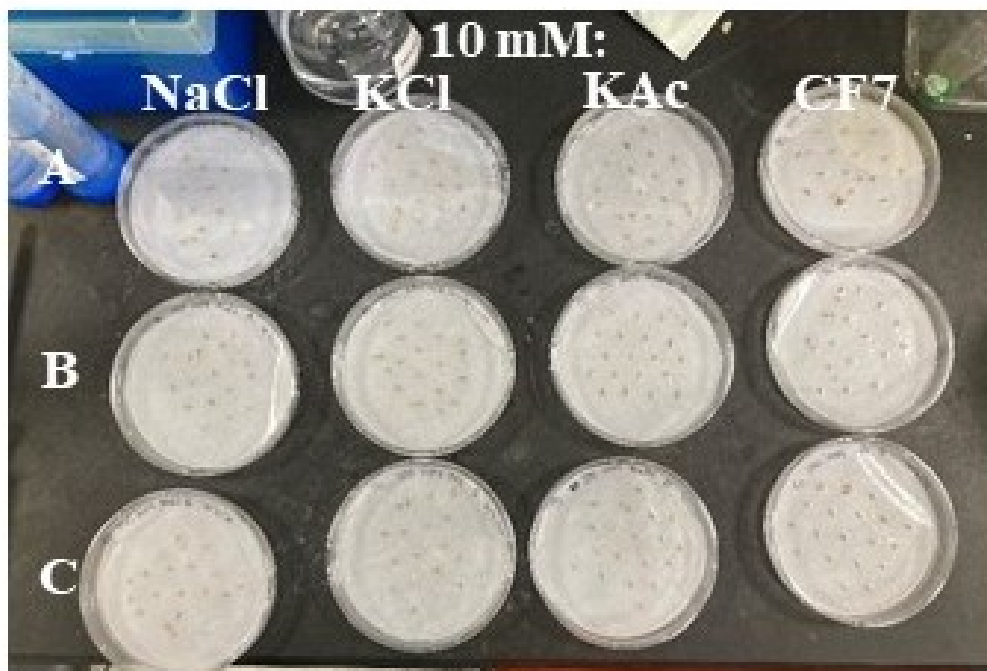
Figure 2.1. A visual of the experiment design, 20 seeds were placed in 3 petri dishes (A, B, and C) for each treatment; 10 mM treatments of NaCl, KCl, KAc, and CF7 are displayed (NaAc is excluded from the image)

After 15-day germination experiments, the length of the root and shoot were measured for growth analysis. Data was used to calculate the root:shoot length ratio, percent germination, and Vigor Index (VI = % germination * (mean root length + mean shoot length)). Additionally, electron microscopy examination was conducted to observe root morphology and accumulation of ions on the roots. Seedling roots were removed and root cross-sections were cut for analysis with a Scanning Electron Microscopy (SEM; Hitachi 3030 Plus with Quantax 70). Energy Dispersive X-ray (EDX) analysis was

performed to see if sodium or potassium was accumulating in the root cells, which can help determine if the toxicity was caused by osmotic stress or direct ion toxicity.

2.2.3 Results and Discussion

Germination of both sheep fescue and switchgrass was inhibited as the salinity increased in all salt solutions, as shown in Figure 2.2. Low salinity has no apparent effect on germination for any salt, but as concentrations increase germination success declines. Both species were more sensitive to increased salinity with acetate-based salts than chloride salts. Generally, switchgrass seeds were affected at a lower concentration for both acetate and chloride salts than sheep fescue. At 250 mM, the germination rate was less than ~10 % for both grass species regardless of salt make-up in comparison to the control (Lake Superior water). Only one seed of sheep fescue was germinated in KCl at 250 mM. The significance of the differences in the mean between test groups (p value < 0.05) was determined with a two-way analysis of variance (ANOVA) and Tukey post-hoc test (see Tables 2.4 and 2.5 in Chapter 2 Supplementary Information). The 10 mM and 20 mM solutions did not significantly differ in germination from the control group, but as salinity increased to 50 mM KAc and CF7 saw substantial decreases in germination, with smaller decreases in KCl and NaCl.

Figure 2.2. Percentage of (a) sheep fescue and (b) switchgrass seeds that germinated in a salt soution as a function of concentration. Control is the filtered Lake Superior water. Error bars represent standard deviation. * indicates treatment group which was significantly differet from the control (p<0.05)

In comparing the response of the two species, both had similar germination inhibition from the acetate salts, but sheep fescue was more robust to salinity stress in a NaCl or KCl solution. Toxicity endpoints as EC_{50}, Effective Concentration at which 50% of seeds are affected, are reported in Table 1. The range of EC_{50} across treatments is 5-16 g/L, all higher than what would be the expected concentrations in the soil. The EC_{50} is 5 times higher for NaCl than CF7 in sheep fescue, and twice as high in switchgrass. As a whole, all chloride-based solutions had higher EC_{50} than acetate ones. The EC_{50} of CF7 is slightly lower than KAc for both species, but pair wise comparisons of the difference in germination between KAc and CF7 at the 100 mM and 250 mM concentrations does not yield significant differences, indicating that the

additives in CF7 are not resulting in increased toxicity of the commercial product when compared to the pure salt.

Table 2.1. EC50 endpoints of sheep fescue and switchgrass germination by chloride- and acetate-based salts and CF7

	Sheep Fescue		Switchgrass	
	mM	*g/L*	*mM*	*g/L*
NaCl	170	9.9	105	7.8
KCl	149	11.1	84	4.9
KAc	67	6.6	63	6.2
NaAc	52	7.1	63	8.6
CF7	52	5.1*	51	5.0*

*g/L values for CF7 as expressed as g/L of KAc in CF7

Potentially, the sensitivity of acetate-based salts to the germination of grasses could be due to basic nature of acetate-based salts (pH of concentrated CF7 is 10.7). Additional experiments were performed to evaluate the role of pH in contributing to decreased germination with the germination of sheep fescue in a repeat of the control (pH = 8.2) and control water adjusted to a higher pH with potassium hydroxide at pH 8.35 and 8.6. However, germination increased with pH, going from 77% in the control, to 80% in pH 8.35, and 85% in pH 8.6. The pH of acetate salts or CF7 does not appear to contribute to germination inhibition.

In comparison to the results with the literature on seed germination in NaCl solutions, sheep fescue and switchgrass in this study have a similar or more sensitive tolerance to salinity. Dudley et al., 2014 found minimal impact to germination of sheep fescue until the 3 g/L (50 mM) solution, which is comparable with this study. Almodares et al. (2007) found sorghum had a slightly greater tolerance for salinity with much reduced germination occurring at a 200 mM NaCl solution. Shitole and Dhumal (2012) reported a very similar reduction in germination percentage as switchgrass and sheep fescue from a control to 100 mM NaCl solution for senna plant. Finally, cotton seed was reported to be more tolerant of salinity than grasses as germination only slightly decreased in a 200 mM NaCl solution (Chachar and Verhoef, 2008).

Seedlings were observed for morphological changes in their root and shoot, and it was noted that sheep fescue seeds were more fragile and likely to fall apart while measuring root and shoot growth at higher concentrations. Some seeds of both species grew double or triple roots, an indication of stress, while some sheep fescue grew shoot sheathes that were much darker in color at 50 mM and above (Figure 2.3).

Figure 2.3. Dark shoot sheathes of sheep fescue exposed to 50 mM KAc

Of the seeds that did germinate, root and shoot lengths were measured to evaluate the effects of the anti-icing/de-icing salt on growth as well as germination success. The growth difference between each treatment group and the control is shown in Figures 2.4 and 2.5, with positive root or shoot growth shown and provided as millimeters above the control, and negative length indicating the control grew more than the treatment. As expected, when germination success decreases with increased salinity, so does root and shoot growth. The results indicates even if grass seeds are successful in germinating at an increased salinity, their growth appears to be inhibited.

The differences of root and shoot length to those in the control were greatest in the 50 and 100 mM solutions (Figure 2.4 & 2.5). While increased germination was not seen at low salinities, seedling growth appears to be enhanced in some cases at low salinities, perhaps due to the cation acting as a nutrient to increase growth. A comparison between root and shoot growth finds that shoot growth is generally less affected by salinity below 100 mM. Root growth was more affected by acetate salts than chloride salts, as Figure 2.4 shows acetate salts have significantly decreased growth at 50 mM in the roots while NaCl and KCl groups do not have major differences in root length until the 100 mM concentration.
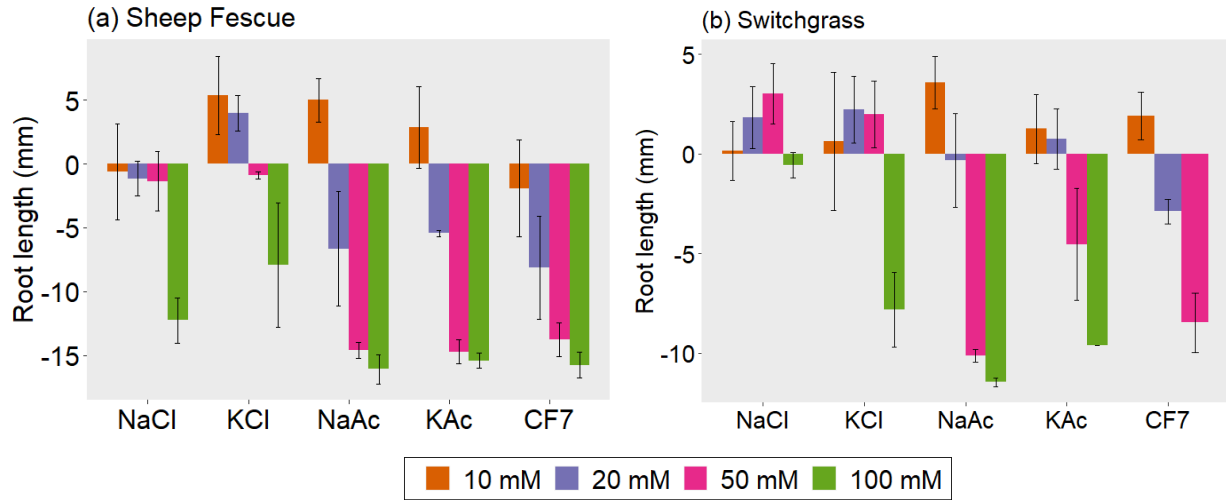
Figure 2.4. The difference in root length (mm) from the control in (a) sheep fescue and (b) switchgrass germinated in a salt soution as a function of concentration. Control is the filtered Lake Superior water. Error bars represent standard deviation.

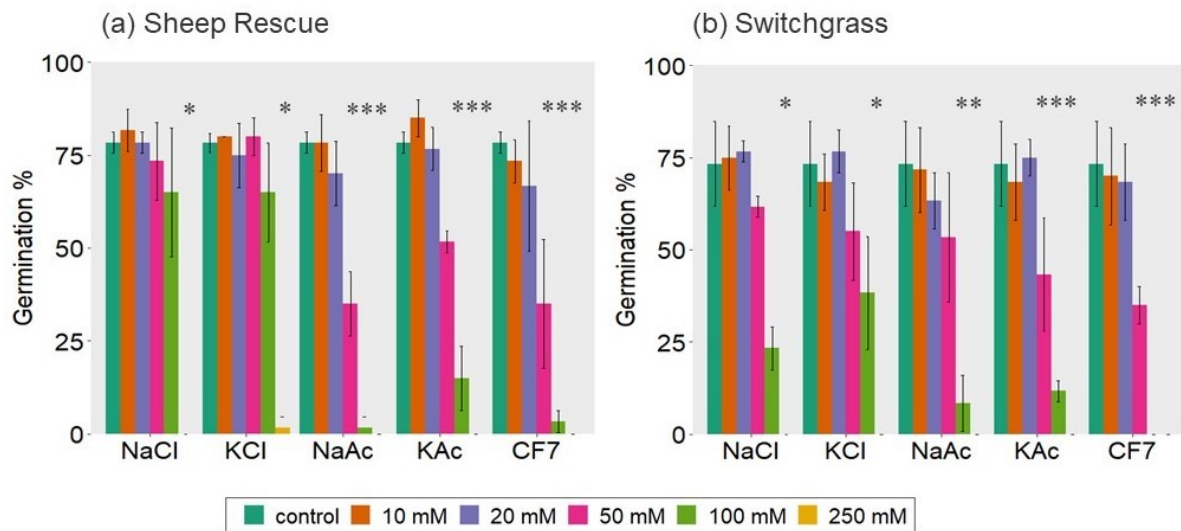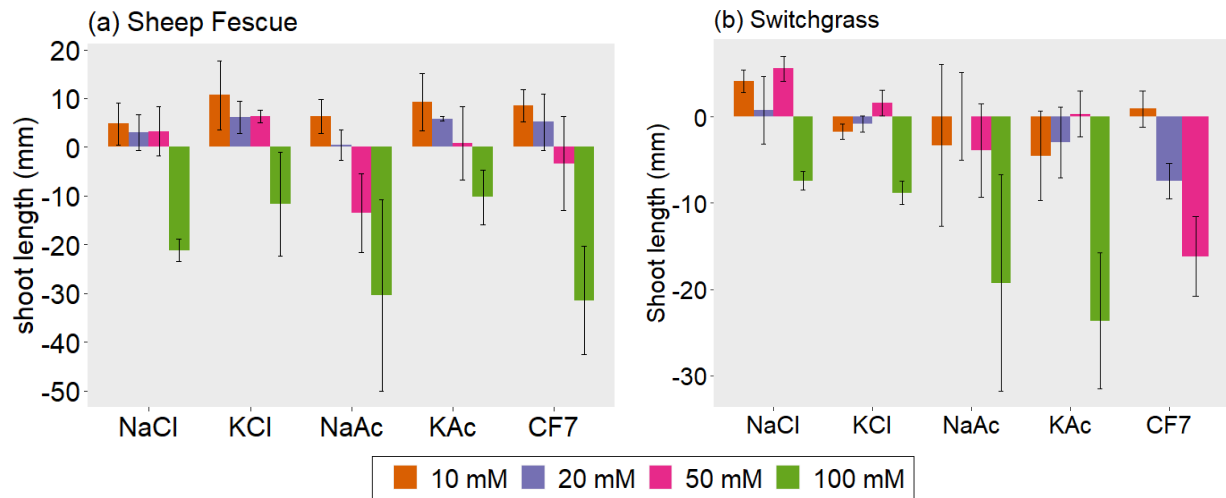**Figure 2.5. The difference in seedling shoot length (mm) from the control in (a) sheep fescue and (b) switchgrass germinated in a salt soution as a function of concentration. Control is the filtered Lake Superior water. Error bars represent standard deviation.**

The root to shoot (R:S) ratio was calculated as another indicator of seedling growth into straight length measurements, as changes in the root to shoot ratio indicate altered growth. The control R:S ratio is 0.4 for sheep fescue and 0.27 for switchgrass. The R:S ratio indicates where the seeds are prioritizing growth when under stress. Generally, the R:S ratio decreases with increasingly salinity, indicating the roots were more affected by salinity stress than the shoots (Figure 2.6). The R:S ratio is important to a plant as

adequate roots are necessary to support further growth above ground. The decreased R:S ratio at high salinities indicates that growth of the germinated seeds under salt stress is likely to be impaired as smaller roots have less ability to allocate and transport nutrients and resources (Maskova and Herben, 2018). Similar to germination rate, R:S ratio indicates that the growth of germinated seed appears to be more sensitive to acetate salts than chloride salts, which was not clear from the length of roots and shoots (Figure 2.4 & 2.5).
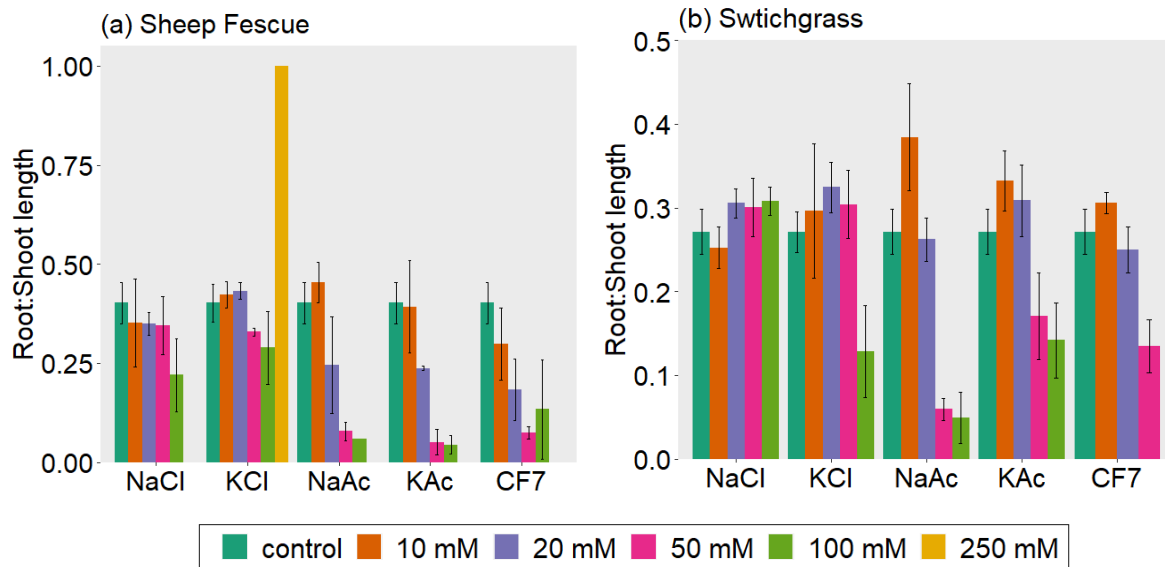
Figure 2.6. Root to shoot ratio in (a) sheep fescue and (b) switchgrass germinated in a salt soution as a function of concentration. Control is the filtered Lake Superior water. Error bars represent standard deviation. Note that there was only one data point for sheep fescue exposed to 250 mM of KCl as only 1 seed was germinated for the treatment.

Taken together, the Vigor Index was calculated as a measurement that combines the effects of salt on both germination and growth:

$$VI = \% \text{ germination} * (\text{mean root length} + \text{mean shoot length})$$

The Vigor Index decreases with increasing salinity, with a larger decline in acetate salts as was seen for the germination and growth measurements that contribute to the index (Figure 2.7). The Vigor Index is useful as it is commonly reported in seed germination studies, making comparison of germination possible across studies that express salinity in mM, g/L, mPa, or dS/cm. The Vigor Index of the control is very similar for both species, at 4574 ± 430 for sheep fescue and 4261 ± 261 for switchgrass. An increase in the Vigor Index at 10 mM is particularly notable in sheep fescue due to positive influence of low concentration salts to root and shoot growth, while switchgrass did not see a significant change to the index until high salinity reduced index values.
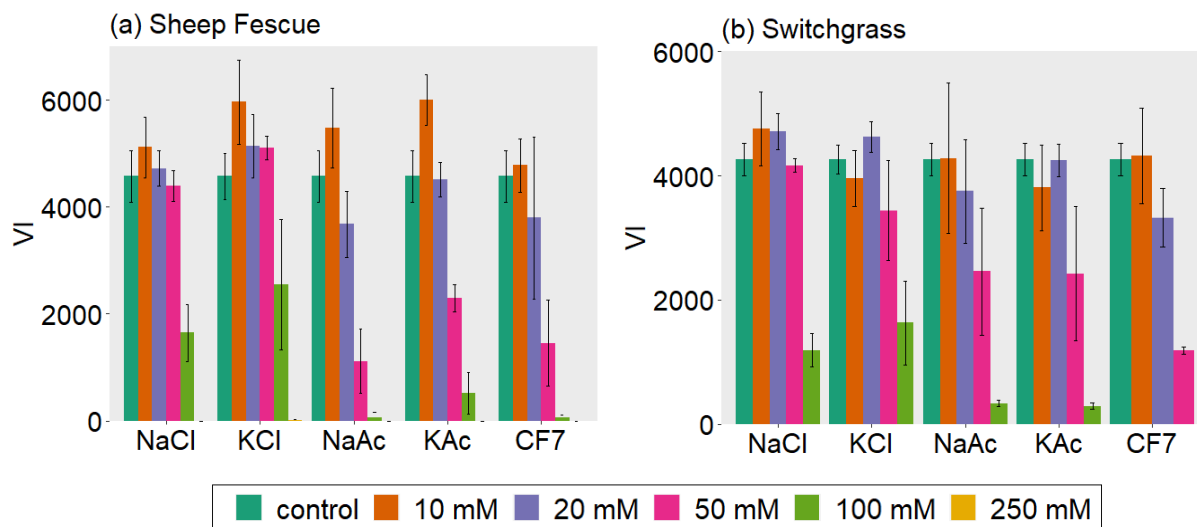
Figure 2.7. Vigor Index (VI) in (a) sheep fescue and (b) switchgrass germinated in a salt soution as a function of concentration. Control is the filtered Lake Superior water. Error bars represent standard deviation.

2.2.3.1 Microscopic observation of salt accumulation in grass roots

Root morphology and potential salt accumulation in roots were examined using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX) analysis to determine whether sodium or potassium was accumulating in the root cells. Figure 2.8 is an exemplary electrogram of the cross section of a root observed by SEM. The chemical composition of the germinated root surface was quantified by the EDX analysis. The majority (greater than 90%) of each cross section was found to be carbon (C) and oxygen (O) as plant matter along with K, Na, Cl, Ca, and Mg. The normalized percentage of each ion is given as atomic weight, all ion percentages were under 5%. Generally, seeds germinated in the salt solutions did uptake ions into the root when excess ions were available in the solution. The dominant ions except for C and O in root cells reflect the treatment solution, with up to a 50-fold increase in the percent of the ion compared to the control. For example, the atomic percentage of K in root cells was greater in salt solutions containing potassium such CF7, KAc, and KCl (Figure 2.9). It is noted that acetate (Ac) cannot be discerned from root tissues as it is an organic compound (C and O).
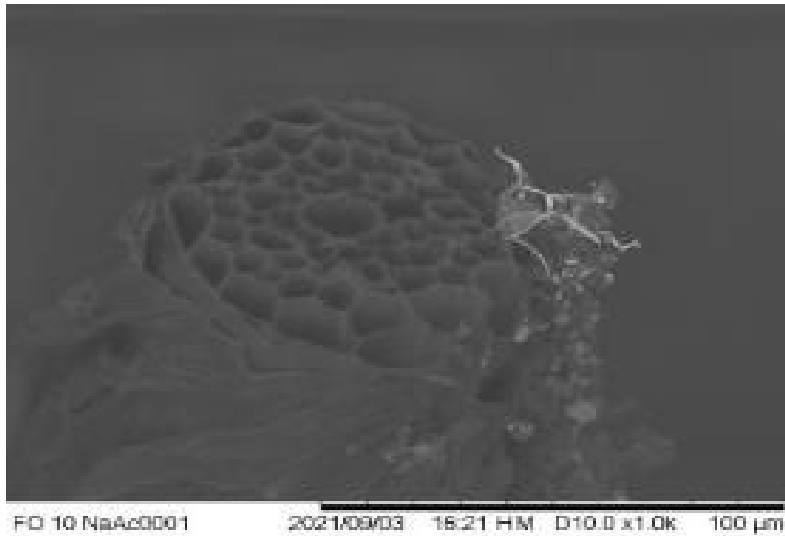
Figure 2.8. Cross section of sheep fescue root germinated in 10 mM NaAc solution

The increase in the percent of the K, Na, of Cl in the root indicates that, as the salinity of the environment increases, roots are taking in additional ions. While the accumuluation was only steady for potassium in KCl (Figure 2.9) and sodium in NaAc (Figure 2.10) solutions, the general trend of all plots is that the ions added in the salt solution increased with increasing concentration, especially in comparison to the control. As Ca and Mg were not components of any salt solutions, they were found on root cells at a relatively constant level regardless of the salt treatments, which were similar to control samples (Figure 2.11). They are likely to be in Lake Superior water (media) at low concentration.
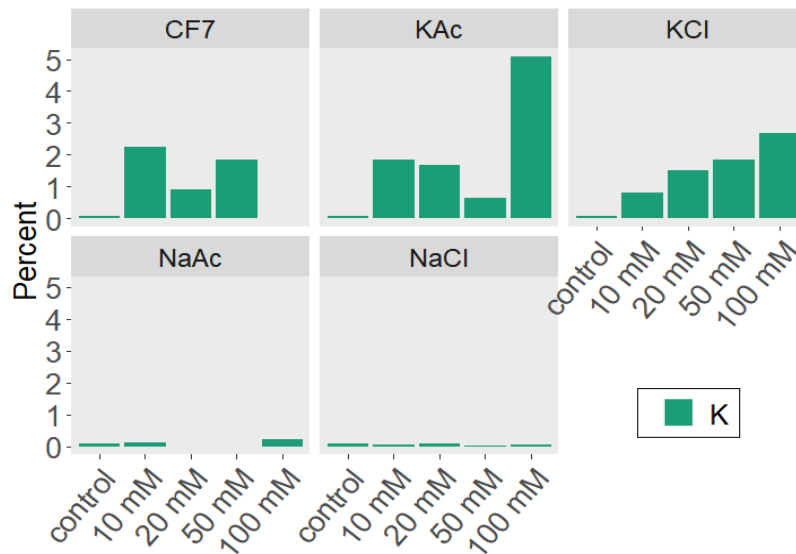
Figure 2.9. Atomic percent of potassium (K) in switchgrass root cross sections from EDX analysis. There were no seeds germinated in 100 mM CF7 solution.

56
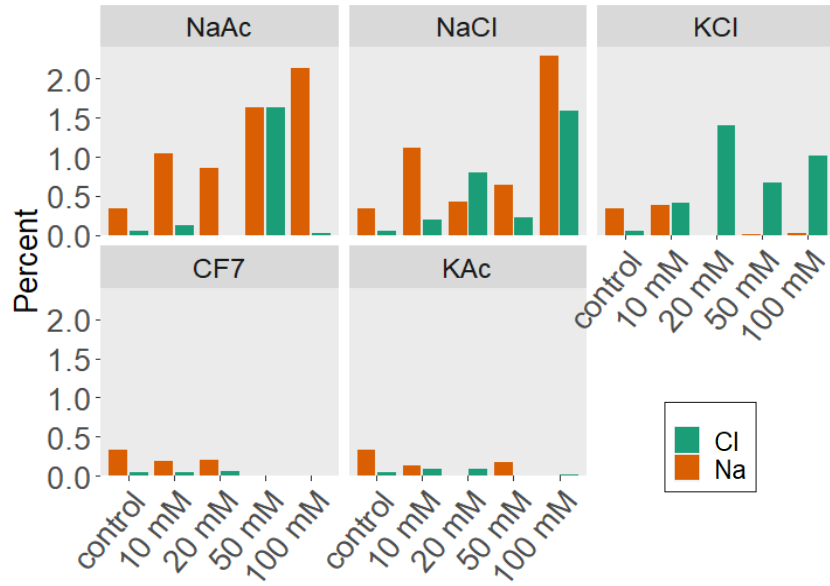
Figure 2.10. Atomic percentage of sodium (Na) and chloride (Cl) in switchgrass root germinated from salt solution from EDX analysis
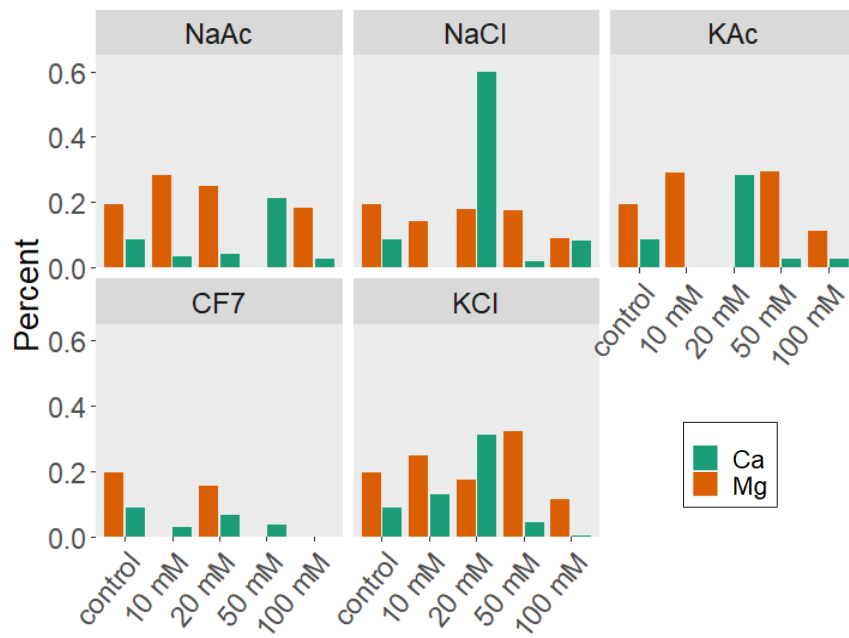
Figure 2.11. Atomic percentage of calcium (Ca) and magnesium (Mg) in switchgrass root germinated from salt solution from EDX analysis

2.3 AQUATIC TOXICITY OF SALTS ON WATER FLEAS

The application of CF7 to roadways will result in addition of the anti-icer/deicer, particularly potassium and acetate to freshwater as stormwater is deposited into receiving water bodies. Increased concentrations of chloride-based anti-icers/de-icers have been shown to be toxic to aquatic life. As KAc-based CF7 is considered as alternative anti-icer/deicer, it is important to determine the toxicological endpoints of CF7. The information helped us understand if the application of CF7 on roadways will result in toxic concentrations to aquatic organisms in light of the field evaluation reported in Chapter 3.

2.3.1 Experimental methods

Cladocerans, commonly known as water fleas, are commonly chosen for toxicity assays due to their important role in the freshwater food web, sensitivity to contaminants, and history as a model organism for aquatic toxicity tests. In this work, the organisms *Daphnia magna* and *Ceriodaphnia dubia* were used as model organisms for acute toxicity tests of the alternative anti-icer/deicer, CF7 and relative salts.

48-hour acute toxicity tests of CF7, KAc, and NaAc to *D. magna* and *C. dubia* were conducted at 25˚C, with an additional test at 20˚C for *D. magna*. Five concentrations of CF7, KAc, and NaAc solutions were made in amended Lake Superior Water: a range of 21-346 mg/L CF7 as K^+, 31-500 mg/L as K^+ from KAc, and 125-2000 mg/L as Na from NaAc. Concentrations were verified by acetate analysis on an HPLC. During the experiments, pH was maintained and monitored at 6.5-9.

The toxicity tests were conducted in a water bath under a 16:8-hour light/dark cycle. The organisms were obtained from culture units of the Great Lakes Toxicology & Ecology Division, EPA. Five organisms of less than 24 hours old were used for each treatment in triplicate designated as A, B, and C. Organisms in the A and B replicates were fed a mixture of yeast, cereal leaves, algae, and trout chow prior to the addition of the salt solution. The C replicate was not fed to determine if food affected the toxicological response. Survival was recorded at 24 and 48 hours and the LC_{50}, lethal concentration causing the death of 50% of a group of a test organisms, was determined.

2.3.2 Results and Discussion

LC_{50} endpoints are reported in Table 2.2, with the lowest LC_{50} as 0.13 g/L CF7 as K and the highest LC_{50} at 8.4 g/L for NaAc. LC_{50} values of K^+ were comparable to both *C. dubia* and *D. magna* between the CF7 commercial product and pure KAc salt, indicating that the proprietary mixture does not contribute meaningfully to toxicity. The LC_{50} of KAc and CF7, when expressed as K concentration, are similar to the LC_{50} values of K^+ (KCl salt) for *C. dubia* using Lake Superior water from the previous study of Mount et al., 2016. This suggests that K^+ is responsible for most of the acute toxicity of CF7 to Cladocerans. The LC_{50} for KAc and CF7 is between 0.46 g/L and 0.93 g/L, while the LC_{50} for NaAc is much higher at 7.26~8.4 g/L. This indicates that potassium is the likely driver of toxicity in the acetate salts. LC_{50} endpoints did not change as organism survival was recorded at 24 and 48 hours, or between 25˚C and 20˚C.

Table 2.2. LD$_{50}$ of CF7, KAc and NaAc for C. dubia and D. magna

Salt (g/L)	*C. dubia* 25°C	*D. magna* 25°C	*D. magna* 20°C
CF7 (K$^+$)	0.73 (0.13)	0.87 (0.15)	0.93 (0.16)
KAc (K$^+$)	0.46 (0.18)	0.46 (0.18)	0.46 (0.18)
NaAc (Na$^+$)	7.26 (1.23)	8.34 (1.41)	8.4 (1.42)

There are other studies that report the 48-hour LC$_{50}$ of CF7 for *C. dubia*, shown in Table 2.3. The LC$_{50}$ determined in this experiment is 0.73 mg/L for *C. dubia*, close to the endpoint found for Mussato and Guthrie (0.66 g/L), and lower than for Pilgrim (1.3 g/L). As mentioned earlier, Mount et al. (2016) found that the *C. dubia* LC$_{50}$ for K$^+$ (in KCl) is 0.18 g/L, an identical endpoint to the K$^+$ as KAc endpoint determined here, emphasizing the role of K$^+$ and not the anion in toxicity.

Table 2.3. LC50 and IC25 toxicological endpoints (g/L) reported in the literature for CF7

Species	LC$_{50}$	IC$_{25}$	Source
Ceriodaphnia dubia	0.66 (2 days)	0.16 (7 days)	Mussato and Guthrie (2000)
	1.29 (2 days)		Pilgrim (2013)
	0.53 (7 days)	1.8[a] (7 days)	Pilgrim (2013)
	0.66 (7 days)		Mussato and Guthrie (2000)
Pimephales promelas	1.67 (4 days)		Pilgrim (2013)
	0.74 (7 days)	2.06[b] (7 days)	Pilgrim (2013)
Selenastrum capricornutum		0.22 (3 days)	Mussato and Guthrie (2000)
		0.03[b] (4 days)	Pilgrim (2013)
Oncorhynchus mykiss	2.28 (4 days)		Mussato and Guthrie (2000)

[a]IC$_{25}$ for young production
[b]IC$_{25}$ for growth

The toxicity tests indicated that potassium is the driver of toxicity in CF7. The driver of toxicity is important to know, as the concentration of K$^+$ can be monitored to determine if CF7 will impact *cladocerans*. The concentration of K$^+$ found in the field after application of CF7 through a field evaluation (Chapter 3) was less 0.01 g/L in Lake Superior as receiving water body even though the concentration was much greater (up to 2.0 g/L in stormwater) in stormwater runoff. Samples were collected from Lake Superior in three locations where stormwater carrying runoff from roads treated with CF7 was entering the lake, and at two locations no traces of the anti-icer/deicer was found due to dilution. At another, more protected site, K$^+$ peaked at 0.66 g/L during spring melt, five times greater than the lowest LC50 for K$^+$ (0.13 g/L). However, this was the only time K$^+$ was observed above the LC$_{50}$, the other samples with K$^+$ detected at this site were below 0.13 g/L. It is unclear how if the concentration of K surpassed the LC50 for greater than 48 hours.

Aquatic toxicity tests of KAc and other salts were performed at 20 and 25˚C, which is known as optima temperature, making the LC_{50} endpoints comparable to others in the literature. Toxicity testing was also done at 20˚C for *D. magna* to determine if a lower temperature affects toxicity. Survival of *D. magna* at 25˚C was no different from survival at 20˚C (Table 2), indicating temperature does not play a role in toxicity. However, this is only a change of 5 degrees, while in the field daphnia are exposed to CF7 in water temperatures at or less than 4˚C. Unlike the laboratory toxicity experiment condition, temperature in the field is variable and colder than the optimal temperature during snowmelt season. To extrapolate laboratory toxicity data to ecosystem receiving snowmelt water, one needs to understand the effect of temperature on organismal response and sensitivity to ions.

Although toxicological experiments of KAc and other salts at cold temperatures were not conducted, temperature-dependent toxicity data of other chemicals on water fleas may be useful to predict toxicological response of water flea to K^+ at cold temperatures. Huegens et al. reported that *D. mamga*'s sensitivity (e.g internal threshold concentration and killing rates) to cadmium enhanced with increasing temperature above 25˚C (Huegen et al 2003). Similar temperature-dependent toxicity trends were observed for common pharmaceuticals (Kim et al, 2010) but zinc toxicity on *D. logispina* was not affected by temperature (Van de Perre et al, 2018). These studies indicate that warmer waters over 25 ˚C increase toxicity but colder temperature (10-20 ˚C) have less (or no) influence on their sensitivity to chemicals. The phenomena are likely attributed to changes in metabolic and locomotory activities by temperature: toxicity of chemicals to cladocerans increases with increasing temperature due to the increased metabolism and uptake of that compound (Huegen et al 2003). Presumably, toxicological effect of K^+ on cladocerans at cold temperatures may be similar to those at the optimal temperature (usually 20 ˚C) due to slower metabolism and less uptake of K^+.

2.4   CHAPTER 2 SUMMARY AND IMPLICATIONS

The toxicity of CF7, a KAc-based alternative anti-icer/deicer to terrestrial and aquatic fauna and flora was assessed to understand if the anti-icers/de-icers in receiving water bodies and on the roadside after CF7 application affect vegetation and aquatic life in proximity to roads. This study reports toxicological endpoints of CF7 and its relevant salts for roadside grasses and water fleas for the evaluation. Germination experiments of roadside grasses, sheep fescue and switchgrass, were designed for the toxicity test for terrestrial flora. To assess aquatic toxicity of CF7, water fleas (*cladocerans*) were selected as sensitive indicators for acute toxicity tests. In addition to determination of toxicological endpoints, the toxicity experiments were designed to inform which ionic species (K^+, Ac^-, the combination or CF7 additives) was responsible for toxicological effects on each case.

Overall, both CF7 and pure KAc salt have lower toxicological endpoints (EC_{50} and LC_{50}) for both roadside grasses and water fleas in compassion to the conventional anti-icer/deicer, NaCl, indicating the organisms were more sensitive to KAc at lower concentration than NaCl. Based on toxicological endpoints, there was no statistical difference between CF7 and KAc, suggesting the contribution of additives in CF7 to overall toxicity was minimal. Interestingly, the acetate anion (Ac^-) of KAc was found to

be responsible for sensitivity of grass seed germination while potassium ion (K^+) was attributed to acute toxicity for water fleas.

The seed germination experiment revealed effects of salt on seed germination began between 20 and 50 mM. Even though seed germination was affected by CF7 at lower concentrations than sodium chloride, the concentration at which germination was impaired was rarely reached in the field. The concentration of 20 mM CF7 at which deleterious effects occur was equivalent to 2 g/L CF7 as KAc. Soil concentrations of NaCl have been reported to reach 1.5 g/L (Pederson et al., 2000), and were unlikely to reach the 5 g/L of the EC_{50} of CF7 due to dilution from roadside snowmelt.

However, for aquatic toxicity, the LC_{50} endpoints could be surpassed if CF7 were applied to roads draining into a smaller water body than Lake Superior. The field evaluation (Chapter 3) of CF 7 application to Blatnik bridge and I-35 whose runoff enters to Lake Superior indicated K^+ concentration did not reach concentrations causing acute toxicity to aquatic life in Lake Superior except for at one location. It was observed that the concentration of K^+ may briefly surpass the LC_{50} endpoint in the protected bay site (Rice's Point) during spring melt but was likely to be diluted quickly. However, if CF7 application were expanded, other roadways that have runoff draining into smaller waterbodies, the probability of surpassing the LC_{50} in waterbodies with less dilution would be greater.

Future work in modeling will be useful to use the biodegradation constants obtained in the lab to predict the concentration of CF7 found in other receiving water bodies. LC_{50} endpoints for *C. dubia and D. magna* are valuable in determining if the runoff carrying CF7 will result in toxic effects in receiving waterbodies. Future work in vegetative toxicity could expand the roadside species tested and move beyond petri dishes to a field study. Salinity causes toxicity by osmotic potentials preventing water uptake or direct ion toxicity, but in the field, the soil texture and chemistry would be additional factors that could impact vegetation. Likewise, growth of seeds in soil rather than salt solutions would also take cation exchange capacity into consideration, as high inputs of a cation from the anti-icer/deicer has been shown to replace other cations such as calcium and magnesium on exchange sites, removing them from potential uptake by the plant (Hartl and Erhart, 2002).

Lastly, it is important to conduct toxicity tests for several aquatic and terrestrial flora and fauna relevant to the application sites, as previous studies have reported variable toxicological response to anti-icer/deicer salts among different organisms. For example, Joutti et al. (2003) also found that KAc anti-icer/deicer was much more toxic to onions and duckweed than NaCl, similar to the results in this work, but potassium (K^+) was identified as an agent of toxicity, which differs from the findings of this study. Conversely, Gerasimov (2021) found that KAc and sodium formate anti-icers/de-icers were less harmful to wheat root growth and biomass than NaCl. Despite that, minimal variation between grass species was observed in this study, with the Vigor Index showing sheep fescue has increased growth at 10 mM, and the germination of sheep fescue is slightly more sensitive to salinity of acetate salts than switchgrass. While two grass species were studied among the many grasses, forbs, and wildflowers found along roadsides, the similarity in response of switchgrass and sheep fescue to salinity is promising in that these effects can be broadly applied to grass species.

2.5 CHAPTER 2 SUPPLEMENTARY INFORMATION

Table 2.4. Significance of differences in salinity within salt groups for germination of sheep fescue according to Tukey post-hoc test

	NaCl	KCl	NaAc	KAc	CF7
control vs 10 mM	ns	ns	ns	ns	ns
control vs 20 mM	ns	ns	ns	ns	ns
control vs 50 mM	ns	ns	***	*	***
control vs 100 mM	ns	ns	***	***	***
control vs 250 mM	***	***	***	***	***
10 mM vs 20 mM	ns	ns	ns	ns	ns
10 mM vs 50 mM	ns	ns	***	***	***
10 mM vs 100 mM	ns	ns	***	***	***
10 mM vs 250 mM	***	***	***	***	***
20 mM vs 50 mM	ns	ns	***	*	***
20 mM vs 100 mM	ns	ns	***	ns	***
20 mM vs 250 mM	***	***	***	***	***
50 mM vs 100 mM	ns	ns	***	***	**
50 mM vs 250 mM	***	***	***	***	***
100 mM vs 250 mM	***	***	ns	***	ns

ns: not significant, p: 0.05, * p < 0.05, ** p < 0.005, * p < 0.0005

Table 2.5. Significance of differences in salinity within salt groups for germination of switchgrass according to Tukey post-hoc test

	NaCl	KCl	NaAc	KAc	CF7
control vs 10 mM	ns	ns	ns	ns	ns
control vs 20 mM	ns	ns	ns	ns	ns
control vs 50 mM	ns	ns	ns	*	**
control vs 100 mM	***	**	***	***	***
control vs 250 mM	***	***	***	***	***
10 mM vs 20 mM	ns	ns	ns	ns	ns
10 mM vs 50 mM	ns	ns	ns	ns	***
10 mM vs 100 mM	***	*	***	***	***
10 mM vs 250 mM	***	***	***	***	***
20 mM vs 50 mM	ns	ns	ns	*	**
20 mM vs 100 mM	***	**	***	**	ns
20 mM vs 250 mM	***	***	***	***	***
50 mM vs 100 mM	**	ns	***	*	**
50 mM vs 250 mM	***	***	***	***	**
100 mM vs 250 mM	ns	**	ns	ns	ns

ns: not significant, p: 0.05, * p < 0.05, ** p < 0.005, * p < 0.0005

3 Environmental Field Evaluation and Persistence of KAc in Meltwater, Runoff, and Receiving Water

Prepared by:

Chan Lan Chun[2]
Jerry Henneck[2]
Kathryn Cassidy[2]
John S. Gulliver[1]

[1]St. Anthony Falls Laboratory, University of Minnesota
[2]Natural Resources Research Institute, University of Minnesota Duluth

3.1 OBJECTIVE

This research conducted an environmental field evaluation of a road salt alternative, potassium acetate (KAc, commercial product CF7), in Duluth, Minnesota. KAc is an organic, liquid anti-icer/de-icer that is being applied on I-35 and Blatnik Bridge for winter road safety. The meltwater from these roadways travels through stormwater drains or (runoff pipes) and eventually enters Lake Superior. The objective of this project was to conduct an environmental field evaluation of KAc concentration and water quality in meltwater, road runoff and receiving water bodies. The field measurements were performed at MnDOT District 1's field sites of KAc application in Duluth. Two years of winter field sampling was conducted, with the first, 2019-2020, focusing on the methodology and logistics of sampling stormwater in the winter, and the second, 2020-2021, using knowledge developed in the first season to increase KAc sample size.

Stormwater samples were collected from I-35, Central Entrance, and Blatnik Bridge during or following snow events in the winters of 2019-2020 and 2020-2021. Receiving waterbody samples were collected from Lake Superior, where the stormwater was being discharged. We investigated temporal and spatial changes of KAc concentration and water quality including biochemical oxygen demand (BOD5), major ions and the microbiological indicator, Escherichia coli (E. coli) in meltwater, road runoff, and receiving water bodies. In addition to a field evaluation, a degradation experiment of CF7 was conducted to understand the fate of CF7 in Lake Superior water. The outcome of this study will inform decision makers on the environmental impact of using KAc as a road salt alternative.

3.2 FIELD SAMPLING CAMPAIGN

MnDOT treated KAc anti-icer/de-icer on the Blatnik Bridge and I-35 roadways. When sites were chosen, Central Entrance was also expected to be treated with KAc and was selected as a third field site. MnDOT informed the research team that NaCl was co-used with KAc on this roadway during Year 1, so samples from Central Entrance were considered to be control (NaCl) sites in comparison to KAc treated sites. To

determine the impacts of KAc application on the receiving water body, stormwater was collected off roadways where KAc was applied, and samples were collected from water bodies that received the stormwater runoff. Samples of snow meltwater and road runoff were collected at three major routes where KAc was applied as a de-icing agent: I-35 (green in Figure 3.2), Central Entrance (yellow), and Blatnik Bridge (blue). Field study sites were identified by visiting the KAc application sites with project teams of the University of Minnesota- Duluth (UMD), MNDOT, Iowa State University (ISU) and the City of Duluth. Storm drains were selected based on 1) safety of parking and sampling 2) NaCl and KAc drains had similar drainage basin sizes and land uses 3) storm drains were constructed so that they could be entered and field equipment could be effectively installed. Table 3.1 summarizes the final study sites with sample ID, shown in Figure 3.5. CF7 was applied on Bong Bridge (purple in Figure 3.2) but this was determined to be unfeasible for sampling due to safety concerns.

In the first year, the sites at I-35 and Central Entrance included an upstream control site where solely chloride-based anti-icers/de-icers were applied, a treatment site which contained snow meltwater and road runoff from KAc application, and downstream sampling sites (Lake Superior) which received runoff from both chloride-based anti-icers/de-icers and KAc application. Blatnik Bridge did not have an upstream NaCl site but did have a KAc runoff collection site and downstream sampling site in Rice's Point of Lake Superior. In the second field season, sites applied with chloride-based salts were not resampled but additional KAc sites were added at I-35 and Blatnik Bridge to increase sample size. Sampling was conducted from November 2019 through March 2021 after snow events. Sampling during Year 1 is shown in Figure 3.1. Monthly sampling events were co-conducted with the project team of ISU, working on Minnesota Department of Transportation, MnDOT Agreement No. 1034774.
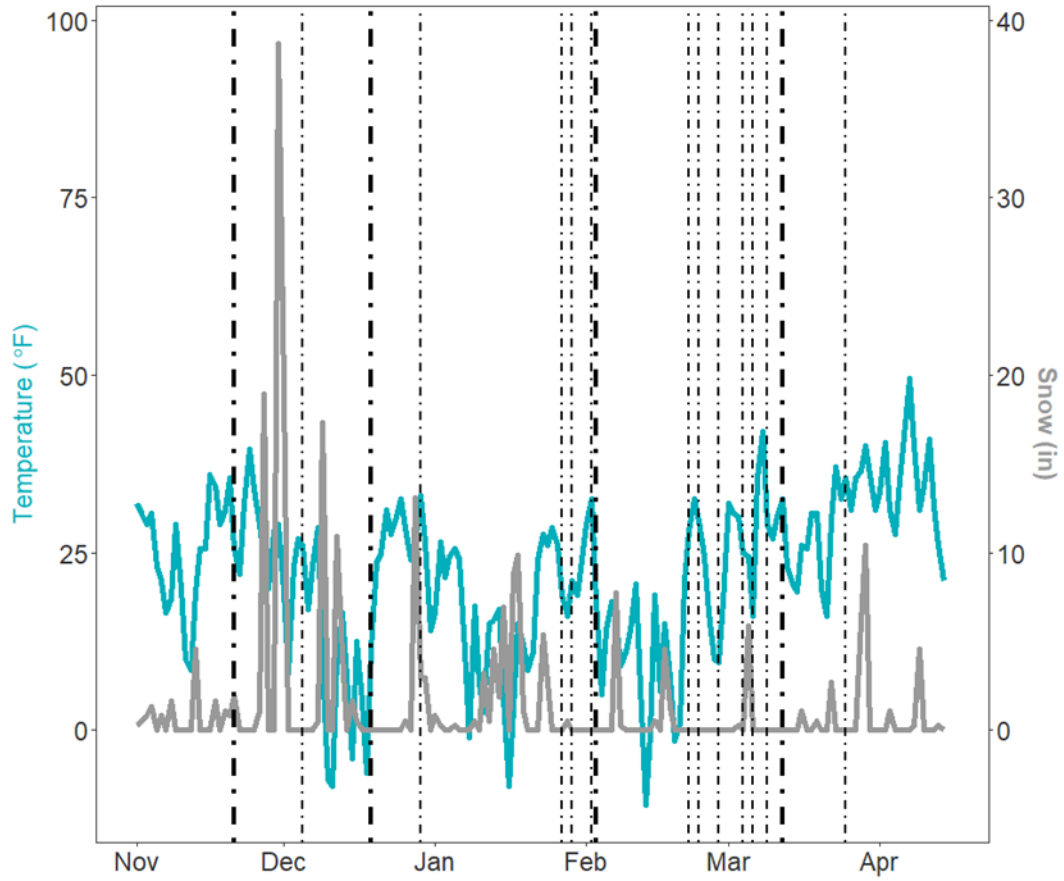
Figure 3.1. Monthly and event runoff collection dates in 2019-2020 winter with temperature and snowfall. Lines indicate field sampling campaigns (bold lines: sampling with the ISU team.

Figure 3.2. Site routes of planned KAc application in yellow (Central Entrance), green (I-35), blue (Blatnik Bridge), and purple (Bong Bridge)

3.2.1   2019-2020 Locations

3.2.1.1   I-35 route (3 sites)

Three sampling locations at I-35 were selected: an upstream stormwater collection system within the city of Duluth above I-35, a stormwater drain of I-35, and Lake Superior water as stormwater receiving water (Figure 3.3). The upstream stormwater sample (green star on Figure 3.3 marked on 16th Avenue) I-35-NaCl was collected from the stormwater collection system at the intersection of London Road and 16th Avenue where chloride-based anti-icers/de-icers (mostly NaCl) are applied above I-35. Snowmelt water from I-35 where KAc is applied will be collected from the MnDOT stormwater collection system

located on the eastside of Duluth Lakewalk (pink star; I-35-KAc-A). Lake Superior water (blue star; I-35-LS) near the collection system will be collected as stormwater receiving water.

3.2.1.2 Central Entrance route (3 sites)

Sampling locations on Central Entrance were selected in a similar manner with I-35 routes: an upstream collection system above Central Entrance on Pecan Avenue (green star on Figure 3.3; CE-NaCl), a road runoff collection system from Central Entrance (pink star, CE-KAc), and Brewery Creek (blue star; CE-BC) where both runoffs enter. Brewery Creek was accessed from Marshall School and the access trail was maintained since it is a CrowdHydrology site (http://www.crowdhydrology.com/)
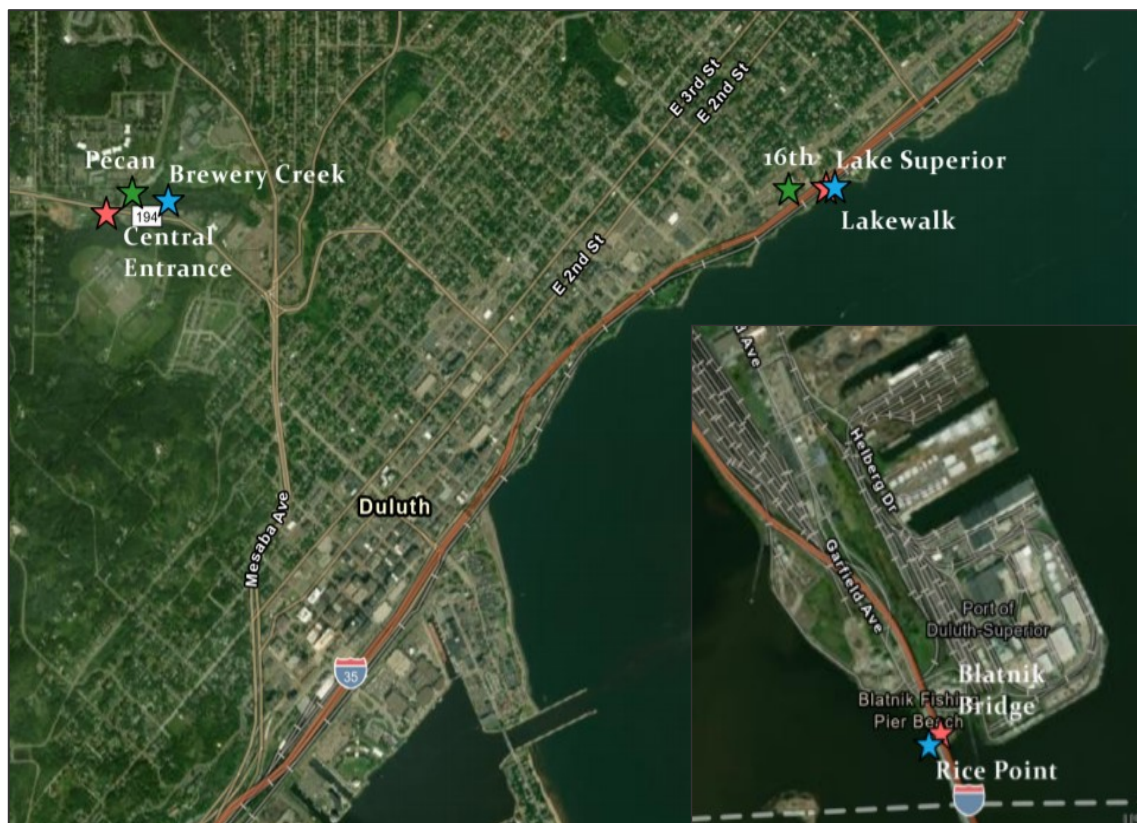
Figure 3.3. Study sites for Year 1 for snowpack meltwater, road runoff and receiving water body including upstream NaCl sites (green), KAc sites (pink), and waterbody receiving stormwater runoff (blue)

3.2.1.3 Blatnik Bridge (2 sites)

With site visits and discussion, runoff from the bridge was collected from a longitudinal pipe collection system (pink star in Figure 3.3; BB-KAc-A) from Blatnik Bridge deck that drains bridge runoff into Rice's Point (Lake Superior). The drainage pipes were about 60 ft off the ground, making collection difficult. The initial drainage pipe that was selected had to be moved to a pipe further down the bridge as the initial site served as a MnDOT snow collection site and the sampling location was inaccessible after November 2019. In addition to collecting bridge runoff, the Lake Superior water sample at Rice's Point was collected as stormwater receiving water (blue star; BB-RP-A).

3.2.2 2020-2021 Locations

3.2.2.1 I-35 route (3 sites)

Instead of NaCl sites, additional KAc sites for both I-35 and Blatnik Bridge were added in Year 2 to increase stormwater carrying KAc sample size (Figure 3.4). Two storm drains were sampled from I-35: I-35-KAc-A is the same site used in the first year of the study and I-35-KAc-B was added as an additional sampling point. Site I-35-KAc-B was added to have additional KAc stormwater samples and is a sediment basin as a best management practice for stormwater coming from I-35. Stormwater from this site is directly discharged into Lake Superior. Stormwater from I-35-KAc-A also travels into this site along with runoff from an additional stretch of I-35 so it was a good location to collect the composite stormwater runoff from I-35. As the basin was open to the air, the stormwater was completely frozen during February and March of 2021. Due to that, limited samples were taken from this site for most of February and March. The receiving water body for I-35 runoff remained the sample place in Lake Superior. The Lake Superior sampling point was less than 10 ft away from where the stormwater is deposited into the lake.

Figure 3.4. Sampling locations of Year 2 at (A) Blatnik bridge and (B) I-35. KAc runoff sites are shown in pink and receiving water body sites in blue.

3.2.2.2 Bridges (4 sites)

Sites BB-KAc-A and BB-RP-A remained from the first year of sampling, but additional sites (BB-KAc-B and BB-RP-B) were added in the 2020-2021 winter sampling season (shown in Figure 3.4). BB-KAc-B was added to have an additional sampling point to capture bridge runoff, as bridge runoff collection was challenging in the 2019-2020 winter due to high drain point and wind. BB-RP-B was chosen as an additional receiving water site as a pipe from the bridge discharges road meltwater directly into the lake about 3 m (less than 10 ft) from shore. At BB-RP-A, bridge runoff is not directly mixing with the lake, but rather traveling over the parking lot or blowing over the lake and into the water. With the more direct connection of the bridge and BB-RP-B, this site was added to examine if the runoff is detectable when bridge runoff is mixed with lake water, and if so, if the CF7 in that runoff impacts lake water chemistry.

Table 3.1 summarizes the description of the sampling sites shown in Figures 3.3 and 3.4 and gives site IDs.

Table 3.1. Study site description and ID of both field seasons.

Roadways	Anti-icer/de-icer application	Site ID	Year sampled	Description
1-35	NaCl	I-35-NaCl	Year 1	A storm drain on 16th Ave above I-35
	KAc	I-35-KAc-A	Year 1 & 2	A storm drain on Lakewalk receiving runoff from I-35
	KAc	I-35-KAc-B	Year 2	A stormwater BMP on the Lakewalk; receives runoff from I-35 before being discharged into the lake
	Receiving water	I-35-LS	Year 1 & 2	Lake Superior receiving road runoff from both chloride-based anti-icer/de-icers and KAc application
Central Entrance	NaCl	CE-NaCl	Year 1	A storm drain on Pecan Avenue above Central Entrance
	KAc	CE-KAc	Year 1	A storm drain receiving Central Entrance runoff
	Receiving water	CE-BC	Year 1	Brewery Creek receiving road runoff from both chloride-based anti-icer/de-icers and KAc application
Blatnik Bridge	KAc	BB-KAc-A	Year 1 & 2	Runoff pipe from Blatnik bridge
	KAc	BB-KAc-B	Year 2	Runoff pipe from Blatnik bridge
	Receiving water	BB-RP-A	Year 1 & 2	Lake Superior at Rice's Point where bridge runoff enters
	Receiving water	BB-RP-B	Year 2	Lake Superior at Rice's Point; sampled by wading into the lake

3.2.3 Sampling Methods

Runoff collection from stormwater collection systems was conducted with a combination of grab sampling and automatic samplers (ISCO 6712 and 3700), while runoff-receiving water samples were collected through grab sampling. Sampling protocol evolved over the first field season as we developed the most efficient method to sample in the winter and made changes based on sampling challenges.

Sampling methods in Year 2 were improved for safe and effective sample collection based on the first winter's experience.

Samples were collected with 1L polyethylene bottles that were washed and bleached. When grab samples were taken, bottles were rinsed in the sample water three times. Field measurements of dissolved oxygen, pH, temperature, and conductivity were taken with a YSI pro plus multimeter. Stormwater samples collected in ISCO units were open to the atmosphere before collection, which may have increased dissolved oxygen concentrations in I-35 and Central Entrance sites. The collected samples were immediately placed on ice for transportation to the Natural Resources Research Institute for sample processing.

Downstream sampling at Lake Superior and Brewery Creek was done by grab sample. Samples were taken from shore at Brewery Creek, from a dock at BB-RP-A, and by wading into the water at BB-RP-B. While the initial plan was to sample I-35-LS by reaching into the water for a grab sample as in Rice's Point, the icy rocks along shore created unsafe conditions so samples were taken from with a bucket on a rope. When ice formed at Rice's Point, an ice pick was used at BB-RP-A. Ice at BB-RP-B reached down to the bed of the lake so samples were only taken in early winter and during Spring melt.

3.2.3.1 Stormwater collection sites:

Stormwater was collected daily in Year 1 with automated water samplers (ISCO 6712) that were deployed in the KAc sites located at Central Entrance (CE-KAc) and I-35 (I-35-KAc-A). The ISCO units were stored inside the lockbox and were powered by a solar panel that supplies continuous power to a 12V deep cycle battery (Figure 3.5A and C). Samplers were programmed on an 8-hour time interval to accumulate a 0.75 L runoff sample each day. Each sample was collected in a separate ISCO bottle. A total of 24 bottles were held in a single sampler at a time but the bottles were collected weekly and after each snowstorm or snowmelt event. The weekly visit was also required for maintenance to clear snow in solar panels and ice in the tubing. These ISCO units worked well at holding charge but ice in the tubing created sampling difficulties. Tubing within the manhole rarely froze, and the section of tubing from the manhole cover to the box could be insulated with foam and hand warmers. The problematic section was the few inches going through the manhole cover. There was not enough of a gap to warm the tubing and ice would block sample from entering the unit. Visits to the sites to conduct repetitive flushing of the tube before snowfall helped clear the tubing. When ISCO units malfunctioned due to disconnection from the battery, poor suction, or ice in the line, grab samples were taken at I-35-KAc-A directly from the storm drain. Continuous autosamplers could not be installed at the I-35-NaCl and CE-NaCl sites as the NaCl storm drains were located in the street, but 3700 ISCO samplers were installed the day before each sample collection to capture composite stormwater runoff.

Figure 3.5. Setup at I-35-KAc-A site (A) ISCO sampling unit box and (C) ISCO set up with battery inside the box. The I-35-KAc-A storm drain (B) was sampled with a flow meter and ISCO tubing attached to a spring ring, and a weir to back up flow.

In Year 2, the ISCO unit within a lockbox remained at I-35-KAc-A, but as Central Entrance sites were no longer in use the ISCO box was moved from CE-KAc to I-35-KAc-B. Site I-35-KAc-B (Figure 3.6) was added to have additional KAc stormwater samples and is a sediment basin as a best management practice for stormwater coming from I-35. Stormwater from this site is directly discharged into Lake Superior. Stormwater from I-35-KAc-A also travels into this site along with runoff from an additional stretch of I-35 so it was a good location to collect the composite stormwater runoff from I-35. As the basin was open to the air, the stormwater was completely frozen during February and March, 2021. Due to that, limited samples were taken from this site for most of February and March. Units were programmed to take a composite sample of 330 ml three times per day, for a total sample volume of ~ 1L. Bottles were collected as soon as possible after a snow event, typically within one day and a maximum of five days depending on air temperature. When the ISCO unit malfunctioned at I-35-KAc-B, samples were not able to be taken as this site is a stormwater basin with a grate preventing grab samples.

Figure 3.6. (A) ISCO sampling unit box used to collect stormwater from the sedimentation basin, I-35-KAc-B site, (B) ISCO tubing and conductivity/temperature sensor through the metal screen to collect stormwater in the basin, and (C) frozen stormwater in the basin during February-March, 2021

Initially, the plan was to rely on UMD's two 3700 series and ISU's two 6712 series ISCO automated samplers to pump composite stormwater samples into collection bottles. However, as the winter progressed, grab samples were taken at most sites due to challenges with the ISCO batteries being unable to stay charged with the below freezing temperatures and ice formation in the tubing blocked

samples from being drawn. When ISCO sampling failed, grab samples were taken upon bottle retrieval. Particularly, stormwater runoff samples from NaCl storm drains were largely represented by grab samples.

It became clear after initial site inspection that flow in the storm drains was variable and not sufficient for autosampling or flow measurements. To improve stormwater sample collection and flow measurements from low flow of runoff, a volumetric weir (Thel-Mar) was installed in all storm drain sites along with an ISCO spring mount ring with a 2150 ISCO Flow Module and a weighted sample strainer (Figure 3.7). Flow measurements were taken at each stormwater site with a 2150 ISCO Flow Module, which uses continuous wave Doppler technology to capture flow data with an area velocity (AV) probe. The AV probe and autosampler tubing were fastened to a spring ring to hold equipment in place in the storm drain. At some locations, there were challenges with water flowing under the weir (see Figure 3.44 in Chapter C Supplementary Information) and wet cement and foam was applied to keep the weir in place without leaks. I-35-KAc-A was a particularly difficult site to sample. Due to weathering of concrete in the drain, the weir did not seal properly which caused water to flow under the weir during the Year 1 study. This was improved for Year 2 with assistance from the City of Duluth which led to the successful installation of a weir (Figure 3.5B) in the drain, necessary to back up flow in order for the ISCO tubing to be submerged to take a sample.
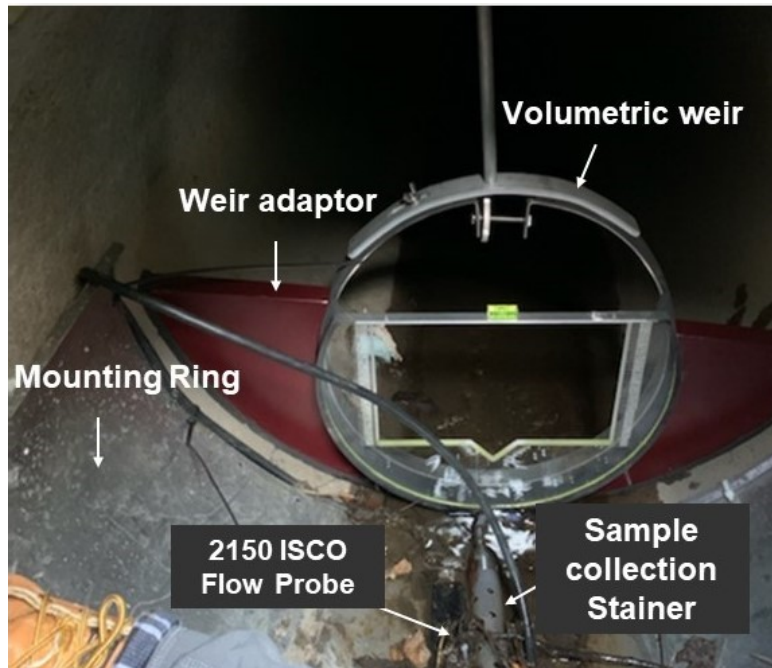
Figure 3.7. Runoff sampling set-up in storm drain with weir, adapter, spring mounting ring, flow probe and sample collection strainer.

Flow measurements at the storm collection systems are shown in Figure 3.8. CE-KAc and I-35-NaCl have long term accurate flow data. At I-35-KAc-A and CE-NaCl, obtaining accurate flow measurements was a continuous challenge due to uneven piping and Flow module battery failures. I-35-NaCl and the I-35-KAc-A had continuous flow most of Year 1, while flow at CE-KAc and CE-NaCl slowed to a trickle or stopped entirely unless melt was actively occurring. During Year 2, the only storm drain able to be outfitted with a Flow Module was I-35-KAc-A, however, much of the winter is missing due to frozen stormwater in the drain January-February and battery issues in March (total snow fall: 0.33 in and average temperature: -0.6 ~15.7 F in February).
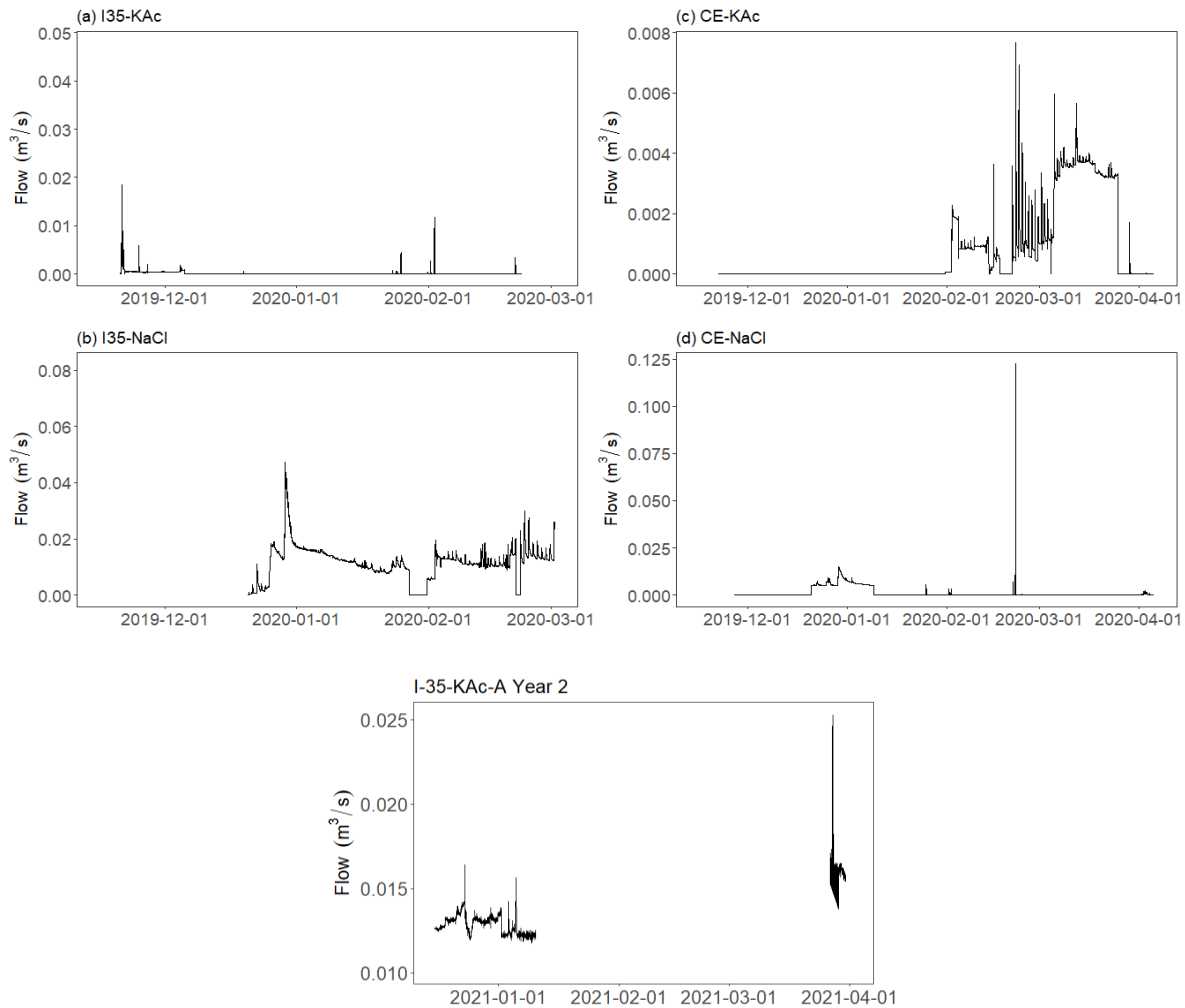
Figure 3.8. (a) Flow at the I-35-KA-Ac site Year 1. Only peak melt events are captured as the weir was not backing up enough flow for the AV probe to be submerged most of the season. The flow dataset ends early due to equipment failure (b) Flow at I-35-NaCl site Year 1. (c) Flow at CE-KAc site Year 1. (d) Flow at CE-NaCl site Year 1. While flow was often nonexistent or a trickle at this site, the data is low quality as there was an ill-fitting weir installed much of the season. (e) Flow at I-35-KAc-A site Year 2.

3.2.4 Blatnik Bridge and Rice's Point:

Blatnik Bridge sampling was challenging due to the drainage pipe installed 60 ft above ground. The initial sampling location chosen with MnDOT was located at a snow removal site. Once snow began being deposited, the collection barrel was buried (Figure 3.9A) and the site was moved to be underneath another pipe further down the bridge (Figure 3.9B). The bridge snowmelt would fall from this pipe and travel over the parking lot into the Rice's Point sampling location (Figure 3.9C). A rain chain was proposed, but due to concerns about water freezing around it and blocking the drain along with the potential hazard of the chain blowing around the parking lot in the wind, was not installed. Initially, a 55-gallon rain barrel was placed underneath the bridge deck outlet pipe to catch the runoff (3.9A). The barrel was fixed with cinder bricks and fences. The barrel collected more than a sufficient amount of sample in early winter when snow was mixed with rain, but as it got colder and windy the barrel was only able to catch a little runoff from the bridge. Additionally, this posed problems with ice build-up in the bottom of the barrel blocking the nozzle, so it was modified to catch the stormwater in a 5-gallon bucket placed on top of the rain barrel with a screen cover on the top of the barrel (Figure 3.9B).

Figure 3.9. Bridge runoff collection sites at Blatnik Bridge: (A) initial runoff site, (B) current runoff site, and (C) receiving water at Rice's Point

Blatnik Bridge was visited at each sampling date, but samples were only collected four times throughout the Year 1 winter. We observed that melt was typically very gradual. On multiple occasions when melt

volume was large at the other sampling locations, at Blatnik Bridge drops of meltwater were seen falling from the pipe and dissipating and scattering by wind over the parking lot. Water samples were collected from the BB-RP-A even on the dates when not enough bridge runoff was in the bucket as the runoff travels over the parking lot to enter the waterbody the Rice's point (~50 ft away from bridge drain pipe).

In Year 2, sites BB-KAc-A and BB-RP-A remained from the first year of sampling, but additional sites (BB-KAc-B and BB-RP-B) were added in the 2020-2021 winter sampling season. BB-KAc-B (Figure 3.10A) was added to have an additional sampling point to capture bridge runoff, as bridge runoff collection was challenging in the 2019-2020 winter due to high drain point and wind. BB-RP-B (Figure 3.10B) was chosen as an additional receiving water site as a pipe from the bridge is discharging road meltwater directly into the lake about 3 m (less than 10 ft) from shore. At BB-RP-A, bridge runoff is not directly mixing with the lake, but rather traveling over the parking lot or blowing over the lake and into the water. With the more direct connection of the bridge and BB-RP-B, this site was added to examine if the runoff is detectable when bridge runoff is mixed with lake water, and if so, if the CF7 in that runoff impacts lake water chemistry.

Figure 3.10. (A) BB-KAc-B; with the collection bucket; (B) BB-RP-B, with an arrow pointing to the discharge pipe over the sampling location

In addition to the second KAc sampling point at BB-KAc-B, changes were made to this site in Year 2 to increase sampling success. MnDOT District 1 reconnected pipes to reach the ground at the beginning of the winter season. This assistance greatly helped to solve issues with bridge runoff dissipating in the wind, which was the major challenge to capture the runoff from the bridge in the 2019-2020 winter. During the 2020-2021 winter season, bridge meltwater at BB-KAc-A and BB-KAc-B was collected either as a grab sample when melt was actively happening, or with a collection bucket placed ahead of snow/melt events. BB-RP-A was sampled from a dock, during both years, and BB-RP-B by wading into the water. During January and February, BB-RP-B and to a lesser extent BB-RP-A were frozen, in some cases down to the shore of the lake, making sampling impossible. On one such occasion, an ice/meltwater sample was taken from the surface of the ice at BB-RP-B where bridge runoff was falling on the ice and melting it. When the ice was not too thick to sample, BB-RP-A and BB-RP-B were sampled with the aid of an ice pick.

As it was no longer safe to climb down to the lake and the arm sampler typically used in these situations was not long enough, a bucket and rope was used to collect lake water. At Rice's Point, Lake Superior, and Brewery Creek, a handheld YSI ProPlus was used for in situ measurements such as pH, DO, conductivity, and temperature. Stormwater flow was not sufficient for the probe to be submerged so YSI measurements were taken in the lab.

3.2.5 Sample Processing and Analysis

Samples were processed within 24 hours of collection. Any large debris was removed from the sample by filtering the entire sample with 70 μm mesh. Water chemistry analytes are listed in Table 3.2. The sample was divided into four aliquots: non-filtered/non-acidified (frozen), non-filtered/acidified, filtered/non-acidified, and filtered/acidified for water quality analysis (Figure 3.11). Aliquots were vacuum filtered through .22 μm pore size membrane filters, acidified with 1% HNO_3, and stored in 50 ml centrifuge tubes at 4 ˚C.

Table 3.2. Water chemistry analytes and processing methods

Analytes	Analyzer	Volume (mL)	Filtration	Acidification
Dissolved cations (Na^+, K^+, Fe^+, Ca^{2+}, Mg^{2+})	UMD	30	Yes	1% HNO_3
Total (dissolved and particulate) cations (Na^+, K^+, Fe^+, Ca^{2+}, Mg^{2+})	UMD	30	No	1% HNO_3
Anions (Cl^-, Ac^-, NO_3^-, PO_4^{3-} and SO_4^{2-})	UMD	50	Yes	None
Nitrogen species (NO_3^-, NH_4^+)	ISU	20	Yes	None
Dissolved metals	ISU	30	Yes	1% HNO_3
Total metals	ISU	30	No	1% HNO_3
Total org. C/inorg. C	ISU	80	No	0.5% HCl
Biochemical oxygen demand	UMD	100	No	None
E. coli	UMD	100	No	None
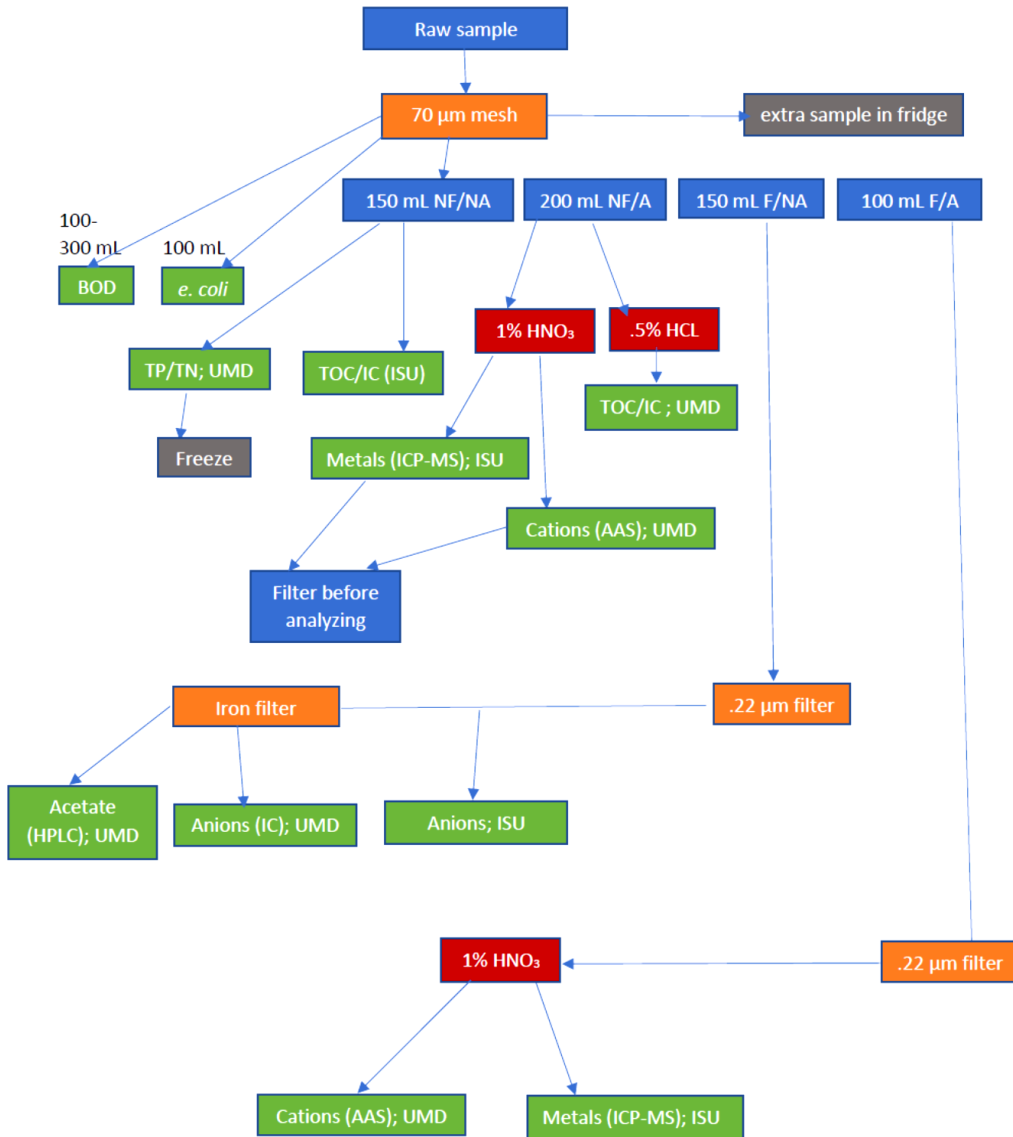
Figure 3.11. Flow chart of water sample processing

Five-day Biological Oxygen Demand (BOD_5) tests were done on the unprocessed (only mesh filtered) samples following EPA Standard Method 5210 B. The desired dilution range and dilution solutions were determined by the third sampling event. Dissolved oxygen (DO) for BOD analysis was measured with a YSI 5000 DO meter calibrated before each use. *Escherichia coli (E. coli)* enumeration (Most Probable Number; MPN) was conducted through the Colilert-18 Quanti-Tray Method (USEPA, 2003). During the University's lab hibernation due to the COVID-19 pandemic, BOD_5 and *E. coli* measurements could not be performed in late Spring 2020.

Major cation (Ca^{2+}, Mg^{2+}, Fe^{2+}, Na^+, and K^+) concentrations were determined with a Shimadzu flame atomic absorption spectrophotometer. Samples aliquoted for dissolved cation analysis were filtered and

acidified, while samples aliquoted for total cation analysis were acidified and not filtered until before analysis. Anion samples were filtered and not acidified, then pretreated to remove transient metals with OnGuard II M cartridge before analysis. Anion (Fl^-, Cl^-, Br^-, NO_2^-, NO_3^- PO_4^{3-}, SO_4^{2-}) concentrations were determined with a Dionex 2000 Ion Chromatography System and a IonPac^{TM} A22 column (4 × 25 mm, Dionex) with an isocratic flow rate of 1.2 ml/min. Acetate was quantified with High Performance Liquid Chromatography (HPLC) on an Dionex Ultimate 3000 with a Rezex ROA column (300 × 7.8 mm, Phenomenex) with a guard column (50 × 7.8 mm) under an isocratic flow rate of 0.8 ml/min and a wavelength of 210 nm for UV detection.

3.3   DEGRADATION EXPERIMENT OF CF7 ANTI-ICER/DE-ICER IN THE LABORATORY

The degradation of CF7 anti-icer/de-icer was evaluated in different conditions of temperature and concentration in the laboratory. The experiments were conducted to determine 1) the degradation rate of acetate in the field conditions (4°C vs room temperature) and 2) the stability of acetate in the sample during storage before analysis (filtered vs unfiltered). Lake Superior water was spiked with varying amounts of CF7 anti-icer/de-icer (100-5000 mg/L as acetate) and incubated at 4°C and room temperature (20-23°C). Each set was repeated with filtered and non-filtered lake water. Experiments were conducted for each concentration in triplicate. Samples were taken at certain time intervals and acetate concentrations were monitored using the HPLC described above.

3.4   RESULTS AND DISCUSSION

3.4.1   Potassium Acetate:

Higher concentrations of Ac^- were found in Blatnik Bridge and I-35 runoff as compared to NaCl sites (Figure 3.12). Ac^- was not observed at CE-KAc as MnDOT used primarily NaCl instead of KAc on the Central Entrance site. While the CE-KAc site was originally intended to be a KAc site, it is evaluated as a NaCl site for BOD and bacteria results given the lack of KAc applied and measured in this site. Bridge runoff smelled strongly like vinegar (acetic acid, which is the acid form of acetate) when sampling, indicating high concentrations of KAc in the sample. This was confirmed upon analysis, as acetate concentrations in BB-KAc-A and BB-KAc-B were much higher than in I-35 stormwater (Figure 3.12 & 3.13). Blatnik Bridge sites had significant acetate concentrations in all but two samples, with an average of 3,376 mg/L and a maximum concentration sampled at 11,375 mg/L at BB-KAc-A. BB-KAc-B had slightly lower acetate concentrations, with an average of 2,429 mg/L and peak of 4,975 mg/L.

Figures 3.12 and 3.13 show variable acetate concentrations especially in bridge runoff, which results from several reasons such as total precipitation amount, CF7 application rate versus snow precipitation, and the time gaps between the melt event and sampling. Interestingly, acetate concentrations could be very different between BB-KAc-A and BB-KAc-B on the same sampling date when samples were taken within an hour of each other. This indicates KAc concentrations in runoff were variable and highly concentrated runoff may flush out quickly to the receiving water body.
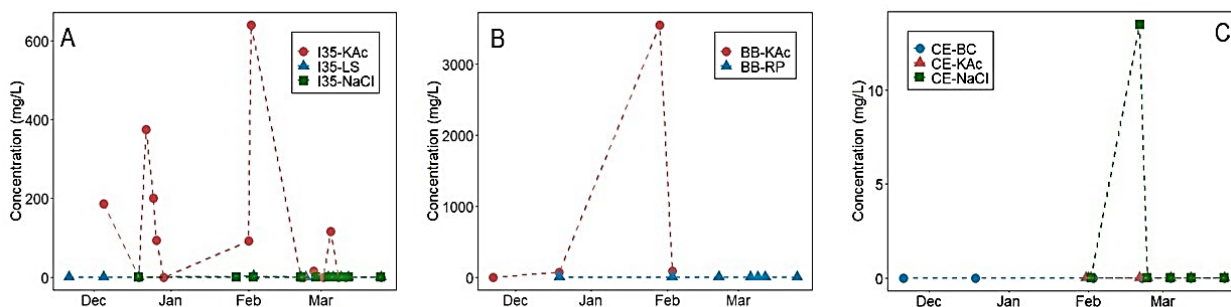
Figure 3.12. Acetate (Ac-) concentration in winter stormwater runoff and receiving water at (A) I-35, (B) Blatnik Bridge, and (C) Central Entrance in Year 1. KAc and NaCl indicates stormwater runoff collected from KAc and NaCl application, respectively. Lake Superior (LS), Rice's Point (RP), and Brewery Creek (BC) are downstream runoff-receiving water bodies.
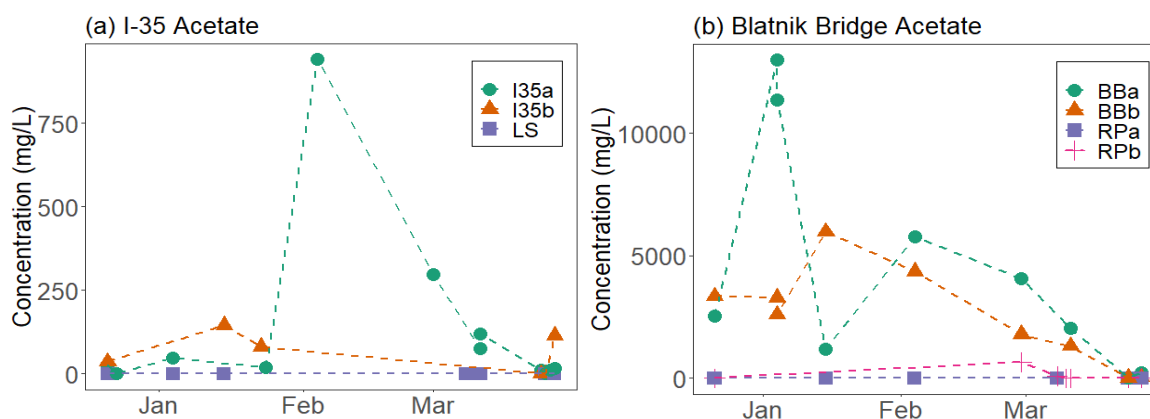

Figure 3.13. Concentration of acetate at (A) I-35 sites and (B) Blatnik Bridge sites in Year 2

Although Blatnik Bridge runoff was highly concentrated, no detectable acetate was found in the receiving water in BB-RP-A or I-35-LS. Low concentrations of acetate in the receiving water body appear to be at background levels in freshwater as acetate is a common organic metabolite (Allen, 1968). Dilution and degradation may result in the low concentrations of acetate in receiving waters. However, acetate was detected in BB-RP-B water in March, as seen in Figure 3.13B as acetate peaked up to 650 mg/L at BB-RP-B. The absence of KAc in I-35-LS and BB-RP-A indicates dilution reduces the effects of stormwater in the lake, but in smaller or less open areas such as BB-RP-B, Ac⁻ in stormwater can impact water chemistry.

Potassium and acetate concentrations in runoff from KAc application sites (Blatnik Bridge and I-35) generally trend together (Figure 3.14, 3.15, & 3.16), indicating that the spikes in K^+ and Ac⁻ were likely capturing the KAc application and not natural background levels. KAc dissociates into K^+ and Ac⁻ (1:1 molar ratio). While Ac⁻ can be consumed by natural microorganisms to be degraded into bicarbonate, carbon dioxide, K^+ is conservative in solution as inorganic species. Potentially, spikes in K^+ at KAc

application sites or in receiving water bodies can be used as an indicator of KAc anti-icer/de-icer. The low concentrations of Ac^- and K^+ in receiving waters of Rice's Point and Lake Superior indicate that the KAc anti-icer/de-icer were likely being diluted, as K^+ concentration remains constant across the winter and spring. Despite the co-occurrence trends of K^+ and Ac^- in KAc application sites and receiving water, K:Ac ratios varied by over time, with Ac^- higher than K^+ on occasion. In Year 1 the measured molar concentrations of K^+ were generally lower than those of Ac^- in runoff, with 0.5-1.0 of K^+/Ac^- molar ratio. In Year 2, the average K^+:Ac^- molar ratio at I-35-KAc-A was 1.3, and 1.9 at I35-KAc-B. Ratios in bridge runoff were similar, with an average K^+:Ac^- ratio of 1.8 at BB-KAc-B and 0.8 in BB-KAc-A. The variations are presumably due to different reactivity of K^+ and Ac^- with other constituents in stormwater: degradability of Ac^- by naturally occurring bacteria or inputs of K^+ from sources other than CF7 (K: Ac ratio>1) and sorption affinity of K^+ to negative-charged organic matter or clay mineral in runoff (K:Ac ratio <1).
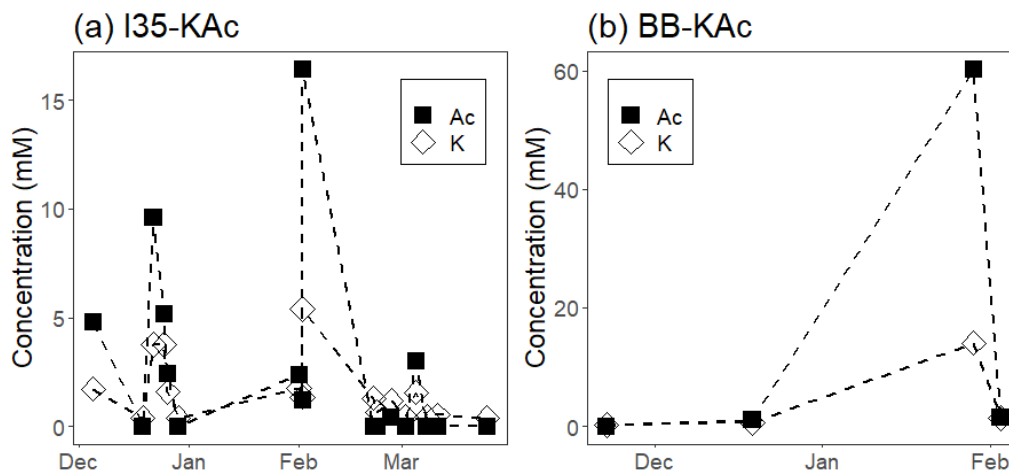

Figure 3.14. Concentrations of acetate and potassium trend together at (a) I-35-KAc-A and (b) BB-KAc-A in Year 1
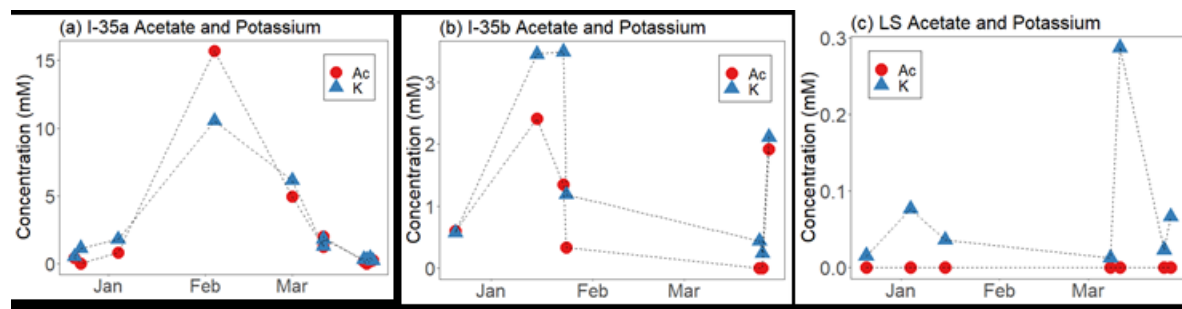
Figure 3.15. Molar concentrations of acetate and potassium at (A) I-35-KAc-A, (B) I-35-KAc-B, and (C) I-35-LS in Year 2

81
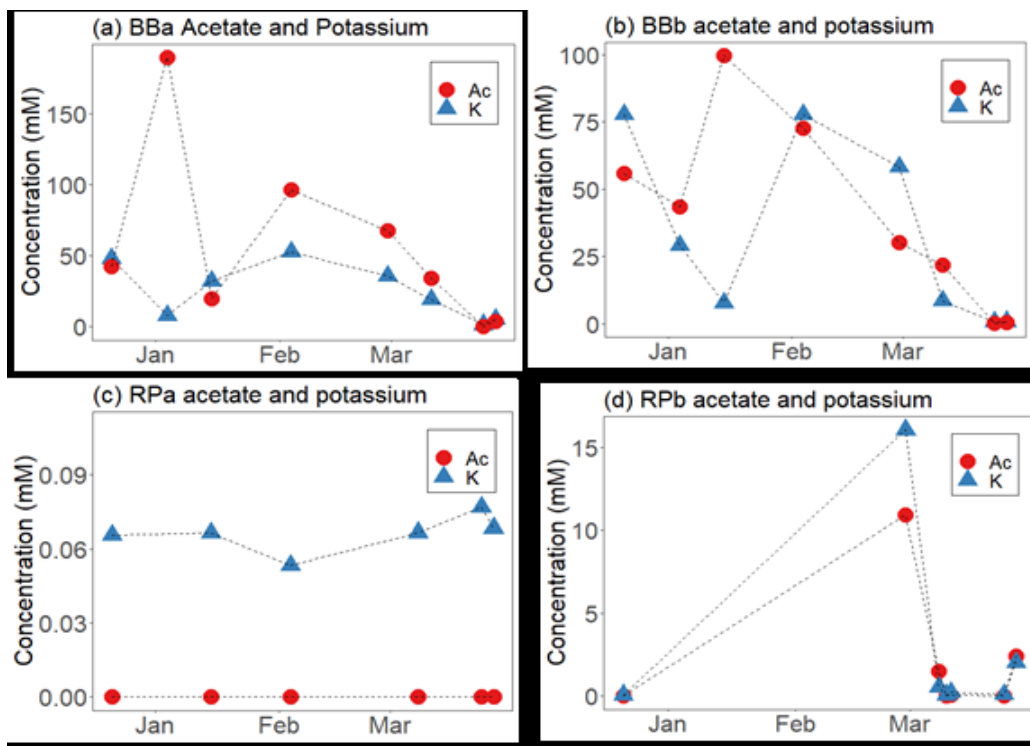
Figure 3.16. Molar concentration of acetate and potassium at (a) BB-KAc-A, (b) BB-KAc-B, (c) BB-RP-A, and (d) BB-RP-B in Year 2

Like Ac^-, K^+ concentrations in both bridge runoff and I-35 stormwater were also high as they surpassed 1,500 mg/L in bridge runoff and 100 mg/L in I-35-KAc-A and I35-KAc-B (Figures 3.17 & 3.18). As K^+ tends to absorb onto negatively charged surfaces in soil minerals such as clays in the stormwater (Sonon et al, 2017), we quantified the concentration of K^+ in both non-filtered and filtered water samples for Year 2. In Figure 3.17 and 3.18, total K^+ concentrations (and other cations such as Na^+, Ca^{2+}, Mg^{2+}, and Fe^{II}/Fe^{III} in Figures below) are reported as non-filtered (NF) while purely dissolved ions are shown as filtered (F). These concentrations were well over what is expected in stormwater runoff, indicating K^+ originated from KAc application. In contrast, the concentration of K^+ was less than 10 mg/L in Lake Superior water (I-35-LS and BB-RP-A), which is close to background levels of surface water.
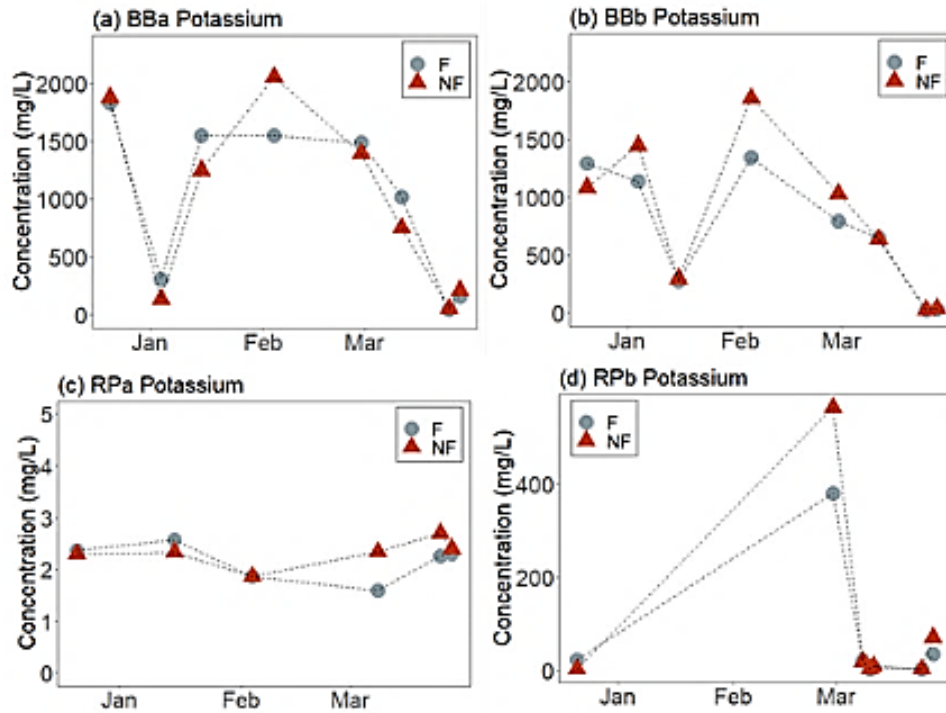
Figure 3.17. Concentration of potassium at (a) BB-KAc-A, (b) BB-KAc-B, (c) BB-RP-A, and (d) BB-RP-B for filtered (F) and non-filtered (NF) samples in Year 2
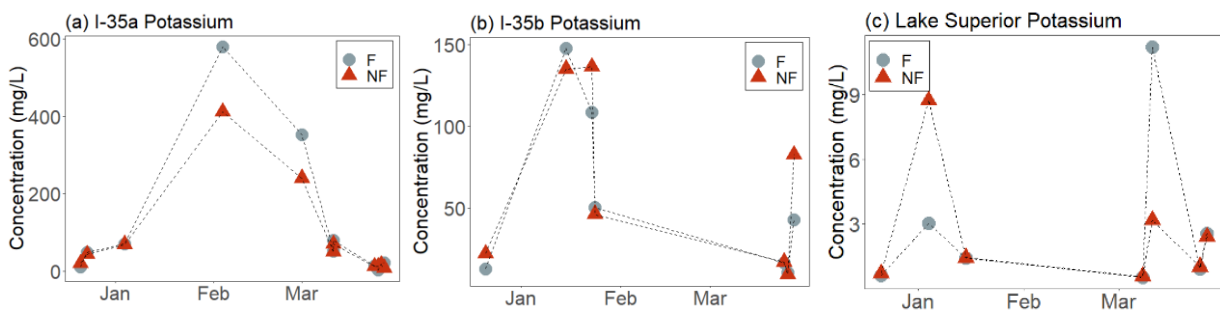
Figure 3.18. Potassium concentrations at (a) I-35-KAc-A, (b) I-35-KAc-B, and (c) I-35-LS for filtered (F) and non-filtered (NF) samples in Year 2

Unlike stormwater samples, low concentrations of Ac⁻ and K⁺ in receiving waters of Rice's Point A and Lake Superior indicate that the KAc anti-icer/de-icer was likely being diluted and their concentrations were influenced by natural background levels of K⁺ and Ac⁻. K⁺ concentration was generally greater than Ac- and remained relatively constant across the winter and spring (Figures 3.15C and 3.16C). However, this was not true for BB-RP-B (3.16D) which was impacted by KAc-containing runoff as a small area of the lake with limited mixing. The K:Ac ratio near 1 in BB-RP-B indicates the K⁺ and Ac⁻ originated from CF7 application.

None of the receiving water bodies had measured high acetate concentrations, although runoff from the I-35 and BB sites had high acetate concentrations. In the 2020-2021 winter season, we observed relative great acetate and potassium concentrations (over 600 mg/L) in smaller or less open areas of receiving water such as BB-RP-B. The lowest documented aquatic toxic concentration of Ac⁻ from KAc anti-icer/de-icer is 19.9 mg/L of Inhibiting Concentration 25% (IC_{25}; level at which the organisms exhibit 25 percent reduction in a biological measurement such as reproduction or growth) for *Pseudokirchneriella subcapitata* (green algae) and 298 mg/L of the median lethal dose (LD_{50}) over 96 hours for *Pimephales promelas* (fathead minnow) (Corsi et al., 2009). As the concentration of Ac⁻ in runoff has been found to be above both these values, there is potential for localized aquatic toxicity to sensitive organisms where runoff is directly entering the water body.

3.4.2 Sodium chloride

The chloride (Cl⁻) concentrations were high enough that a log scale is required to display chloride trends over time (Figure 3.19C & Figure 3.20). Chloride was the dominant ion in I-35 stormwater and Blatnik Bridge runoff, mostly from road salt. Bridge runoff was much more concentrated than I-35 stormwater. The concentration of Cl⁻ in bridge runoff was very high with an average concentration of 11,714 mg/L at BB-KAc-A and 16,994 mg/L at BB-KAc-B. Cl⁻ at I-35-KAc-A ranged from 340-4,400 mg/L with an average of 1,160 mg/L. Lower concentrations were found in I-35-KAc-B, with Cl⁻ ranging from 300-1,300 mg/L and an average of 923 mg/L as it was more composite stormwater from I-35 and was potentially diluted from precipitation as an open system.
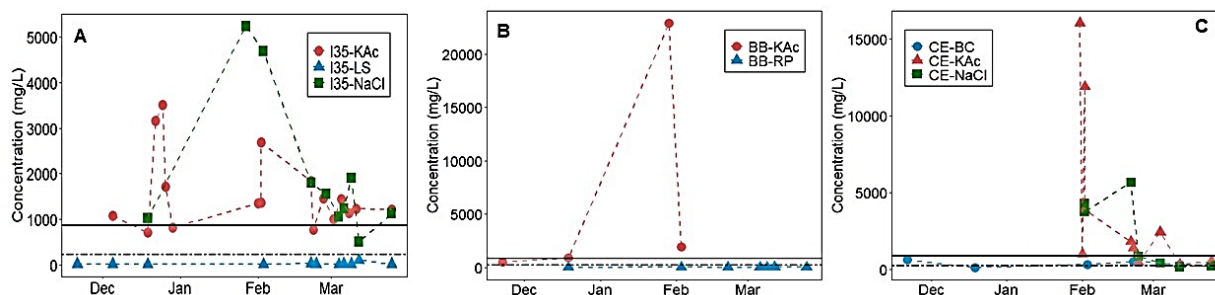
Figure 3.19. Chloride (Cl-) concentration in winter stormwater runoff and receiving water in Year 1 at (A) I-35, (B) Blatnik Bridge, and (C) Central Entrance. KAc and NaCl indicates stormwater runoff collected from KAc and NaCl application, respectively. Lake Superior, Rice's Point, and Brewery Creek are downstream runoff-receiving water bodies. The solid line indicates the acute (1 hour average) Cl- limit of 860 mg/L and the dashed is the chronic (4 day average) Cl- limit of 230 mg/L based on the US EPA recommended water quality criteria for chloride.
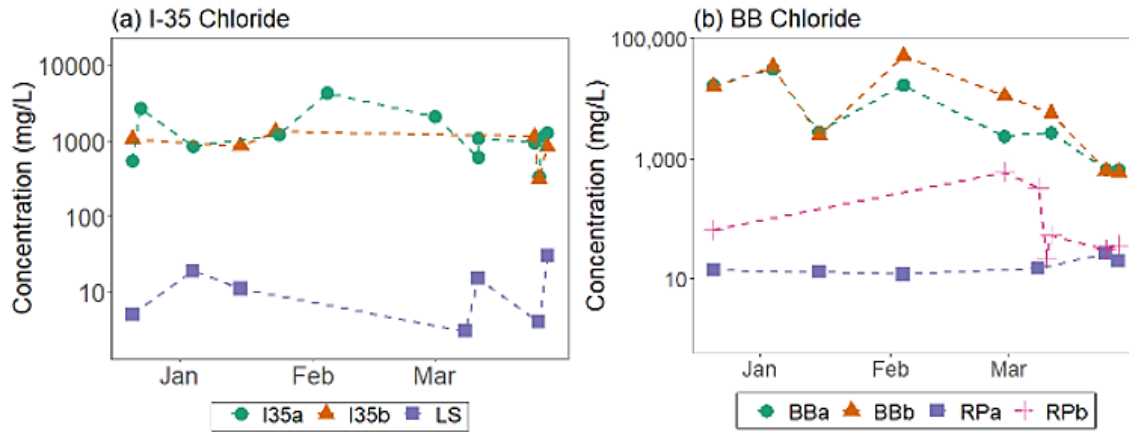
Figure 3.20. Cl- concentration in stormwater in (a) I-35 sites and (b) Blatnik Bridge sites in Year 2

BB-RP-B has an average Cl⁻ concentration of 162 mg/L, with the highest measurement at 597 mg/L. Considering the EPA freshwater acute and chronic Cl⁻ toxicity threshold of 860 mg/L and 230 mg/L, chloride levels in lake water at BB-RP-B appears to surpass the limit. BB-RP-A was much less impacted by Cl⁻, and presumably bridge runoff, than BB-RP-B. The differences are likely due to the proximity from runoff discharge as the BB-RP-B site received runoff directly from bridge in comparison to BB-RP-A (50 ft away from the bridge). Cl⁻ concentrations remained relatively stable across the winter at BB-RP-A with an average of 17 mg/L Cl⁻ and slight increases with spring melt (Figure 3.19B & 3.20B).

Cl⁻ was extremely high at both Central Entrance storm drains, with peaks of 16,035 mg/L in CE-KAc runoff and 5,672 mg/L in CE-NaCl runoff (Figure 3.19c). High Cl⁻ concentration in CE-KAc was attributed from the application of chloride-based anti-icers/de-icers. MNDOT District 1 initially planned to apply KAc on Central Entrance during the 2019-2020 winter season but made a change to use chloride-based anti-icers/de-icers. An average Cl⁻ level of 396 mg/L at CE-BC is unsurprising given the levels of Cl⁻ in runoff in that catchment. Brewery Creek Cl⁻ was regularly above the EPA's chronic Cl⁻ limit of 230 mg/L and would be considered impaired for Cl⁻. While Cl⁻ levels in Lake Superior have yet to trend upwards towards toxic limits, the Cl⁻ impaired streams such as Brewery Creek feed into the lake. Increased Cl⁻ was observed in Lake Superior during January and March, with an average Cl⁻ concentration of 12 mg/L at the I-35-LS site and a peak of 95 mg/L.

Sodium (Na⁺) was the most abundant cation in stormwater, with average total concentrations of 512 mg/L in I-35 samples (Figure 3.21), and 2,338 mg/L in Blatnik Bridge samples (Figure 3.22). While Cl⁻ is the better proxy for NaCl application due to its conservative nature, Na⁺ can also be understood as an indicator of NaCl. Na⁺ and Cl⁻ concentrations were higher than K⁺ and Ac⁻ and remained the dominant salt contributing to conductivity even with the transition from NaCl use to KAc on both roadways. Even though it was a KAc application site, traffic entering the bridge can carry chloride-based anti-icers/de-icers applied from other roads. Additionally, contaminant concentrations in runoff from bridge scuppers and deck generally are more concentrated than those in runoff of highway which is often equipped with catchment or bioswale (Bakr et al. 2020). The high NaCl concentrations on the KAc treated roadways is

likely ascribed to the co-application of sand mixed with ~10% NaCl along with KAc which helps retainment of liquid anti-icer/de-icer, KAc, on the road surface and enhances skid resistance.
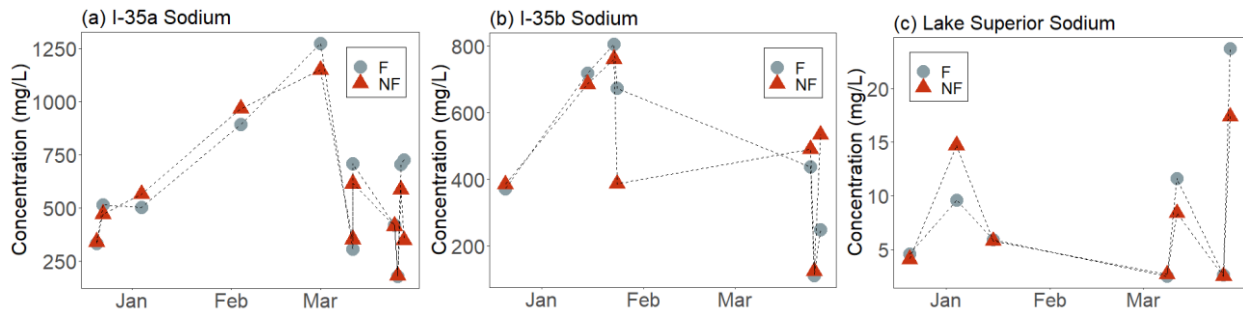
Figure 3.21. Sodium concentrations at (a) I-35-KAc-A, (b) I-35-KAc, and (c) I-35-LS for filtered (F) and non-filtered (NF) samples in Year 2
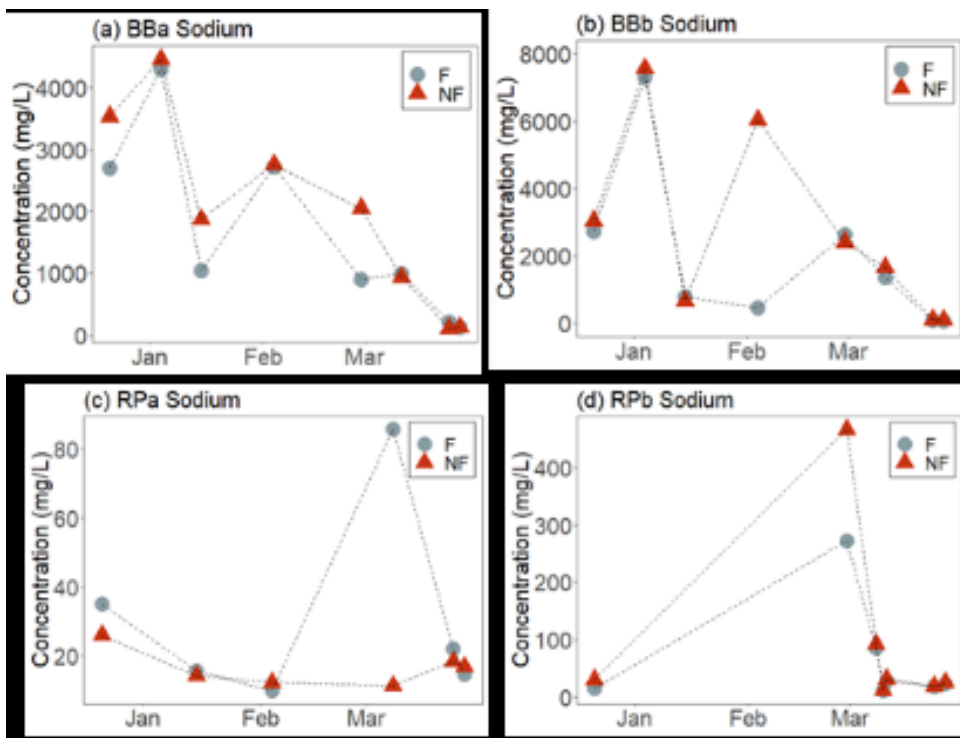
Figure 3.22. Sodium concentrations at (a) BB-KAc-A, (b) BB-KAc-B, (c) BB-RP-KAc, and (d) BB-RP-B for filtered (F) and non-filtered (NF) samples in Year 2

Molar concentrations of Na^+ and Cl^- in the water samples show that Na^+ and Cl^- typically trend together (Figure 3.23 and 3.24), indicating that the Na^+ and Cl^- concentrations were largely derived from road salt application. NaCl deicing salt has a molar ratio of 1:1, so deviations from this indicate additions of an ion

from outside sources or uptake in the soil or water column. Natural sources of Cl⁻ and Na⁺ are from rock weathering. As for the I-35 stormwater, Cl⁻ concentration generally has a higher concentration than Na⁺, with a molar ratio of 0.7 Na:Cl in I-35-KAc-A and 0.8 in I-35-KAc-B. Blatnik Bridge has a lower Na:Cl ratio than I-35, with a 0.5 average ratio in BB-KAc-A and a 0.3 average ratio in BB-KAc-B. Additional Cl⁻ sources in stormwater could be other chloride-based anti-icers/de-icers ($CaCl_2$ or $MgCl_2$).
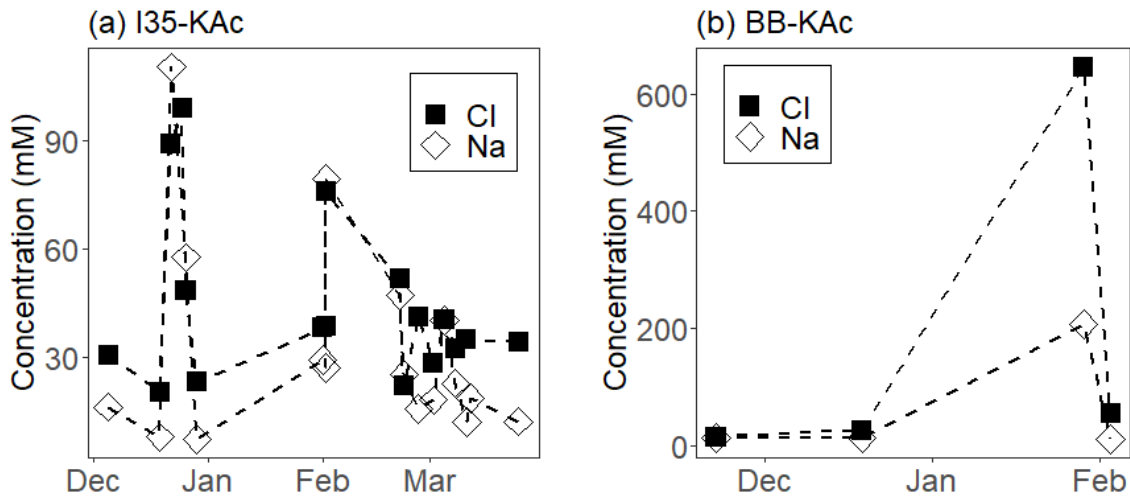
Figure 3.23. Molar concentrations of sodium (Na+) and chloride (Cl-) trend together at (a) I-35-KAc-A and (b) BB-KAc-A in Year 1
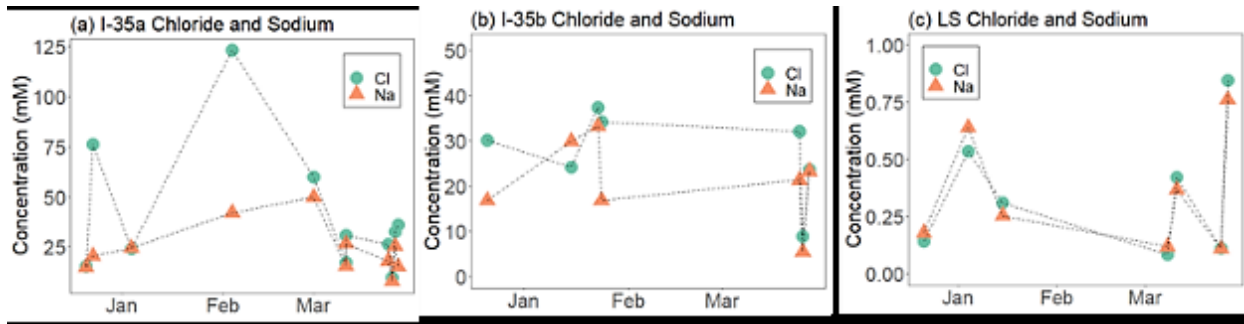
Figure 3.24. Chloride and sodium concentrations at (a) I-35-KAc-A, (b) I-35-KAc, and (c) I-35-LS in Year 2
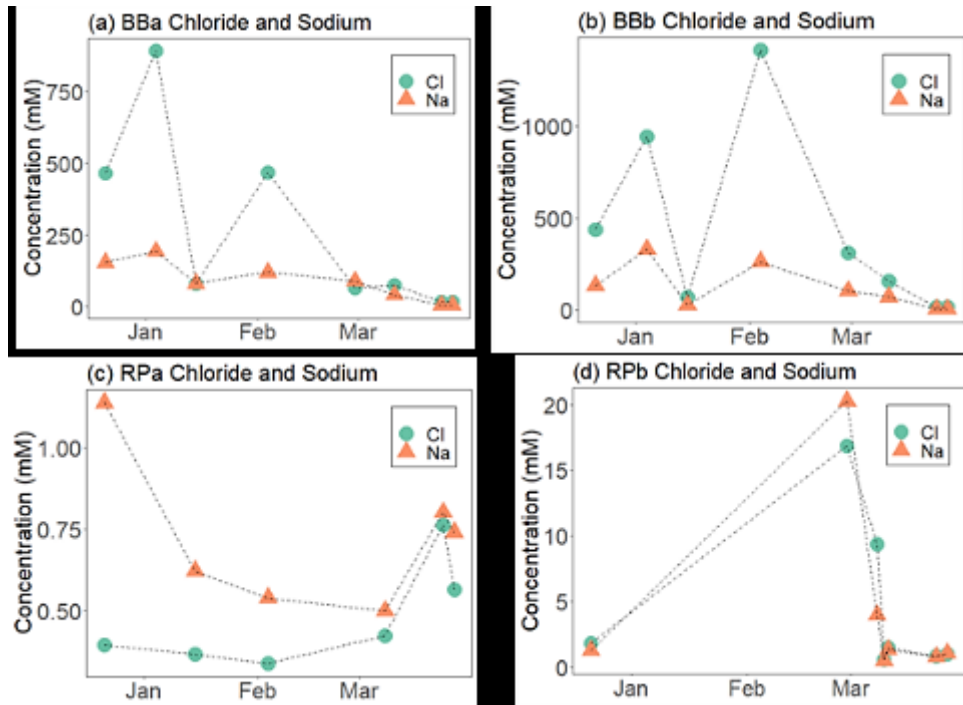
Figure 3.25. Chloride and sodium concentrations at (a) BB-KAc-A, (b) BB-KAc-B, (c) BB-RP-KAc, and (d) BB-RP-B in Year 2

Conductivity is a proxy measurement for the amount of ions in the water. As chloride is the dominant ion, it was the greatest contributor to conductivity. A comparison of chloride (Figures 3.19 and 3.20) and conductivity (Figures 3.26 and 3.27) show how specific conductivity follows the trends of chloride over the season. Conductivity was very high in stormwater, with average concentrations of 18,000 µS/cm (BB-KAc-A) and 21,251 µS/cm (BB-KAc-B) in bridge runoff, and 3,341 µS/cm (I-35-KAc-A) and 2,061 µS/cm (I-35-KAc-B) in stormwater. Conductivity was the lowest in I-35-LS, at 119 µS/cm, and a bit higher in Rice's Point with an average of 139 µS/cm. Higher salinity, as with chloride, is apparent at Rice's Point with RP-KAc-B at 326 µS/cm. Additionally, for Year 2 the conductivity was estimated based on the measured concentration of predominant ions, Na^+, Cl^-, K^+ and Ac^- with molar conductivity (H^+: 0.3498; OH^-: 0.1986, Na^+: 0.0501, K^+: 0.0735, Cl^-: 0.0764, Ac^-: 0.409 $S \cdot Lmol^{-1}cm^{-1}$) of the selected ions (Brown et al. 2018). Overall, the calculated conductivity values have good agreement with the measured conductivity within the same order of magnitude.
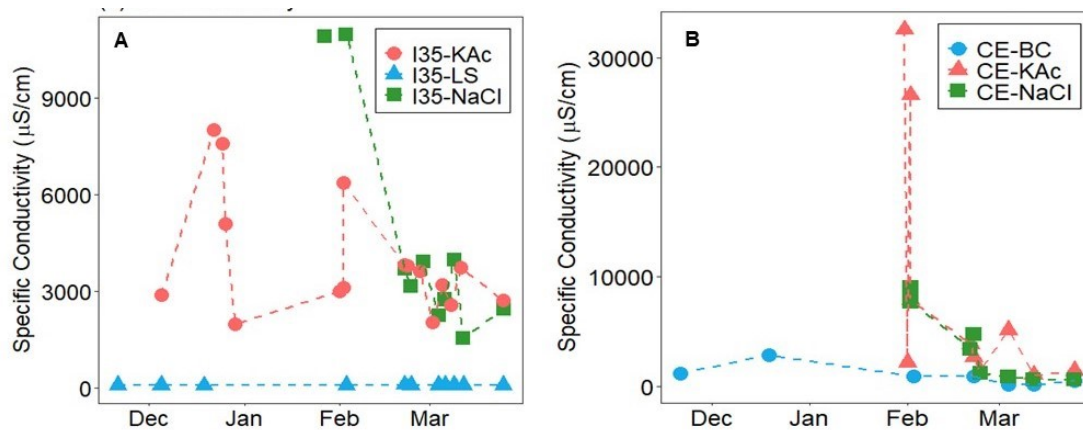
Figure 3.26. Specific conductivity in stormwater runoff and receiving water at I-35 and Central Entrance sites in Year 1
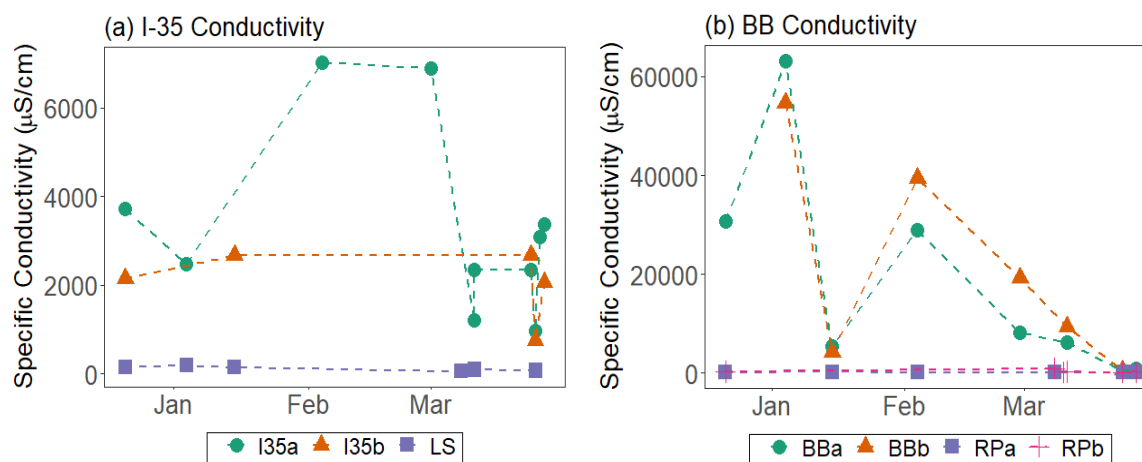
Figure 3.27. Specific conductivity trends at (a) I-35 and (b) Blatnik Bridge in Year 2

3.4.3 Other anions

While Cl⁻ was the dominant anion in stormwater, nitrate (NO_3^-) and sulfate (SO_4^{2-}) were also present in most stormwater and lake water. Bromide and nitrite were present in only a few samples, and phosphate was not detected in Year 2, but was found in some I-35 and Central Entrance stormwater (Figure 3.45 in Chapter 3 Supplementary Information). NO_3^- ranges from 0-270 mg/L in I-35 stormwater. Bridge runoff had more variation in NO_3^- than I-35 (Figure 3.28), with either no detectable NO_3^- or concentrations above 1,000 mg/L. NO_3^- was low (<5 mg/L) in I-35-LS and BB-RP-A but reached 53 mg/L in BB-RP-B from inputs of bridge runoff. NO_3^- is a pollutant which can lead to eutrophication in receiving water bodies, given sufficient phosphorus. Generally, NO_3^- in stormwater is largely due to atmospheric deposition, fertilizer use, and nitrification (Jani et al., 2020) during the summer season. The concentration of nitrate in these winter stormwater samples was considered to be large in comparison to the values reported in the literature for other stormwater samples. The median concentration of NO_3^-

+ NO_2^- is given as 1.2 mg/L in stormwater from freeways in the National Stormwater Quality Database (Pitt et al., 2004).
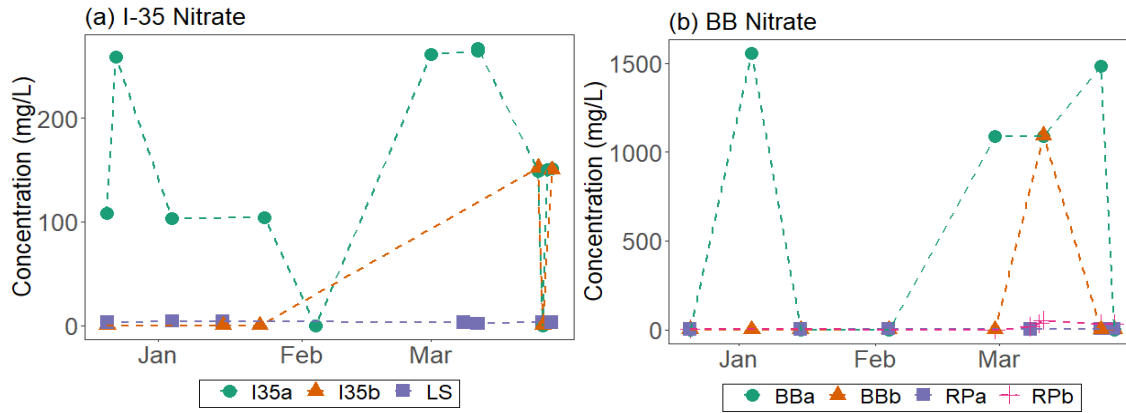
Figure 3.28. Nitrate concentrations at (a) I-35 sites and (b) Blatnik Bridge sites in Year 2

SO_4^{2-} concentrations (Figure 3.29 and 3.46 (Chapter 3 Supplementary Information)) in I-35 stormwater during Year 2 average at 347 mg/L at I-35-KAc-A and 379 mg/L at I-35-KAc-B. As with other ions, the Blatnik Bridge water was more concentrated. There, SO_4^{2-} averages 1,743 mg/L at BB-KAc-A and 1,482 mg/L at BB-KAc-B. SO_4^{2-} was low in I-35-LS, around 5 mg/L while it ranged from 20-60 mg/L at BB-RP-A and BB-RP-B. As both $NO_3^- + NO_2^-$ and SO_4^{2-} are present in CF7® anti-icer/de-icer as trace and other constituents, their greater concentration in stormwater is likely due to KAc application on the roadway.
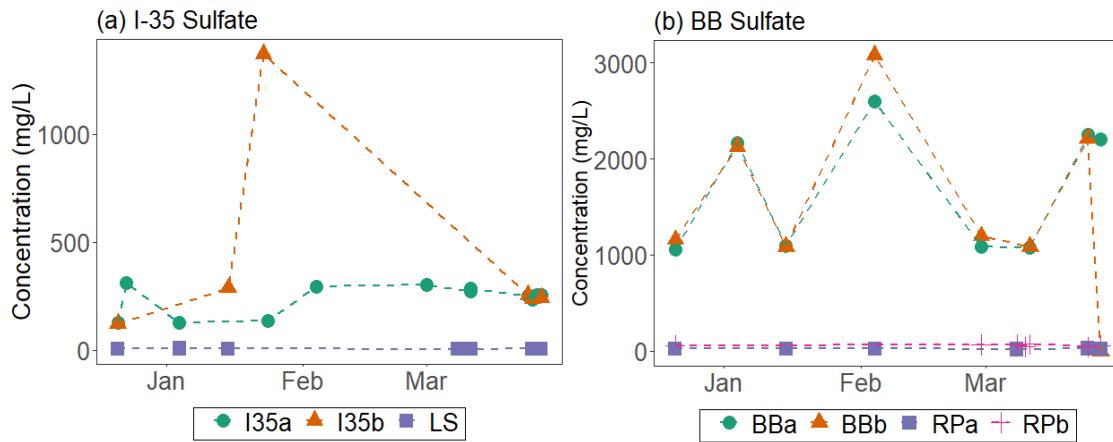
Figure 3.29. Sulfate concentrations at (a) I-35 sites and (b) Blatnik Bridge sites in Year 2

90

3.4.4 Other Cations

3.4.4.1 I-35 sites:

In addition to Na^+ and K^+ concentrations reported above, other cations, $Fe^{II/III}$, Mg^{2+}, and Ca^{2+} were analyzed. Filtered and nonfiltered cation data is shown in this section for Year 2. Filtered cation data for Year 1 is shown in Figures 3.47 and 3.48 in Chapter 3 Supplementary Information. Like Na^+, Fe^{2+} is often found bound to particulate matter rather than dissolved, and total cation concentrations are reported as non-filtered (NF) while dissolved ions are shown as filtered (F). Na^+ and K^+ are by far the most abundant cations, with Ca^{2+}, Mg^{2+}, then $Fe^{II/III}$ as the next most prevalent. As with Na^+ and K^+, the other cations were variable over time (Figures 3.30, 3.31, 3.32). Natural iron, calcium, and magnesium are dissolved in freshwater from rock weathering. Additional Ca^{2+} and Mg^{2+} could be due to the use of alternative road salts containing these species. The average total concentration of Ca^{2+} in I-35 sites is 127 mg/L, and 15 mg/L in I-35-LS. Magnesium averages at 19 mg/L in I-35 stormwater, and 3 mg/L in I-35-LS. Iron, nearly all of which is bound to solids in stormwater (Figure 3.32), has an average of 13 mg/L in I-35 sites and very little present in I-35-LS (0.2 mg/L).
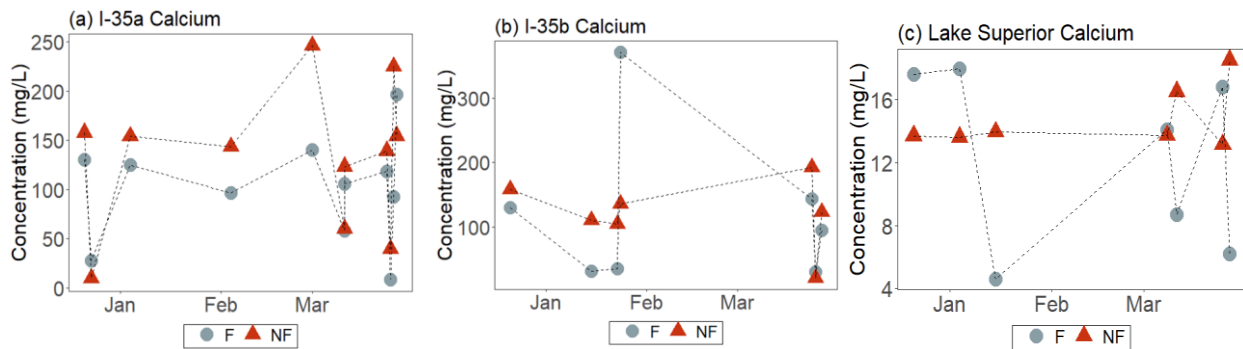
Figure 3.30. Calcium concentrations at (a) I-35-KAc-A, (b) I-35-KAc-B, and (c) I-35-LS for filtered (F) and non-filtered (NF) samples in Year 2
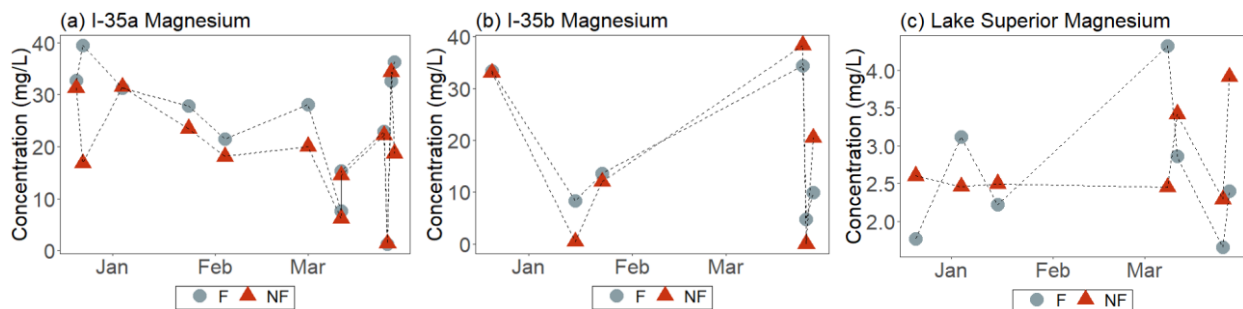
Figure 3.31. Magnesium concentrations at (a) I-35-KAc-A, (b) I-35-KAc-B, and (c) I-35-LS for filtered (F) and non-filtered (NF) samples in Year 2
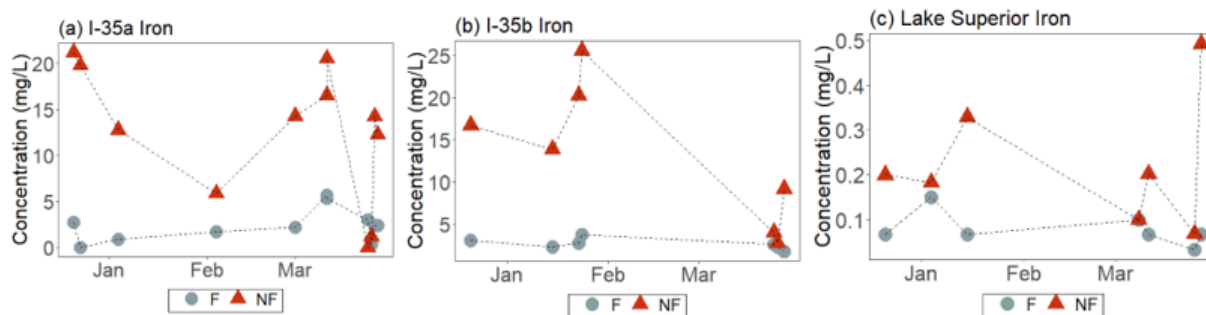
Figure 3.32. Iron concentrations at (a) I-35-KAc-A, (b) I-35-KAc-B, and (c) I-35-LS for filtered (F) and non-filtered (NF) samples in Year 2

3.4.4.2 Blatnik Bridge:

As with the I-35 stormwater, bridge runoff had primarily Na^+ and K^+, then Ca^{2+}, Mg^{2+}, and Fe^{2+} as the positively charged constituents. While Mg^{2+} and Fe^{2+} concentrations in bridge runoff were in similar ranges as at I-35 reported above, the concentration of calcium was twice as high (Figure 3.33) in bridge water than stormwater. Ca^{2+} in bridge sites BB-KAc-A and BB-KAc-B averages 126 mg/L and reaches 570 mg/L. Ca^{2+} in BB-RP-A was a bit higher than in I-35-LS, but significantly higher than that in BB-RP-B. Mg^{2+} is more concentrated in I-35 runoff than the bridge; the average Mg^{2+} concentration at Blatnik Bridge sites was 10 mg/L (Figure 3.34). $Fe^{II/III}$ in bridge runoff (Figure 3.35) was similar to the concentration in I-35 runoff, with an average of 13 mg/L, indicating that iron was originated from soil or particulates.
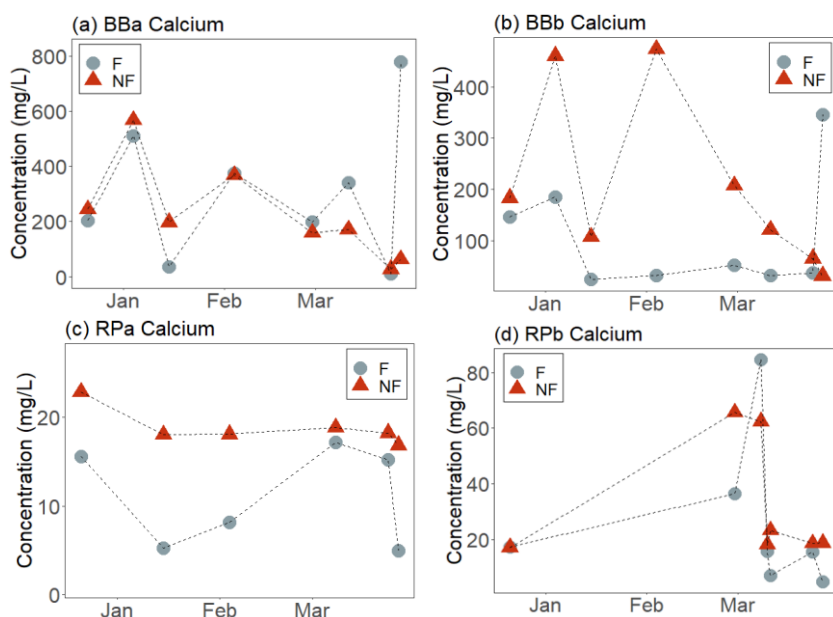
Figure 3.33. Calcium concentrations at (a) BB-KAc-A, (b) BB-KAc-B, (c) BB-RP-A, and (d) BB-RP-B for filtered (F) and non-filtered (NF) samples in Year 2
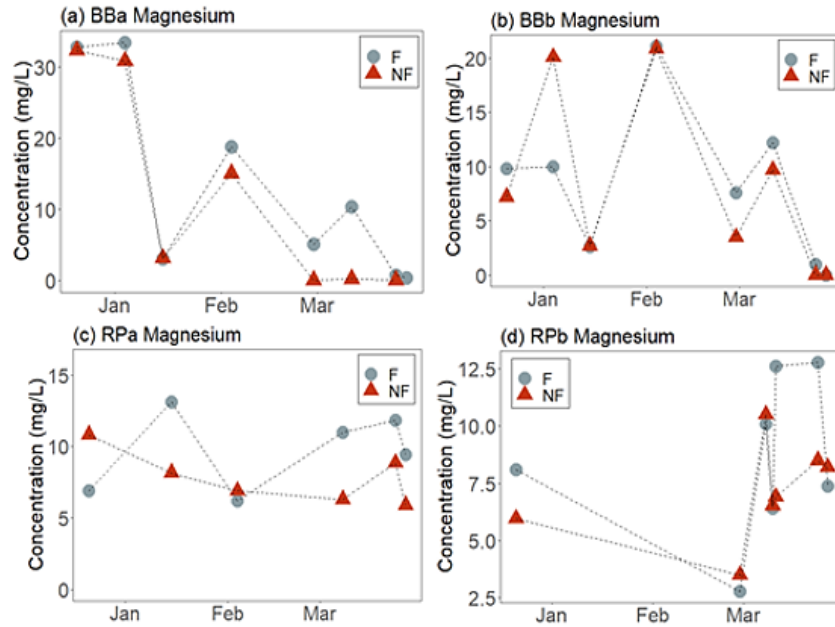
Figure 3.34. Magnesium concentrations at (a) BB-KAc-A, (b) BB-KAc-B, (c) BB-RP-A, and (d) BB-RP-B for filtered (F) and non-filtered (NF) samples in Year 2
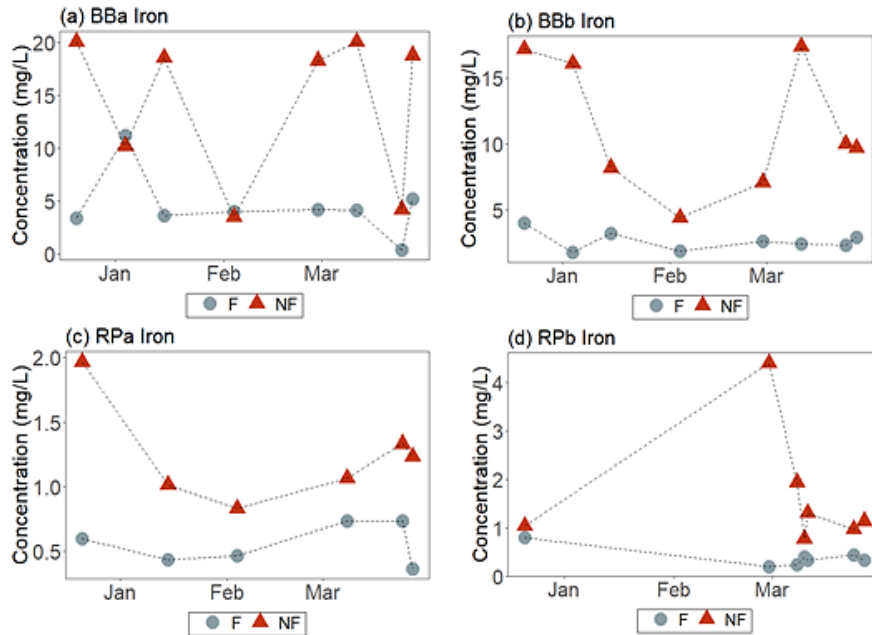
Figure 3.35. Iron concentrations at (a) BB-KAc-A, (b) BB-KAc-B, (c) BB-RP-A, and (d) BB-RP-B for filtered (F) and non-filtered (NF) samples in Year 2

3.4.5 Biochemical Oxygen Demand (BOD₅)

BOD is a hazard to aquatic life when the oxygen demand is greater than the oxygen supplied to the waterbody by photosynthesis and reaeration. The depletion of dissolved oxygen of surface waters receiving KAc-loaded meltwater is potential major concern of KAc application. Previously, the five-day BOD (BOD_5) of KAc anti-icer/de-icer was reported to be up to 180,000 mg/L, high enough to lead to oxygen depletion of receiving water bodies (Switzenbaum et al., 2002). This measurement was for concentrated anti-icer/de-icer, and the BOD of runoff carrying KAc is expected to be much lower. As KAc was applied, it ran off roads into soil or storm drains, and was eventually deposited in surface waters such as Lake Superior.

The BOD_5 was extremely high in both bridge runoff and I-35 stormwater, and fairly high in the lake as well (Figure 3.36). The average BOD_5 at 20° C was 41 mg/L in I-35-KAc-B, 66 mg/L in I-35-KAc-A, 2,102 mg/L in BB-KAc-A, and 2,371 mg/L in BB-KAc-B. These values were much higher than typical BOD_5 values reported for stormwater runoff in the literature, with the national median BOD_5 of freeway runoff reported as 8 mg/L (Pitt et al., 2004). The impact of a high BOD_5 on oxygen levels is relative, as oxygen levels may tolerate varying BOD_5 based on the rate of reaeration, by photosynthesis or mixing with the atmosphere. Oxygen levels below 6 mg/L can reduce salmonoid growth with an EPA acute toxicity limit of 4.5 mg/L, where salmonoids especially have a high oxygen requirement. Generally, BOD_5 concentrations under 2 mg/L indicate pristine waters, BOD_5 2-8 mg/L are mildly impacted, and BOD_5 standards for wastewater effluent fall between 20-30 mg/L. The BOD_5 in all stormwater sites herein is greater than the acceptable BOD discharged from wastewater treatment plants.
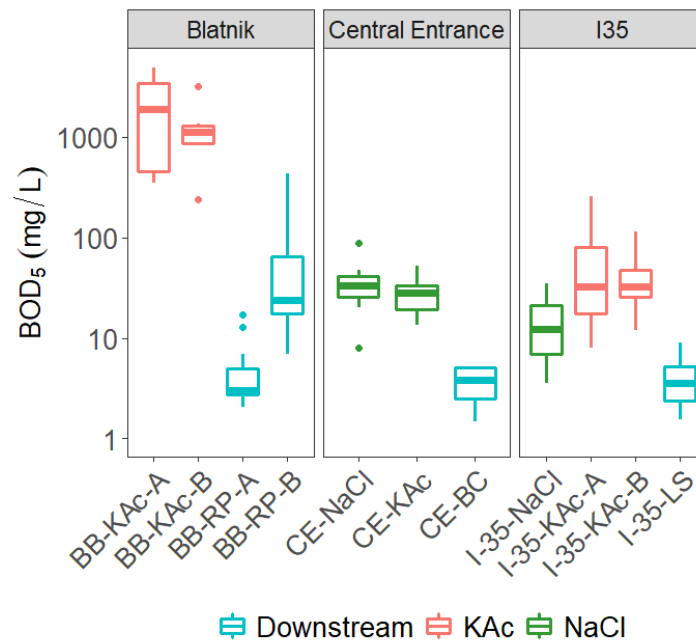
Figure 3.36. Biological Oxygen Demand (BOD5) at all sites Year 1 and 2. Bold line in each box indicates mean values.

94

The levels of BOD$_5$ in receiving water bodies were higher than the levels in pristine waters, with an average of 4 mg/L in Brewery Creek and Lake Superior and 5 mg/L in BB-RP-A, and 99 mg/L in BB-RP-B. The trends of acetate and BOD$_5$ concentration in Year 2 appears to be aligned together in Figure 3.37. I-35-LS and BB-RP-A were excluded from the Figure as Ac$^-$ was ~0 mg/L at these sites. The increase in BOD$_5$ with Ac$^-$ concentration is particularly evident in BB-RP-B (Figure 3.37e). Pearson's correlation coefficient between BOD$_5$ and Ac$^-$ (r = 0.62, p <0.001) indicates moderate positive correlation between them (Figure 3.38).
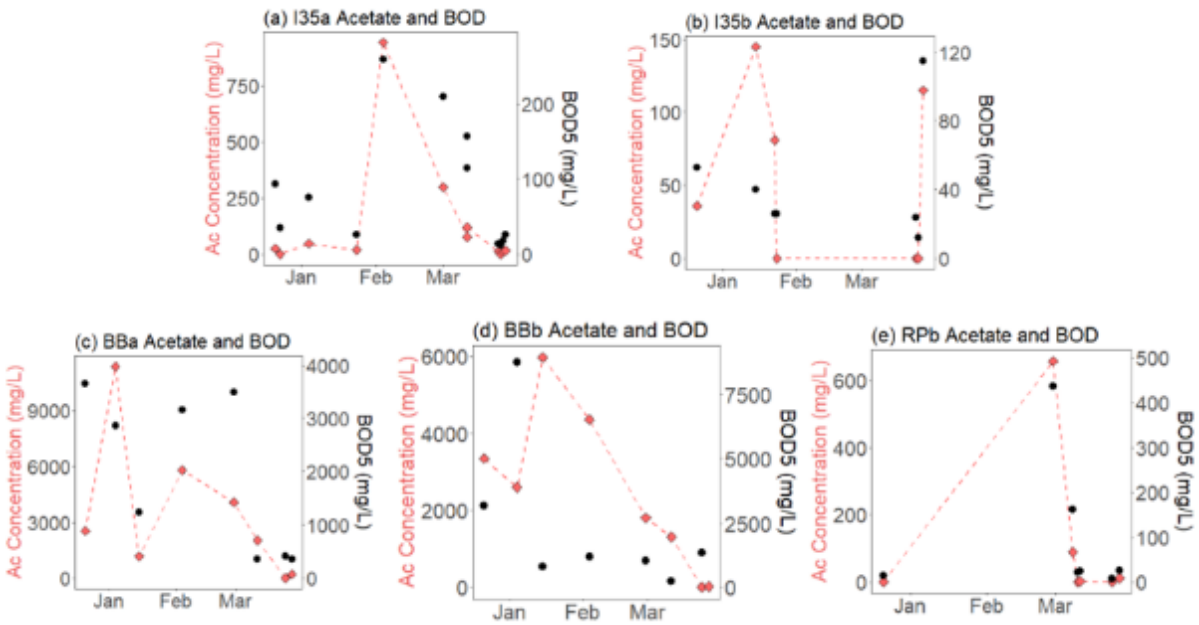
Figure 3.37. Acetate and BOD5 at (a) I-35-KAc-A, (b) I-35-KAc-B, (c) BB-KAc-A, (d) BB-KAc-B, and (e) BB-RP-b in Year 2
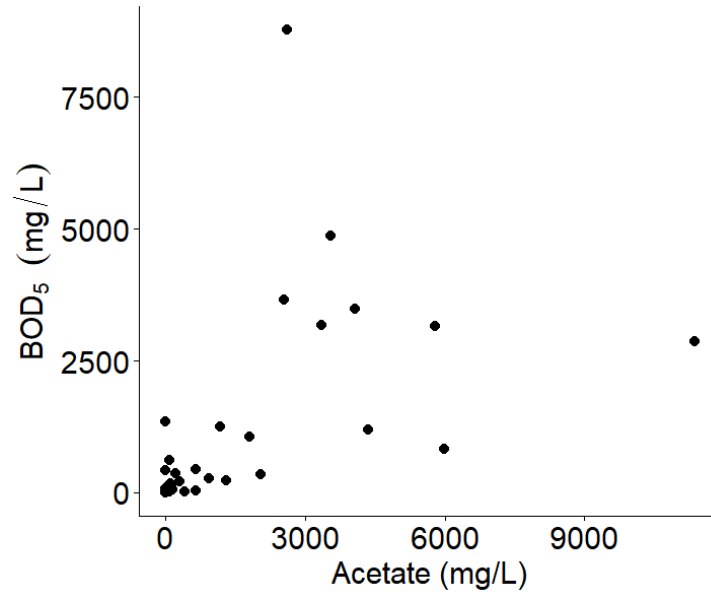
Figure 3.38. Relationship between acetate concentration and BOD5 in both years. Pearson's r = 0.62, p < 0.02.

While BOD_5 is sufficiently high in stormwater and BB-RP-B sites to deplete oxygen, dissolved concentrations remain at healthy ecological levels in the receiving water bodies (Figure 3.39). Dissolved oxygen was higher in lake samples than stormwater, as expected. None of the stormwater samples had particularly low oxygen levels nor were any depletions apparent when KAc application occurred. BOD_5 is traditionally measured at 20˚C, but the BOD of KAc is exerted at much lower temperatures. The cold temperature of the water during the time of year KAc was applied significantly slows oxygen consumption. Horner and Brenner found that acetate in water takes 5 days to completely biodegrade at 20˚C, but 100 days at 2˚C (1992). Water temperatures in Lake Superior averaged between 0.5˚C and 2.5˚C during sampling. The lack of depleted dissolved oxygen in the downstream sites despite the high BOD_5 concentrations measured in runoff can be explained by this as the BOD is exerted over time, and Lake Superior has sufficient aeration and mixing to prevent significant oxygen depletions.
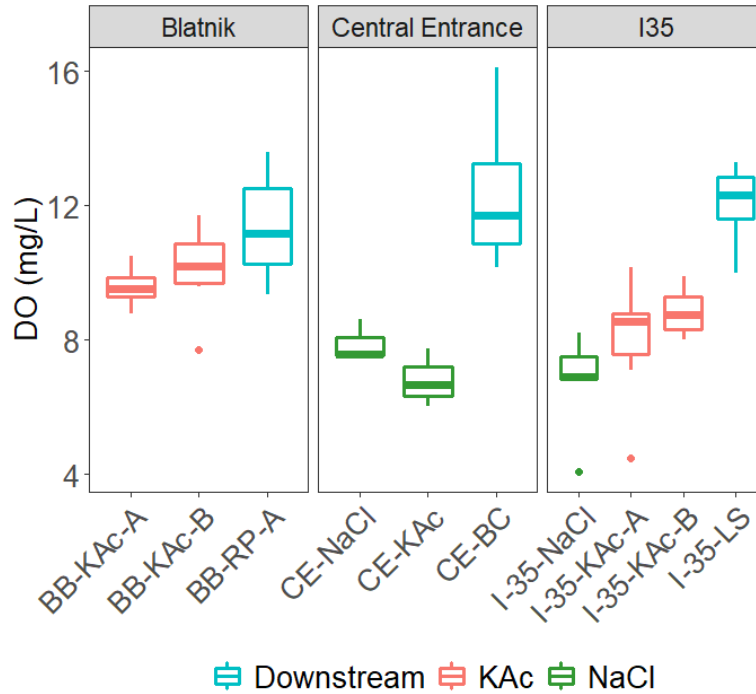
Figure 3.39. Dissolved oxygen (DO) concentrations in difference sites. Bold line in each box indicates mean DO value.

While no oxygen depletion was detected in the receiving water bodies, with an oxygen demand so high it is likely that smaller waterbodies receiving highly concentrated storm water would see oxygen concentrations fall substantially. While there is minimal work on KAc and BOD, LaPerriere and Rea (1989) found that 50 mg/L of Calcium Magnesium Acetate in a receiving water body (pond) is sufficient to cause oxygen depletions past concentrations safe for fish.

3.4.5.1 Microbiological Water Quality: E. coli and Coliform bacteria

Coliform bacteria are measured for their utility as fecal indicator bacteria (FIB). When *E. coli* surpasses standards, it serves as an 'indicator' that human pathogens could be present in the sample. Sources of coliform bacteria in stormwater are primarily animal waste carried through overland flow into the storm system or naturalized bacteria in storm collection systems. As acetate is known as a good substrate for microorganisms, KAc application has the potential to result in increased microorganism populations. Thus, microbiological water quality was evaluated by enumerating indicator bacteria, *E. coli*. and coliform bacteria.

Average concentrations of *E. coli* (Figure 3.40) and coliform bacteria (Figure 3.41) show the highest *E. coli* counts at bridge runoff sites, then at both Rice's Point sites. The range is very wide at CE-KAc, and Brewery Creek has a high *E. coli* count. Sites at I-35 have the lowest bacterial counts, and Lake Superior at I-35 is much lower than the lake at Rice's Point. Average bacteria counts in bridge runoff were 3,587 MPN *E. coli* and 4,460 MPN coliform bacteria at BB-KAc-A, and 164 MPN *E. coli* and 3,852 MPN coliform at BB-KAc-B, which are comparable to their level in wastewater. I-35-KAc-A stormwater had an average *E. coli* count of 74 *E. coli* and 830 coliform, while I-35-KAc-B had an average *E. coli* count of 93 and

coliform of 1115 MPN. Central Entrance sites had an average of 11 *E. coli* and 4245 coliform at CE-NaCl, 2194 *E. coli* and 3127 coliform at CE-KAc, and 165 *E. coli* and 556 coliform at Brewery Creek. Of the lake sites, BB-RP-A had the highest bacterial populations, presumably due to the large gull population seen in the water and on the dock while sampling. Average *E. coli* counts in the lake were 162 at BB-RP-A, 53 at BB-RP-B, and 11 at I-35-LS. Average coliform counts were 881 at BB-RP-A, 1211 at BB-RP-B, and 23 at I-35-LS.
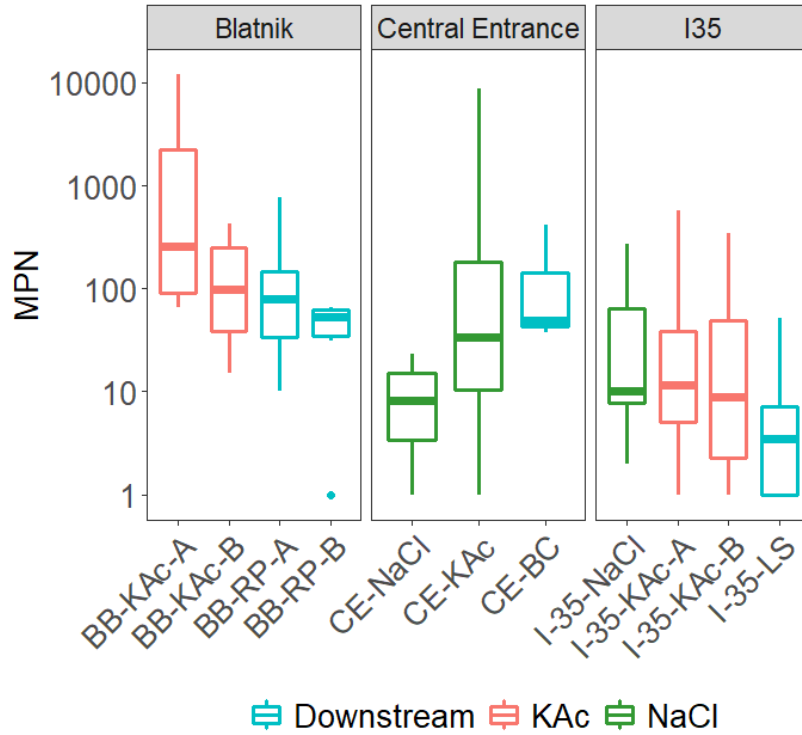
Figure 3.40. E. coli levels at all sites in the winter of 2020-2021. Bold in each box indicates mean most probable number (MPN)
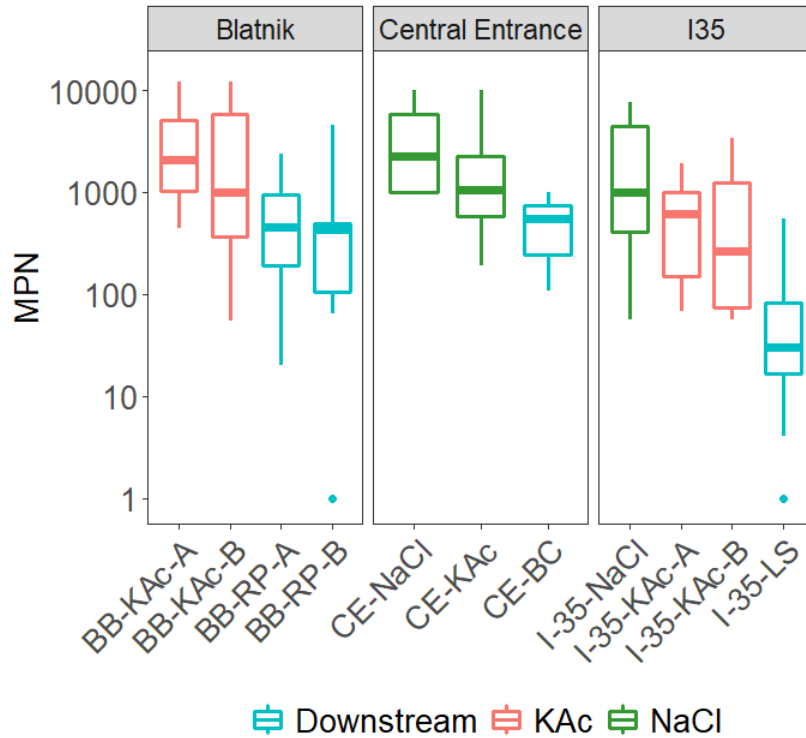
Figure 3.41. Coliform levels at all sites in the winter of 2020-2021. Bold line in each box indicates mean most probable number (MPN)

All sites had very large ranges of *E. coli* and coliform, with MPN increasing in multiple orders of magnitude on different sampling dates. The *E. coli* concentrations in freeway runoff were lower (aside from BB-KAc-A and CE-KAc) than the national average of 1,900 MPN (Pitt, 2004), which is likely due to the fact that most samples included in the national database were taken during the summer. Acetate and *E. coli* have a weak positive relationship (tau = .26, p <0.01), and acetate and coliform also have a weak positive relationship (tau = 0.22, p <0.02). Even though NaCl concentrations were as great as KAc in stormwater runoff, the influence of NaCl on FIB is unlikely as the growth of FIB and *E. coli* is not favorable in high saline environment (Kiaghadi and Rifai, 2019).

3.4.6 Degradation of acetate derived from CF7 in Lake Superior water

In addition to the field evaluation of KAc in stormwater and receiving water bodies, laboratory experiments were conducted to determine the degradation rate of acetate in the field conditions and the stability of acetate in the sample before analysis. Lake Superior water was spiked with varying amounts of CF7 anti-icer/de-icer (100-5000 mg/L as acetate). A set of solutions were incubated at room temperature (20-23°C) and 4°C to evaluate how temperature affects the biodegradation of acetate. Lake Superior water acted as the base as it is populated with naturally occurring bacteria. Non-filtered

samples reflect the conditions in the field while the filtered samples represent the stability of acetate in the stored sample as filtration (0.22 μm) removes bacteria.

Overall, acetate concentration decreased with time at both room temperature and 4°C (Figures 3.42 & 3.43 and Table 3.3). As for non-filtered samples which mimic field samples, acetate in Lake Superior water with low concentrations underwent the faster acetate degradation, particularly in C1 solution with 100 mg/L. Only C1 and C2, with the 100 and 300 mg/L of acetate derived from CF7 reached 0 mg/L over 90 days at both temperatures with no lag time. Lake water with higher concentration (C3, C4, and C5) had a lag time (up to ~28 days) before the degradation occurred.
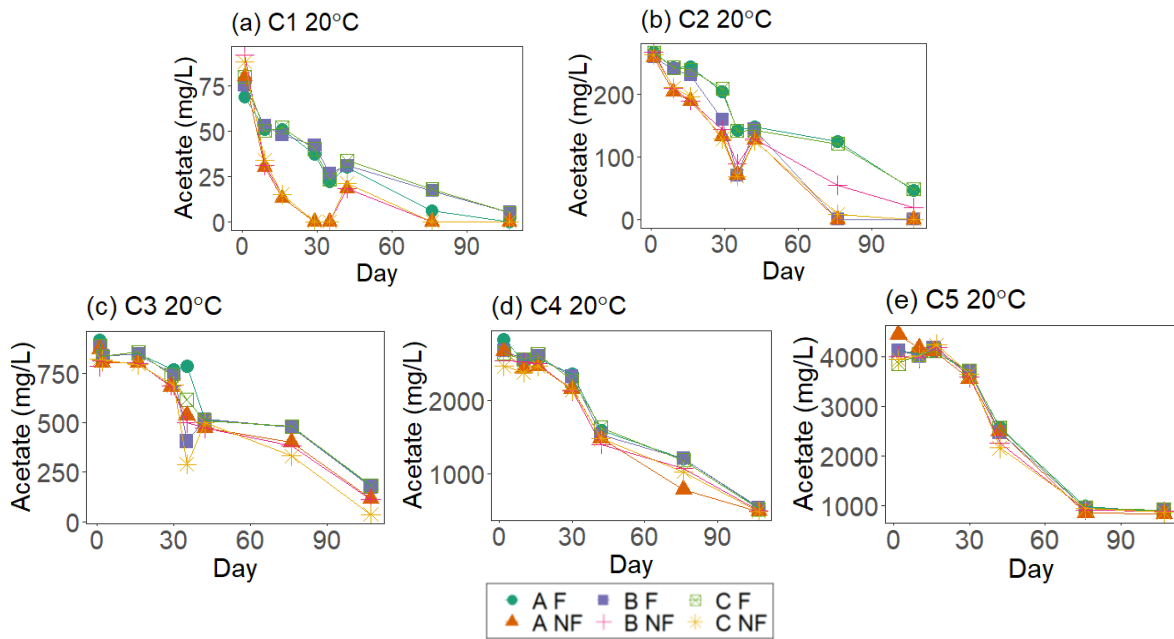
Figure 3.42. Degradation of acetate in filtered and non-filtered Lake Superior water spiked with CF7 as a function of concentration (100-5000 mg/L as acetate in CF7®; C1-C5) in triplicate (A, B, and C) at room temperature (20-23 °C)
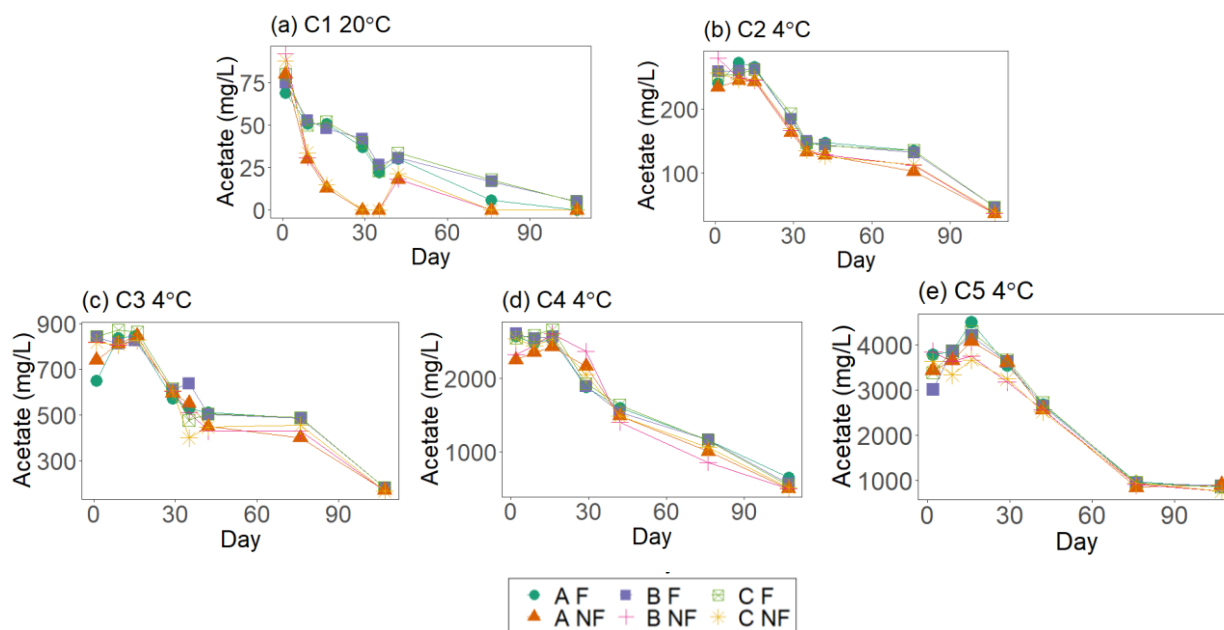
Figure 3.43. Degradation of acetate in filtered and non-filtered Lake Superior water spiked with CF7 as a function of concentration (100-5000 mg/L as acetate in CF7®; C1-C5) in triplicate (A, B, and C) at 4 °C

Table 3.3. Degradation rate of acetate derived from CF7 in non-filtered and filtered Lake Superior water as a function of concentration at 4 °C and room temperature (20-23 °C)

20-23°C			Non-filtered			Filtered[a]	
	Initial Conc.[b] (mg/L)	Lag time[c] (day)	k^d (1/day)	$t_{1/2}$ [e] (day)	Lag time (day)	k (1/day)	$t_{1/2}$ (day)
C1	100	0	0.12±0.004	0.6	>9	0.023±0.003	3.0
C2	300	0	0.033±0.004	2.1	>16	0.019±0.005	3.6
C3	1000	>16	0.021±0.004	3.3	>16	0.014±0.002	5.0
C4	3000	>16	0.025±0.004	2.8	>28	0.015±0.002	4.6
C5	5000	>28	0.025±0.004	2.8	>28	0.015±0.002	4.6
4°C			Non-filtered			Filtered	
	Initial Conc. (mg/L)	Lag time (day)	k (1/day)	$t_{1/2}$ (day)	Lag time (day)	k (1/day)	$t_{1/2}$ (day)
C1	100	0	0.043±0.007	1.6	>9	0.018±0.003	3.9
C2	300	0	0.017±0.002	4.1	>16	0.015±0.005	4.6
C3	1000	>16	0.014±0.002	5.0	>16	0.013±0.002	5.3
C4	3000	>16	0.016±0.001	4.3	>28	0.014±0.002	5.0
C5	5000	>28	0.017±0.002	4.1	>28	0.017±0.002	4.0

[a] Lake Superior water was filtered with a membrane filter with 0.22 µm of pore size; [b]initial acetate concentration of CF7; [c]time period no acetate degradation is experimentally observed; [d]first-order degradation rate constant with 95% confidence range; and [e]half-life

101

Once degradation occurred, the rates of acetate degradation were faster at room temperature than those at 4°C. The rate constant of acetate at room temperature seems to be comparable to acetate oxidation rate constants (0.06-0.36 day^{-1}) observed in the marine water column even though kinetics studies of acetate in freshwater column were limited (Hordijk et al, 1992; Zhuang et al, 2019). A Q_{10} temperature coefficient, a measure of temperature dependence of a process, was estimated at 1.5-1.9 for lake water with a lower acetate concentration and ~1.3 for lake water with over 300 mg/L acetate. Considering that the Q_{10} values for most microbial (biological) systems are known as 2-3, the degradation of acetate in Lake Superior water appears to be less temperature-dependent, resulting in faster degradation in cold temperature (4°C). Additional experiments at different temperatures are needed to confirm temperature sensitivity of acetate degradation. Moreover, there are likely other degradation pathways contributing to acetate degradation in lake water such acetate oxidation by reduced species in natural water or other constituents in CF7® in addition to bacterial oxidation and assimilation.

Additionally, the degradation of acetate in the filtered lake water indicates that acetate degradation did not occur for a minimum of 9 days and up to ~30 days as majority of biomass were removed by filtration. After the lag time, the acetate degradation underwent at a similar rate constant of acetate in non-filtered lake water at 4°C regardless of incubation temperature. This suggests that the acetate degradation in filtered waters at both temperature and non-filtered water at 4°C may not result from biological process. The results also show samples should be analyzed within 20 days of collection to avoid potential degradation of acetate in the sample.

3.5   CHAPTER 3 SUMMARY AND CONCLUSIONS

MnDOT selected KAc, a liquid anti-icer/de-icer as a non-corrosive deicing alterative to NaCl. It can be effective down to -26°F, making it an ideal anti-icer/de-icer for the cold winters (Fay et al., 2015). The environmental impacts of KAc have not been widely studied. KAc anti-icer/de-icer was applied on I-35 and Blatnik Bridge during winter season of 2019-2021. This report presents the water chemistry and microbiological water quality of KAc-containing runoff in Duluth in the 2020-2021 winter as the Year 2 study by collecting and analyzing meltwater runoff and receiving water body samples. The Year 2 study focused on the fate of KAc and other water constituents in runoff at KAc application sites and water bodies receiving the runoff while the Year 1 study evaluated upstream sites from KAc application (NaCl sites) in addition to stormwater drains of KAc application and receiving water bodies.

In the 2020-2021 winter, KAc levels in stormwater samples were observed to be up to 12,000 mg/L while NaCl levels were concerningly high, surpassing 18,000 mg/L in stormwater runoff. KAc concentrations were much greater than those in stormwater samples collected in the 2019-2020 winter. This may be due to the improved sampling methods to capture initial melt water from roadways and prompt analysis of acetate in the samples prior to potential degradation. As acetate is degradable, the potassium level was a good indicator to monitor KAc level in stormwater runoff. In contrast to high concentrations of KAc and NaCl in road runoff samples, the concentration of anions, cations, and BOD$_5$ in Lake Superior water receiving the runoff were low and relatively stable except for BB-RP-B in March when snowmelt occurred.

In contrast to the results of the Year 1 study, KAc application appears to increase the levels of BOD$_5$ and FIBs (indicator for microbiological water quality) moderately. This is particularly true in certain areas of the lake with less mixing and volume like BB-RP-B. The runoffs at BB-RP-A and Lake Superior locations are usually mixed with larger quantities of lake water by waves and are more open compared to the shallow and calm water at BB-RP-B. Currently, KAc is only applied to roadways discharging stormwater into Lake Superior. If KAc application were expanded, runoff from roadways draining into creeks or smaller lakes could result in a high oxygen demand as with BB-RP-B. Interestingly, the lake water at BB-RP-B was oxygenated on the sampling dates when BOD and KAc were high in the water, indicating reaeration were sufficient to avoid deleterious effects of oxygen depletion on aquatic life. However, in cases of runoff with a high BOD entering stagnant or small areas of water, reaeration may not be sufficient to prevent a decrease in oxygen from the BOD of the stormwater.

In addition to field evaluation, the rate and extent of degradation of acetate in Lake Superior water under cold temperatures were determined as a function of CF7® concentration in the laboratory. The biodegradation of acetate in Lake Superior water occurred under cold temperatures (4°C) with lag time of 9-30 days. After the lag time, the half-life of the acetate in the Lake Superior water was 0.6-3 days at room temperature and 1.5-5 days at 4°C. The results also indicate that there may be additional reaction pathways to degrade acetate in addition to biological degradation. The experiments also provided acetate stability and storage time of filtered field samples for the analysis.

The results of field measurement and the laboratory KAc degradation experiment will be useful for modeling the watershed impacts of KAc use as a road salt alternative as initial input parameters and boundary conditions. Particularly, the two-year field measurement data show the spatial and temporal variation of KAc concentration and other water chemistry parameters in stormwater runoff and receiving water. This information can be used to develop various scenarios (e.g., receiving water body size, distance from the road, precipitation, KAc application) for watershed modeling to predict the impact of KAc on DO concentrations of road runoff and receiving water bodies by verifying with the field measurement data.

In summary, a field evaluation of the application of CF7 as an anti-icing/de-icing agent has determined the fate and transport of KAc after application as stormwater eventually ends up in freshwater systems. The range of concentrations of K^+ and Ac^- that are found in the highway or bridge runoff was used for watershed modeling to evaluate impacts of KAc use. While the scope of this evaluation was narrowed to the impact of stormwater on Lake Superior, future work can determine the potential impacts on lakes and streams if CF7 use were to be expanded.

Figure 3.44. Images of weir modification with cements and foam to capture low flow of snowmelt runoff
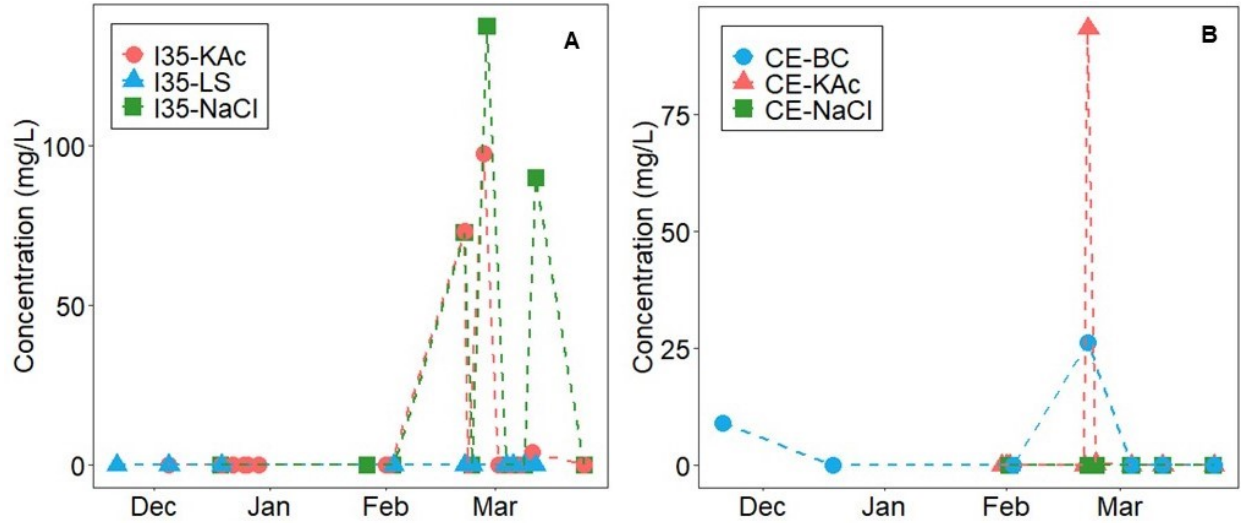
Figure 3.45. Phosphate (PO$_4^{3-}$) levels in winter stormwater runoff and receiving water at (A) I-35 and (B) Central Entrance. No phosphate was detected in Blatnik Bridge runoff and receiving water
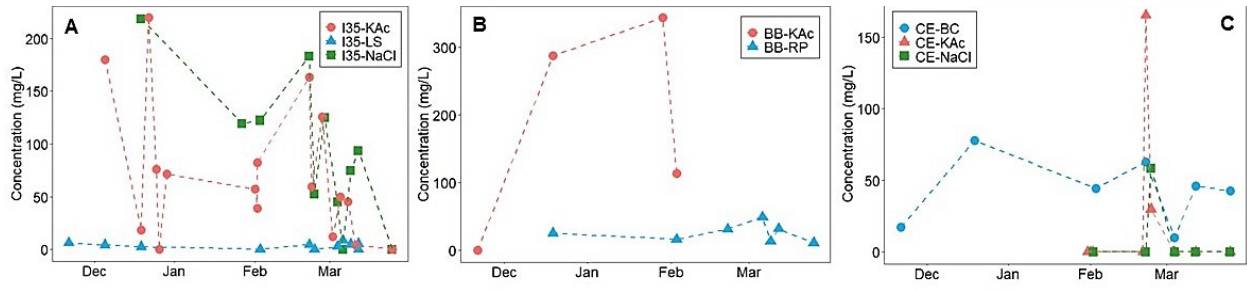
Figure 3.46. Sulfate (SO$_4^{2-}$) levels in winter stormwater runoff and receiving water at (A) I-35, (B) Blatnik Bridge, and (C) Central Entrance in Year 1
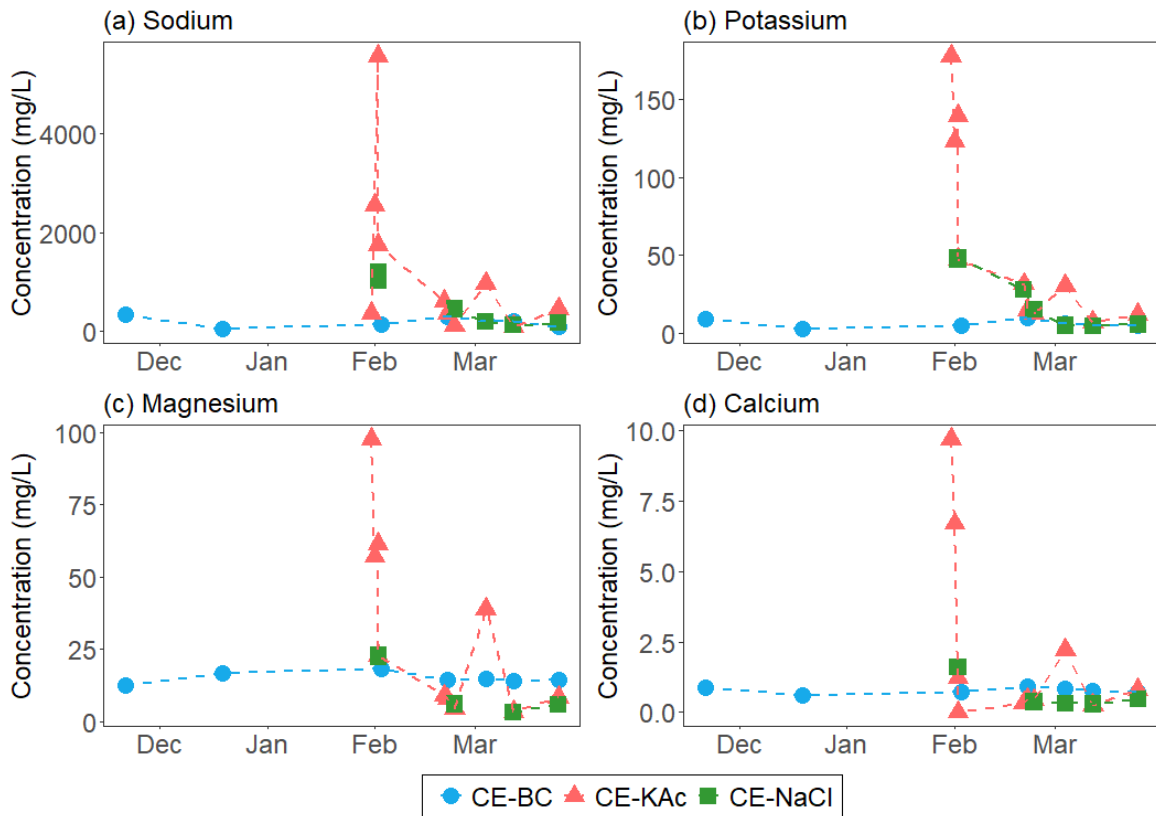
Figure 3.47. Concentration of major cations, (a) sodium, (b) potassium, (c) magnesium and (d) calcium at Central Entrance in Year 1

105
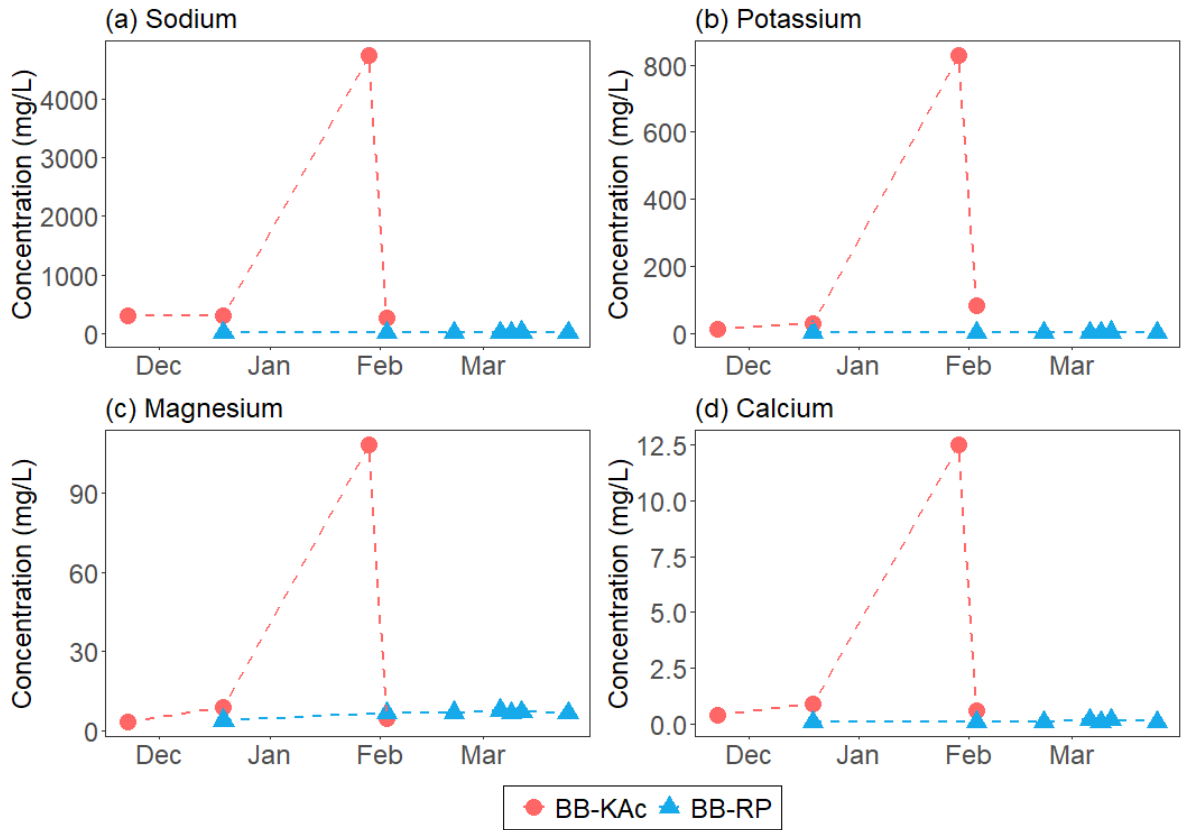
Figure 3.48. Concentration of major cations, a) sodium, (b) potassium, (c) magnesium and (d) calcium at Blatnik Bridge in Year 1

4 Water Quality Modeling

Prepared by:

Andrew J. Erickson[1]
William Herb[1]
John S. Gulliver[1]

[1]St. Anthony Falls Laboratory, University of Minnesota

4.1 INTRODUCTION

To predict the fate and transport of KAc within a watershed properly, a model needs to be able to simulate snowfall and snowmelt, pollutant application and transport, and natural biodegradation of KAc in the environment. P8 was evaluated and found to not have the built-in capabilities or flexibility to model KAc properly. Specifically, the application of pollutants in P8 was connected to sediment accumulation and washoff and cannot be independently characterized. In addition, decay rate equations and other pollutant-related fate and transport functions are model-wide and cannot be specified by sub-watershed or event. Excel was also considered but required model creation from scratch including creating a user interface for input parameters, input equations and calculation steps, and extensive testing for accuracy and bug-fixes. EPA-SWMM was found to have 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 used by several engineering consultants, County Soil and Water Conservation Districts (SWCDs), watershed districts, and city staff in Minnesota. Thus, EPA-SWMM was selected to satisfy project requirements. EPA-SWMM was adapted to model the transport of Kac applied to streets and parking lots. Degradation rate constants obtained from the results of Chapter 2 and the impact of temperature and precipitation were incorporated into the model.

4.2 METHODOLOGY

4.2.1 Example Watershed Application

EPA-SWMM was applied to a small example sub-watershed to demonstrate how end-users would input values to model snowfall, snow plowing, snowmelt, and KAc transport and decay. An aerial photo of this hypothetical subwatershed is given in Figure 4.1. The use of EPA-SWMM to model watersheds, subwatersheds, inlets, pipes, and outfalls such as those shown in Figure 1 will not be described here. It is assumed that the end-users will either already have this knowledge or will have access to the tools and resources to gain this knowledge through training for users. The guidance in this document will describe how end-users can implement tools and select parameters within EPA-SWMM to model snowfall, snow plowing, snowmelt, and KAc transport and decay.
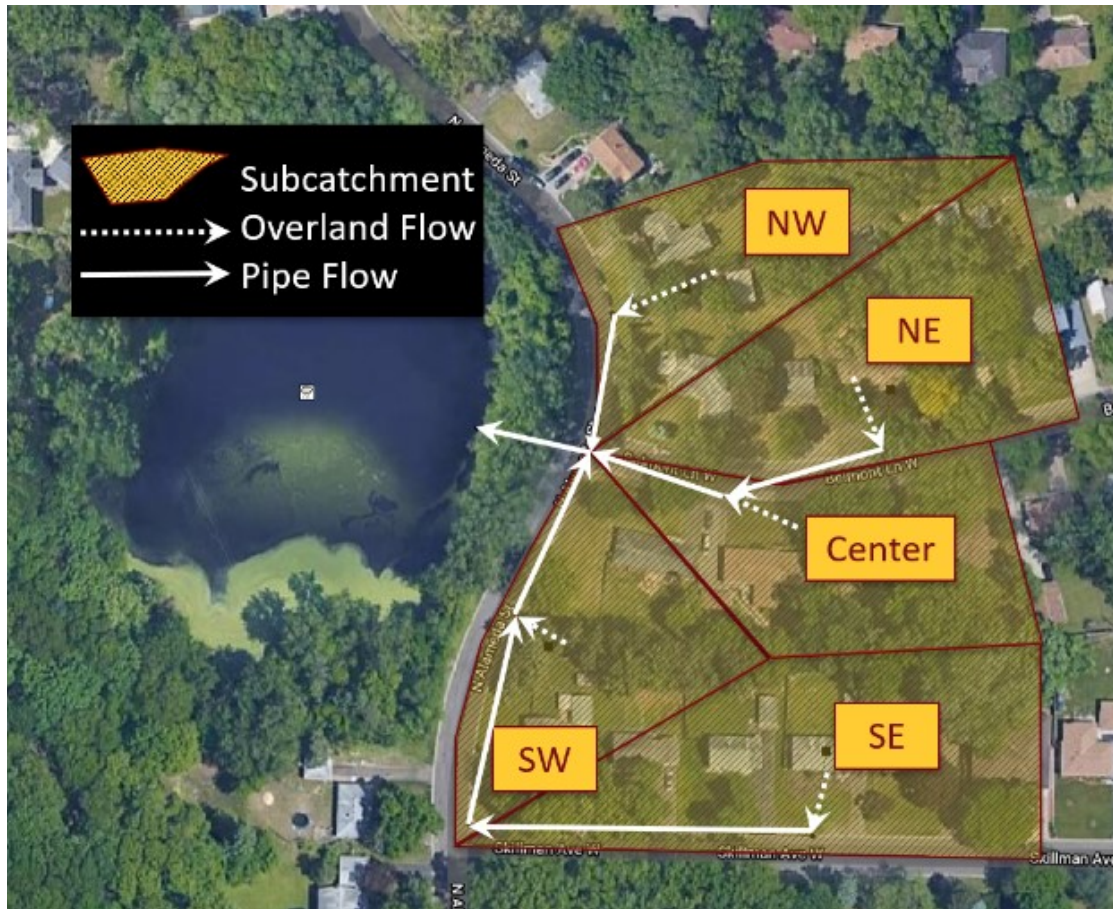
Figure 4.1: Schematic of hypothetical urban subwatershed modeled in EPA-SWMM.

4.2.1.1   Snowfall, Snow Plowing, and Snowmelt

Snowfall occurs automatically within EPA-SWMM when the air temperature (input file) is below freezing temperatures of water (~32°F or 0°C) while precipitation (input file) occurs. This snowfall is then stored on the watershed (i.e., subcatchment) surfaces, both pervious and impervious as "snowpack" until it is plowed (impermeable surfaces, typically) or melts (all surfaces). The snow plow and snowmelt parameters within EPA-SWMM are found in the "Snow Packs" module (Project/Hydrology/Snow Packs) as shown in Figure 4.2.
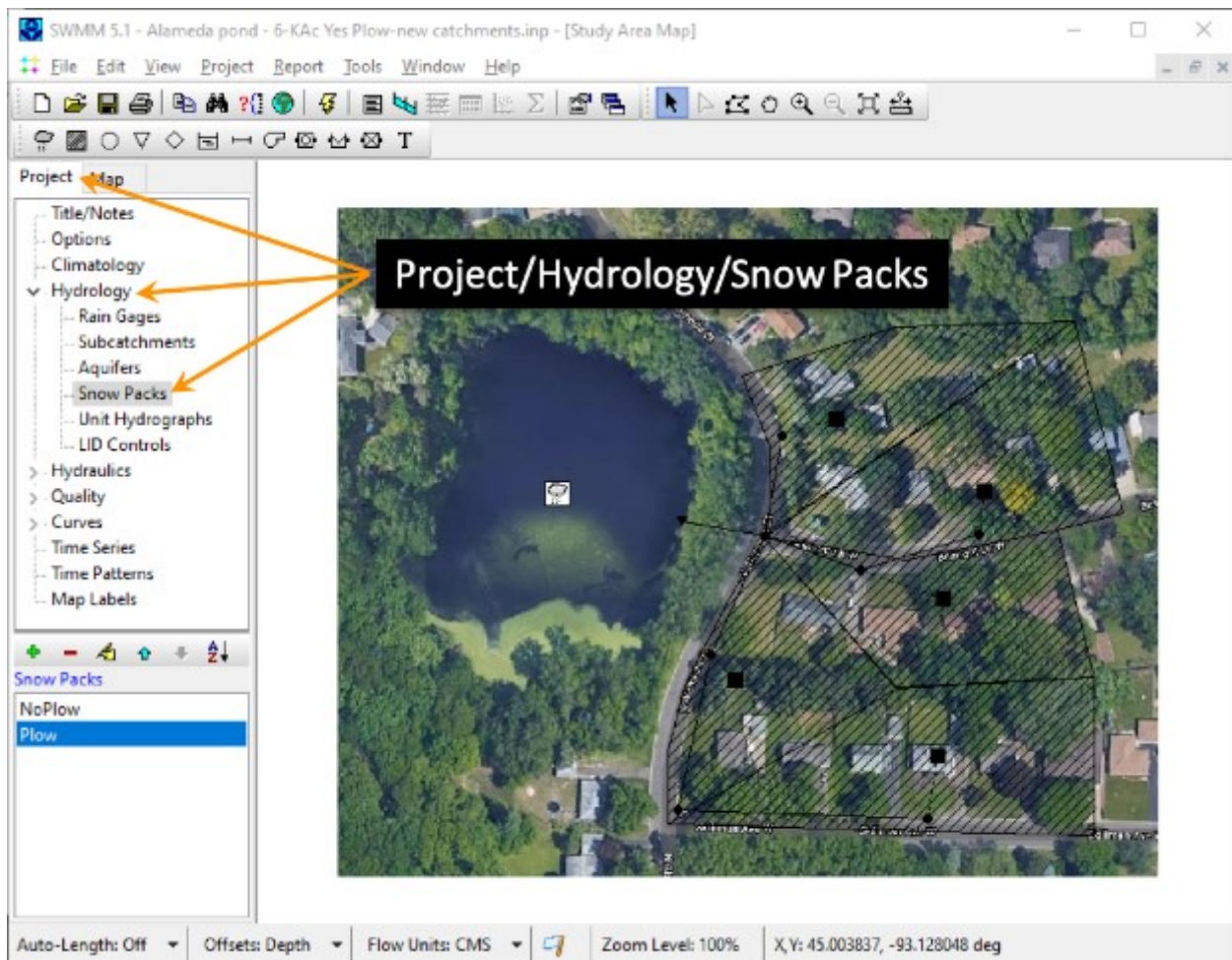
Figure 4.2: Snow pack module within SWMM (Project/Hydrology/Snow Packs).

Multiple Snow Packs can be added and assigned to subcatchments as needed. In this example, one snow pack was created and the parameters were selected to represent portions of the subwatershed that were plowed. Snowmelt parameters appear in the Snow Pack Parameters tab of the Snow Pack Editor window (See Figure 4.3). In this example, snowmelt parameters were now changed from the default values. The snowplow parameters appear on the bottom of the Snow Pack Parameters tab and throughout the Snow Removal Parameters tab within the Snow Pack Editor Window. In this example, The Fraction of Impervious Area That is Plowable was assumed to be 0.95 (i.e., 95% of the impervious area is plowed); the Depth at which snow removal begins was assumed to be 25 mm (i.e., plowing occurs whenever the snow depth on the impervious areas equals or exceeds 25 mm = 1 inch); and Fraction transferred to the pervious area was assumed to be 0.9 (i.e., 90% of the snow on the impervious area is plowed onto the pervious areas), as shown in Figure 4.3.
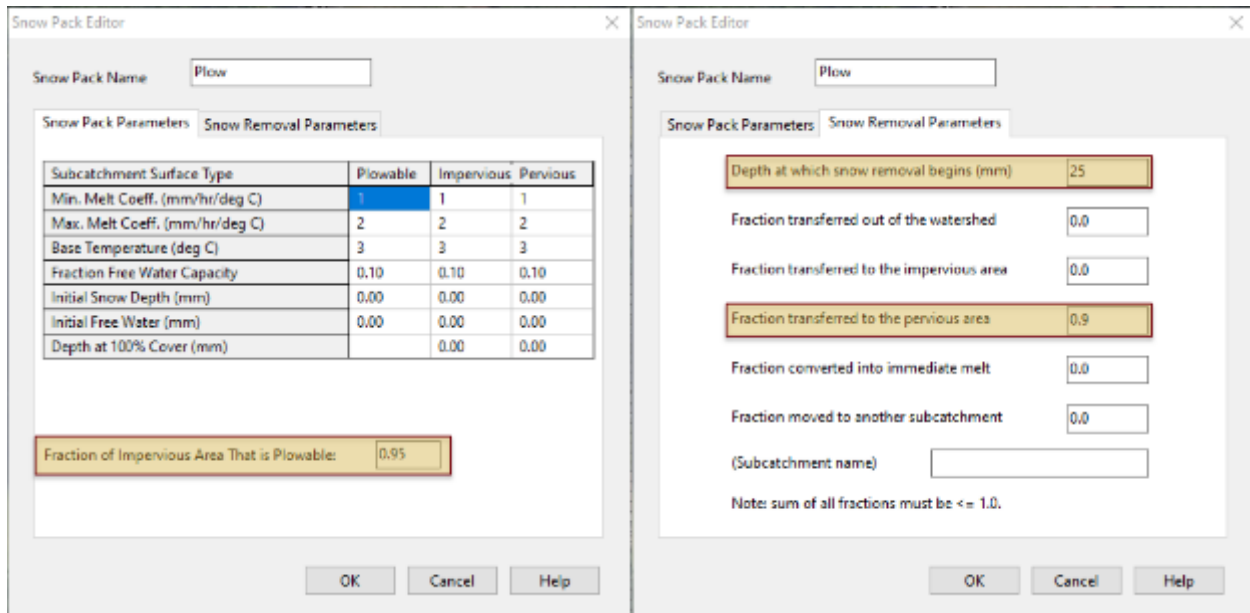
Figure 4.3: Plow Parameters. Highlighted fields were selected to represent areas that are plowed.

4.2.1.2 Pollutants (for modeling Potassium Acetate)

To represent the fate and transport of KAc, a Pollutant must be added within EPA-SWMM using the Pollutant Editor (Project/Quality/Pollutants). In this example, KAc was added as a pollutant using the pollutant parameters as shown in Figure 4.4. The primary parameters used to represent KAc are the decay coefficient (e.g., k = 0.11/day) and Snow Only flag ("Yes").
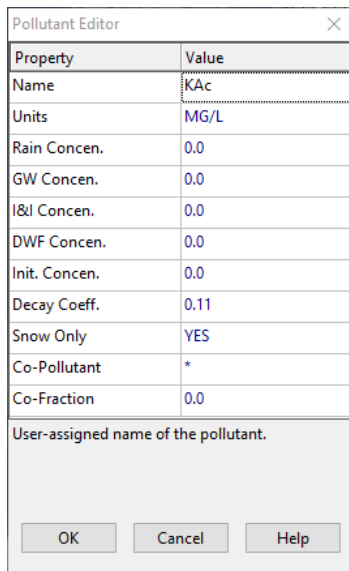
Figure 4.4: Pollutant Editor showing parameters used to represent Potassium Acetate

4.2.1.3 Land Use for applying and washing off KAc

To apply KAc to subcatchments within EPA-SWMM, a Land Use must be defined using the Land Use Module (Project/Quality/LandUse). In this example, a Land Use called "Roadway" was created and defined to represent the roadway surfaces that are plowed and receive KAc as an anti-icing agent (see Figure 4.5). The important parameters in the Land Use Editor are the Buildup and Washoff parameters associated with KAc. Additional research is needed to specify values, range, and sensitivity of EPA-SWMM to the values inputted on these screens. In this example, a Power function was used to describe the buildup (i.e., application) of KAc on the Roadway surface with a Rate Constant of 0.0295 kg/m of curb length and a power constant (i.e., exponent) of 1. These values correspond to an average application rate of KAc of 42.5 gallons per lane mile (the known range of application rate is 25 – 60 gallons per lane mile) and a linear application rate (power exponent = 1). In this example, an exponential function was used to describe the washoff of KAc during snowfall events. A common washoff coefficient of 4.6 / inch = 0.1811 / mm (EPA 2016) was assumed but additional research is needed to calibrate this value to measured values in field applications. Again, a power exponent = 1 was assumed to represent linear washoff of KAc.
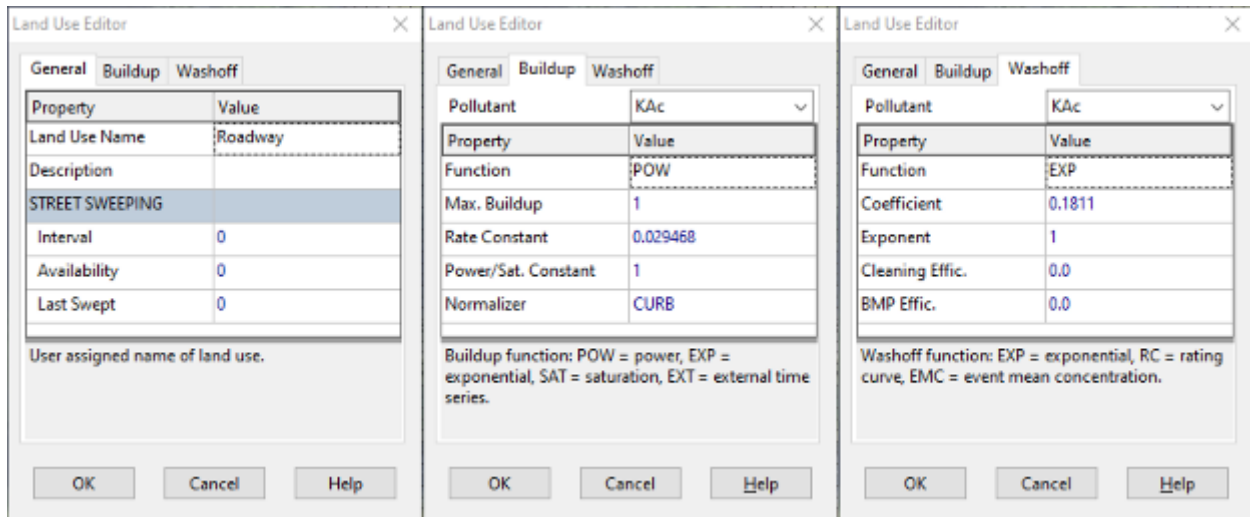
Figure 4.5: Land Use Editor demonstrating the Roadway land use over which KAc is applied.

4.2.1.4 Subcatchment Parameters

Finally, the Snow Pack and Landuse parameters are applied to the subcatchments in which plowing and KAc are used as anti-icing. In this example, all subcatchments were modified to use the Plow Snow Pack and Roadway Land Use as shown for the NW subcatchment in Figure 4.6. The amount of roadway surface that is plowed and receives KAc is 11.6% of the subcatchment area, in this example.

Figure 4.6: Subcatchment Parameters including use of Plow Snow Pack and Roadway Land Use.

4.2.1.5 Preliminary Results

Please note that the above parameters are for a hypothetical residential subwatershed. Values do not represent actual watershed characterization. As such, hypothetical climate parameters were used to test the model functionality. In this scenario, a period of 11 days was modeled in which three precipitation events were simulated 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 4.7.
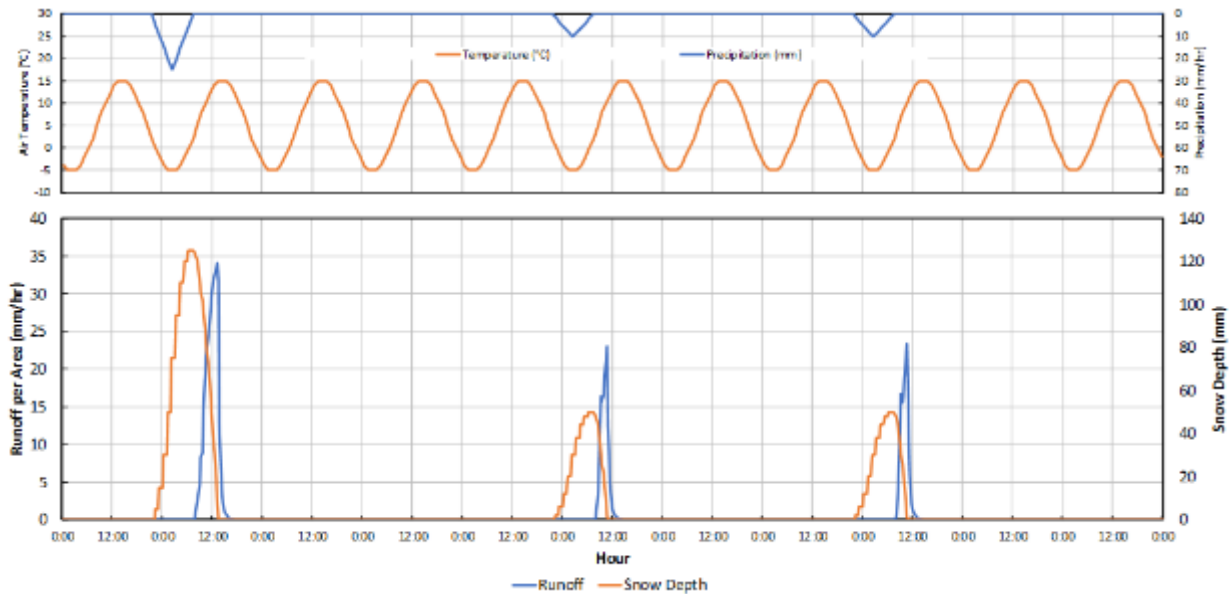
Figure 4.7: Simulated climate, runoff, and max snow depth for hypothetical watershed modeled by EPA-SWMM.

As shown in in Figure 4.7, snowfall accumulates to a max depth of 125 mm for the first event, corresponding to the cumulative snowfall. Shortly after the peak accumulation, the temperature rises above freezing (0°C) and snowmelt begins as represented by the decrease in max snow depth and increase in runoff (mm/hr). The runoff increases until the snowpack is completely melted and then quickly decreases as well. For these hypothetical events, the entire snowpack is melted within a single day.

Pollutant fate and transport was simulated using SWMM for multiple anti-icers/de-icers as part of the concurrent LCCMR project, including Rock salt (NaCl), liquid brine (NaCl and $MgCl_2$, separately) and KAc. The application rates in this hypothetical scenario were as follows:

- NaCl Rock Salt: 500 lbs / lane mile NaCl ≈ 85,486 mg Cl^- per m of curb (mg/L as Cl^-)

- NaCl Brine: 30 gal / lane mile @ 23.3% by mass ≈ 9,973 mg Cl^- per m of curb (mg/L as Cl^-)

- MgCl2 Brine: 20 gal / lane mile @ 21.6% by mass ≈ 7,568 mg Cl^- per m of (mg/L as Cl^-)

- KAc Liquid: 42.5 gal / lane mile @ 49% by mass ≈ 29,468 mg Ac^- per m of curb (mg/L as Ac^-).

The pollutant fate and transport results from this hypothetical scenario are illustrated in Figure 4.8. The peak runoff concentration for each pollutant corresponds proportionally with the application rate described above. As expected, the rock salt application (≈ 85,486 mg Cl^- per m of curb) produced considerably higher runoff concentration than the liquid-applied chemicals. The runoff concentration, however, did not vary based on the event size. We suspect this is because the model is applying the chemicals based on duration of the event and not based on the amount of snowfall during the event.
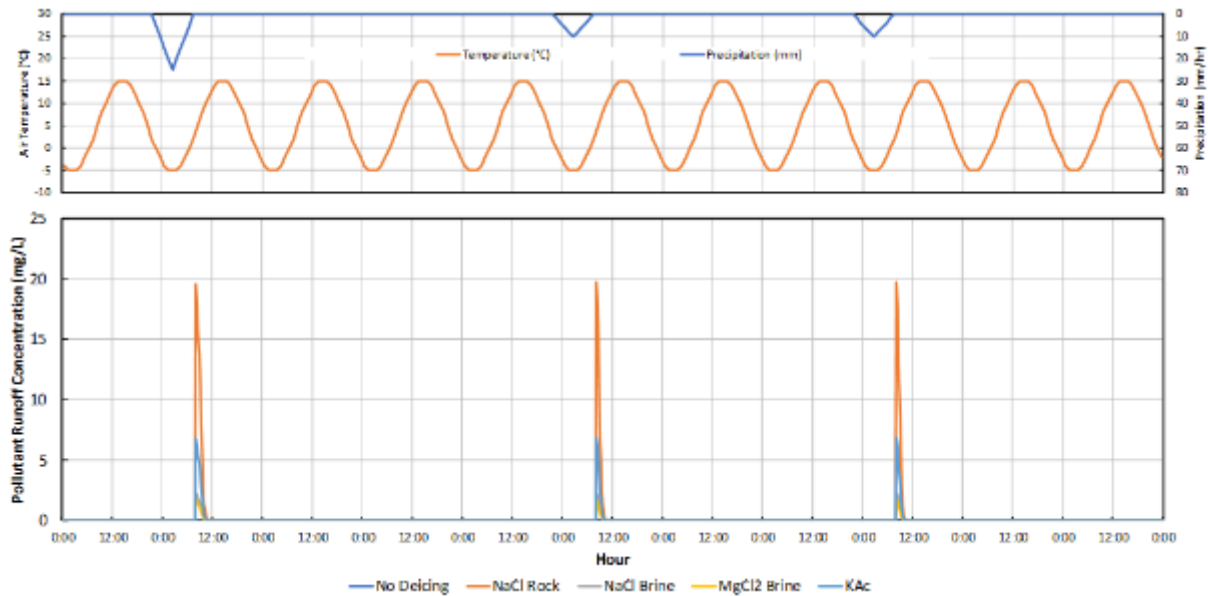
Figure 4.8: Pollutant runoff concentration (mg/L) for rock salt, liquid brine (NaCl and MgCl2), and KAc).

Finally, the transport of 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 determined in Chapter 1 were used to calibrate the model to accurate model biodegradation of KAc.

4.3   MODEL INPUTS AND SETTINGS TO PREDICT ENVIRONMENTAL IMPACTS OF POTASSIUM ACETATE

The project team solicited and received several EPA-SWMM model set-ups from municipalities in Minnesota but were unable to confirm their accuracy. In addition, the project team requested flow monitoring and water level data to confirm accuracy even though this was beyond the scope of the project. The lack of available data prevented calibration or verification of any of these municipal EPA-SWMM model inputs and thus these were not used in the completion of this effort to date.

The analysis included in this chapter used a SWMM model for Miller Creek, in Duluth, Minnesota. The Miller Creek SWMM model was originally developed for temperature TMDL studies (Erickson et al. 2009) and has been subsequently modified and used for climate change adaptation studies (Herb 2021) and an infiltration study (Herb et al. 2020). Miller Creek has a 24 km^2 watershed that includes portions of Duluth and Hermantown, Minnesota, with headwaters near Duluth International Airport and drainage outlet to Duluth Harbor in Lake Superior, as shown in the aerial photo in Figure 4.9. The watershed is 23% impervious and includes a section of State Highway 53 and a mix of residential and commercial development. The topography is a relatively flat plateau in the upper two thirds of the watershed, with an increase in slope as Miller Creek heads towards Lake Superior.

Figure 4.9. Map of the Miller Creek watershed modeled in EPA-SWMM, outlined in black.

The SWMM model for Miller Creek used as a basis for this study has 41 sub-catchments (Figure 4.10) and includes channel segments representing the main stem of Miller Creek, several small tributaries, and some of the major stormwater drainage features (culverts, pipes, detention ponds, etc.).
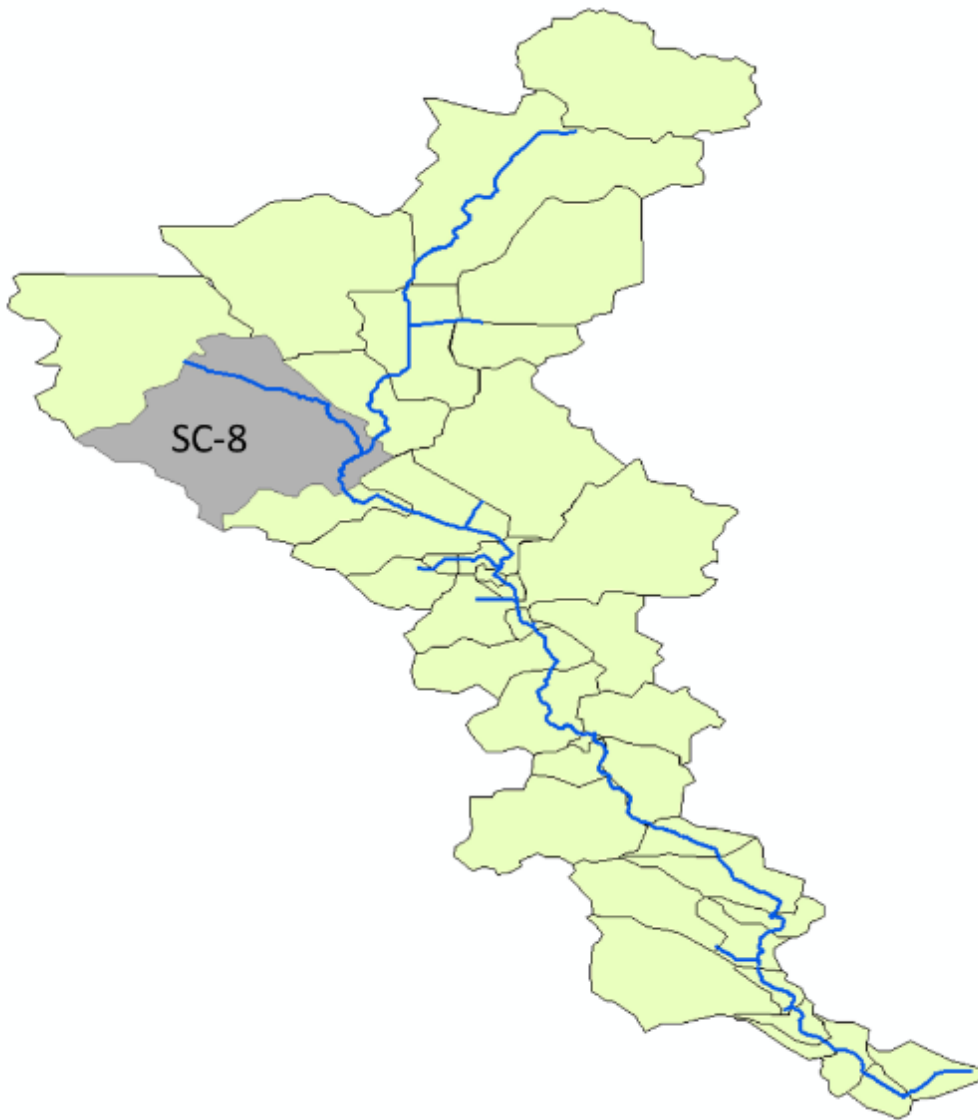
Figure 4.10. Schematic of the Miller Creek SWMM model, showing the sub-catchments (thin black lines) and drainage network (dark blue line).

4.3.1 Model Inputs and Settings

For this chapter, the pre-project EPA-SWMM model for Miller Creek was modified as follows:

- Modeling of snow accumulation and melting was added

- A GIS analysis was performed to estimate the length of roadways in each sub-catchment connected to the stormwater drainage network

- Separate sub-catchments were created in the model for these connected roadway areas, and

- A roadway land use was created in the model to enable application of anti-icer to the connected roadway areas.

Approximately 60% of the roadways in the Miller Creek watershed are drained with pervious ditches. It was assumed that anti-icer applied to these roadways infiltrates to the shallow groundwater aquifers, and does not appear in surface runoff (Meriano et al. 2009, Perera et al. 2013). For connected roadways (i.e., curb-and-gutter), previous studies estimated that 50% of applied anti-icer is plowed over the curb and infiltrates into the pervious areas behind the curb, with the remaining 50% washed off into the drainage network (Meriano et al. 2009, Perera et al. 2013). This 50-50 split of anti-icer was used in the Miler Creek Watershed.

4.3.1.1 Snowfall, Snow Plowing, and Snowmelt

Snowfall occurs automatically within EPA-SWMM when the air temperature (input file) is below a specified temperature threshold (~32°F or 0°C) while precipitation (input file) occurs. This snowfall is then stored on the watershed (i.e., subcatchment) surfaces, both pervious and impervious as "snowpack" until it is plowed (impermeable surfaces, typically) or melts (all surfaces). The snow plow and snowmelt parameters within EPA-SWMM are found in the "Snow Packs" module (Project/Hydrology/Snow Packs).

Prior to analyzing transport of anti-icer in the Miller Creek watershed, the snow accumulation and melting model was calibrated using snow depth data from Duluth International Airport. An example of observed and simulated snow depths is given in Figure 4.11 for the winter of 1998/99 – these snow depths are representative of unplowed, pervious land areas. Note that SWMM simulates snow accumulation and melt depths as water equivalent, rather than actual snow depth. Four snow parameters were adjusted from their default settings under Project/Hydrology/Snow Packs/Snow Pack Parameters for the calibration:

- Min. Melt Coeff. = 0.01 in/hr/ °F

- Max. Melt Coeff. = 0.015 in/hr/ °F

- Base Temperature = 35 °F

- Dividing (i.e., Threshold) Temperature Between Snow and Rain (found under Project/Climatology/Snow Melt) = 35 °F
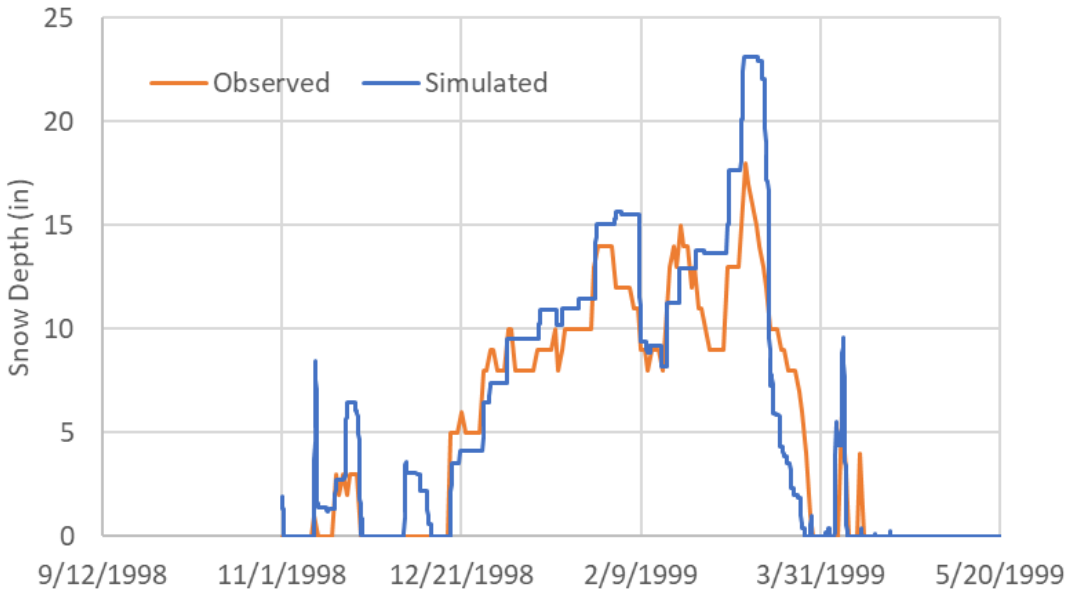
Figure 4.11. SWMM-simulated and observed snow pack depth in unplowed areas for 1998/99 in Duluth, Minnesota.

To simulate snow accumulation, melting, and plowing on roadways, a second snow pack was set up, specifically for roadways. The plow parameters were set as follows in the Project/Hydrology/Snow Packs/Snow Removal Parameters, and as shown in Figure 4.12:

- 80% of the roadway area is plowable (Fraction of Impervious Area That is Plowable

- = 0.8; found in the Project/Hydrology/Snow Packs/Snow Pack Parameters)

- Plowing occurs for snowfall > 0.1 in water equivalent (~ 1 in snow depth accumulation) (Depth at which snow removal begins = 0.1 in of water equivalent)

- 40% of the plowed snow goes to the roadway shoulder (Fraction infiltrated into the soil or transferred to the impervious area = 0.4)

- 40% of the plowed snow leaves the roadway sub-catchment (plowed over the curb) (Fraction infiltrated into the soil or transferred out of the watershed = 0.4)

- 20% of the plowed snow is melted immediately (plow residue melted by anti-icer) (Fraction converted to immediate melt = 0.2)

Specifying immediate melting of 20% of the plowed snow was found to be important to simulate small volume, high anti-icer concentration runoff events, as shown in the next section.

118

Figure 4.12. Plow Parameters for the roadway sub-catchments.

4.3.1.2 Simulation of Sodium Chloride Transport in Miller Creek

The fate and transport of one de-icer and one anti-icer was simulated using the SWMM model: Sodium Chloride (e.g., rock salt) and KAc, respectively. Although this study focuses on KAc, sodium chloride was also simulated as a mechanism to verify that the model was simulating reasonable concentrations in the main stem of Miller Creek in comparison to measured NaCl concentrations (1998-1999). Input time series (Project/Time Series) of chloride (Cl) to the SWMM model were specified as follows:

- For any snowfall event > 1 inch, an application of 250 lbs rock salt per lane mile was assumed.

- An equivalent mass of Cl was calculated (250 x 0.607 = 151.8 lb Cl).

- The application rate was reduced by 50% to account for losses rate of Cl to infiltration and rock salt blowing or bouncing off the road, giving a final application rate of 75.9 lb Cl per lane mile.

- The washoff coefficient was set using an exponential function with a coefficient of 10 and an exponent of 1.

- The decay coefficient of chloride was set to 0 (conservative substance).

Observed chloride concentrations in Miller Creek were obtained through the Lake Superior Streams website (http://www.lakesuperiorstreams.org), with 1999 having the most complete data set. Although some stream gaging data is available for Miller Creek, very little winter stream flow data is available. An interesting feature of the chloride monitoring data is that summer baseflow can have concentrations on the order of 200-300 mg/L, reinforcing the assumption that much of the chloride is infiltrated and subsequently released as stream baseflow. SWMM does not explicitly model the infiltration of

119

pollutants and transport of pollutants through groundwater aquifers. However, a fixed pollutant groundwater concentration can be specified, which then appears in stream baseflow. Based on summer monitoring of chloride in Miller Creek (Figure 4.13) for the summer of 2007, a background concentration of 250 mg/L was specified in the model and used for all simulations.
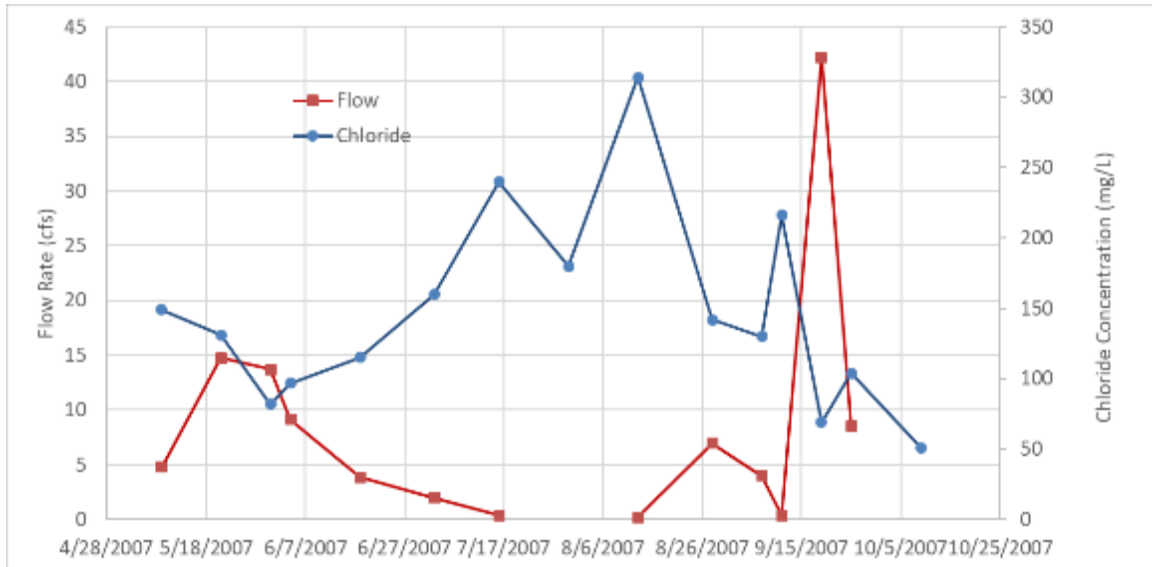
Figure 4.13. Observed chloride concentration and flow rates near the outlet of Miller Creek in 2007.

The simulated stream flow and chloride concentration for the 1998/99 winter season is shown in Figure 4.14 along with the observed chloride concentrations. The SWMM model does not capture the exact timing of peak chloride concentrations – actual rock salt application data is not available, and the amount of initial snow melt associated with each snow event is only roughly estimated as a fixed fraction of total snow depth. However, the peak concentrations of chloride simulated by the SWMM model are similar in magnitude to observed peaks, suggesting that model is effectively capturing the processes of de-icer washoff and dilution in the drainage network.
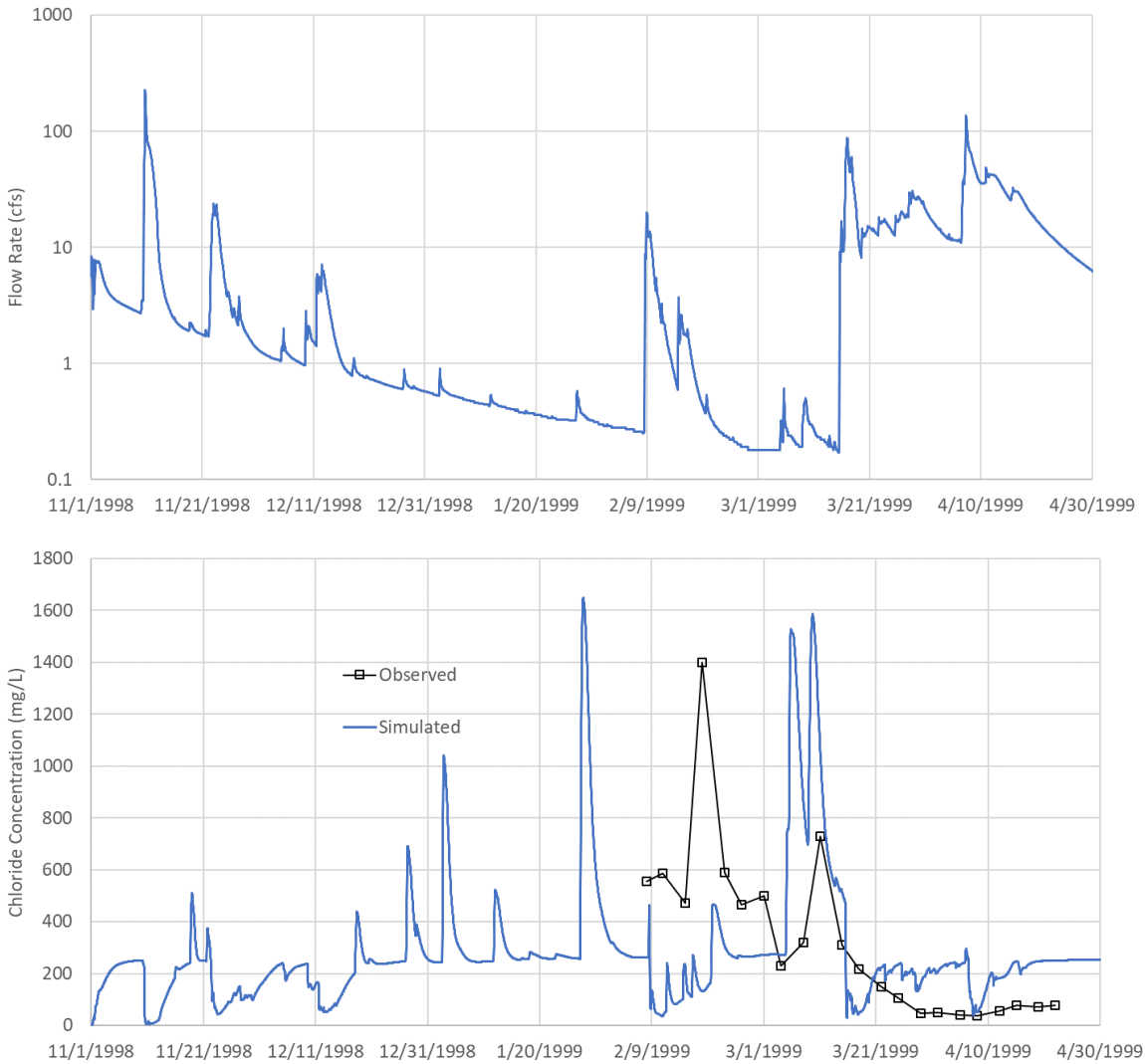
Figure 4.14. Simulated flow rate in Miller Creek (upper pane) and simulated (thin blue line) and observed chloride concentration (black line with open squares) at the Miller Creek outlet (lower panel) for the 1998/99 winter season.

4.3.1.3   Simulation of Potassium Acetate (KAc) Transport in Miller Creek

The transport of KAc in Miller Creek was simulated in a very similar manner to sodium chloride. Potassium and acetate were modeled as separate pollutants, with potassium assumed to be a conservative substance in surface waters and acetate 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). Input time series (Project/Time Series) of potassium and acetate to the SWMM model were specified as follows:

- For any snowfall event > 1 inch, an application of 31gallons solution at 50% KAc per lane mile was assumed.

- Equivalent masses of K (39.8%) and Ac (60.2%) were calculated as 180.1 and 272.5 lb per lane mile, respectively, based on 10.65 lb/gallon of 50% KAc solution.

- The application rate was reduced by 50% to account for losses rate to side-of-the-road infiltration, giving a final application rate of 90.1 and 136.2 lb per lane mile of K and AC, respectively.

- The washoff coefficient was set using an exponential function with a coefficient of 5 and an exponent of 1. The washoff coefficient was adjusted to obtain roadway sub-catchment washoff concentrations similar to those observed at the Blatnik Bridge (see Chapter 3 of this project).

While no in-stream measurements of KAc concentrations were available for this study, concentrations of KAc in direct runoff from treated paved areas are available from Chapter 3 of this report. It was assumed that K^+ is adsorbed by soil or plant matter so that it would not reach the groundwater table (similar to Na^+) and that Ac is degraded with the long residence time of groundwater. Thus, the background concentration KAc in groundwater was specified as 0.

Simulated K^+ and Ac^- concentrations from a roadway sub-catchment are shown in Figure 4.15. The simulated Ac^- concentrations (up to 15000 mg/L) are in line with the maximum observed Ac^- concentrations from the Blatnik Bridge (~ 13000 mg/L) from Chapter 3 of this report. Simulated K^+ concentrations are similar, up to 15000 mg/L. The ratio of K^+ to Ac^- concentrations in the simulations (~ 1:1) do not match the molar ratio for Kac (1:1.5), likely because of Ac^- degradation. The highest concentrations of Ac^- and K^+ correspond to very small hourly runoff depths (< 0.01 in) (Figure 4.14).
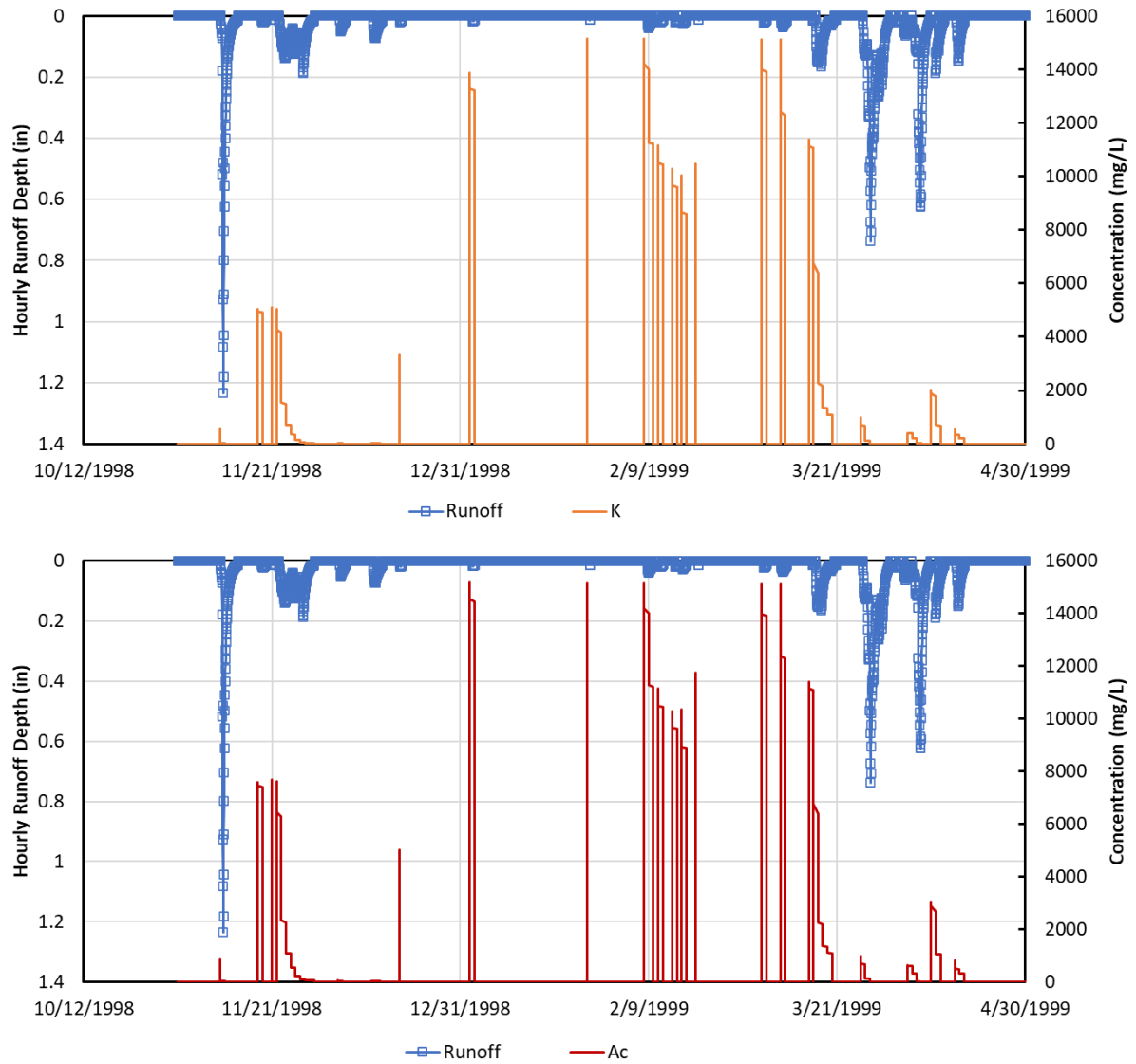
Figure 4.15. Simulated K (upper panel) and Ac (lower panel) concentrations and hourly runoff depths for a roadway sub-catchment during the 1998/99 winter season.

For comparison, aquatic toxicity experiments of KAc and relevant salts on water fleas, *Daphnia magna* and *Ceriodaphnia dubia* were also conducted as part of Chapter 1 of this report. A portion of the results from these experiments are provided in Table 4.1.

Table 4.1. Toxicity endpoints for C. dubia and D. magna. Note all concentrations in g/L. Values in mg/L can be obtained with multiplication by 1000, as in 7.26 g/L x1000 = 7260 mg/L.

	Ceriodaphnia dubia	Daphnia magna	
	LC$_{50}$ at 25˚C	LC$_{50}$ at 25˚C	LC$_{50}$ at 20˚C
CF7	0.73 g/L	0.87 g/L	0.93 g/L
K$^+$	0.13 g/L	0.15 g/L	0.16 g/L
KAc	0.46 g/L	0.46 g/L	0.46 g/L
K$^+$	0.18 g/L	0.18 g/L	0.18 g/L
NaAc	7.26 g/L	8.34 g/L	8.4 g/L
Na^{2+}	1.23 g/L	1.41 g/L	1.42 g/L

4.3.2   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 KAc application scenarios. First, the model was used to model the runoff and outflow concentration of K$^+$ and Ac$^-$ from an individual subcatchment (SC-8, see Figure 4.10). 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 for three winter seasons; October 1, 1991 to April 30, 1992 (1991/92 season); November 1, 1998 to April 30, 1999 (1998/99 season); and November 1, 2006 to April 30, 2007 (2006/07 season). The 1991/92, 1998/99, and 2006/07 winter seasons were the 75th, 50th, and 25th percentile years, respectively, for total snow depth in Duluth, based on snow data from Duluth International Airport for 1991 through 2020.

4.3.2.1   Runoff and Outflow Concentration from an Individual Subcatchment

The Miller Creek EPA-SWMM model was used to model runoff and K$^+$ and Ac$^-$ concentration in the outflow from a single subcatchment (12.8 acres) when KAc application was assumed on all roadways. For the winter periods of 1991/92, 1998/99, and 2006/07, there were 3315 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 4.16.
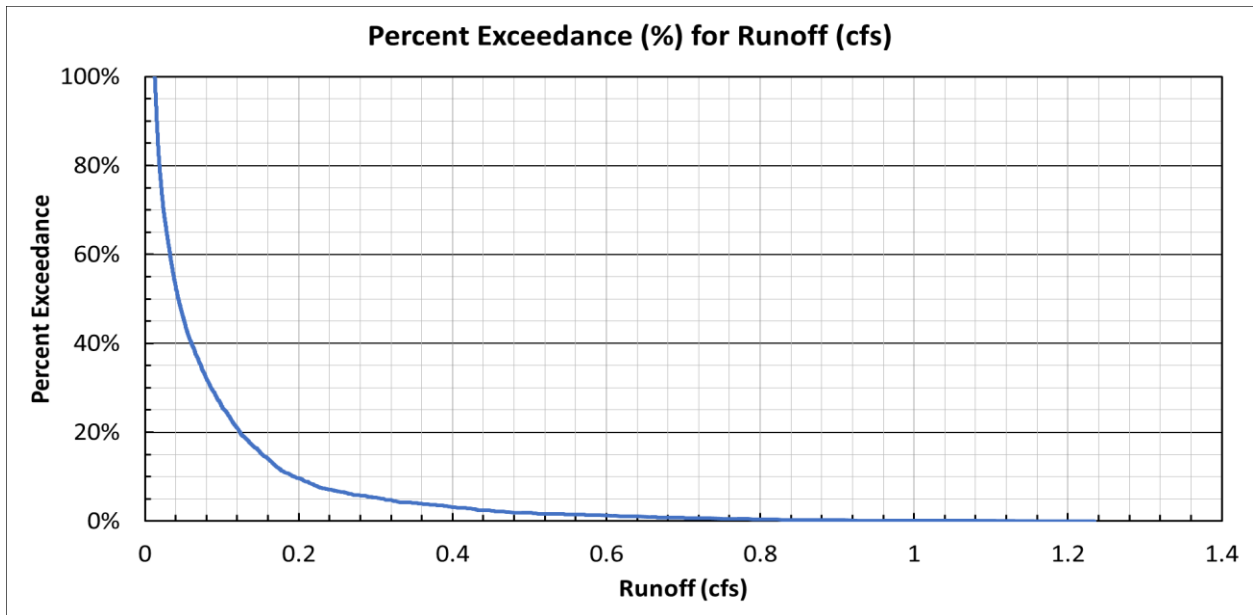
Figure 4.16. Percent exceedance for runoff data from an individual subcatchment within Miller Creek for the 1991/92, 1998/99, and 2006/07 winter periods (n = 3315)

Approximately 50% of the simulated hourly runoff data is less than 0.04 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 4.17-4.18 for K^+ with an assumed toxicity threshold of 0.13 g/L (130 mg/L) for K^+ based on values reported in Table 4.1 above.

Figure 4.17. 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 threshold of 0.13 g/L for K^+ was assumed and the region of concentration above this value is shaded in light red.

Figure 4.18. 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 threshold 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 4.17), the concentration statistics for K⁺ range from 0 to over 15,000 mg/L. It is apparent from Figure 4.17 that the median values of K+ concentration exceed the assumed toxicity threshold (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 ~150 mg/L for the interquartile range and ~2000 mg/L including extreme values. It is also apparent from Figures 4.17 and 4.18 that the concentration 1) varies substantially as a function of flow rate, 2) decreases from low flow rates to high flow rates, and 3) the toxicity threshold is exceeded for nearly all flow rates.

Acetate (Ac⁻) data for low flow rates (Q < 0.2 cfs) and high flow rates (0.2 cfs < Q < 1.3 cfs) are shown in Figures 4.19 and 4.20, respectively. The toxicity threshold for Ac⁻ is assumed to be 7.26 g/L (7260 mg/L) based on values reported in Table 1 above and the decay rate (k) is assumed to be 0.03 per day, corresponding to temperatures below 10°C. Similar to K⁺ (Figures 4.17 and 4.18), Ac⁻ concentrations vary substantially as a function of flow rate and decrease from low flow rates to high flow rates as shown in Figures 4.19 and 4.20. Though the assumed toxicity threshold for Ac⁻ is substantially larger than that for K⁺ (7260 mg/L vs. 130 mg/L), the interquartile range of concentration values for low flow rates still exceed the toxicity threshold below 0.03 cfs, and outliers exceeded the toxicity threshold up to flow rates of 0.17 cfs, as shown in Figure 4.19. All Ac⁻ concentration values were below the assumed toxicity threshold for high flow rates as shown in Figure 4.20.
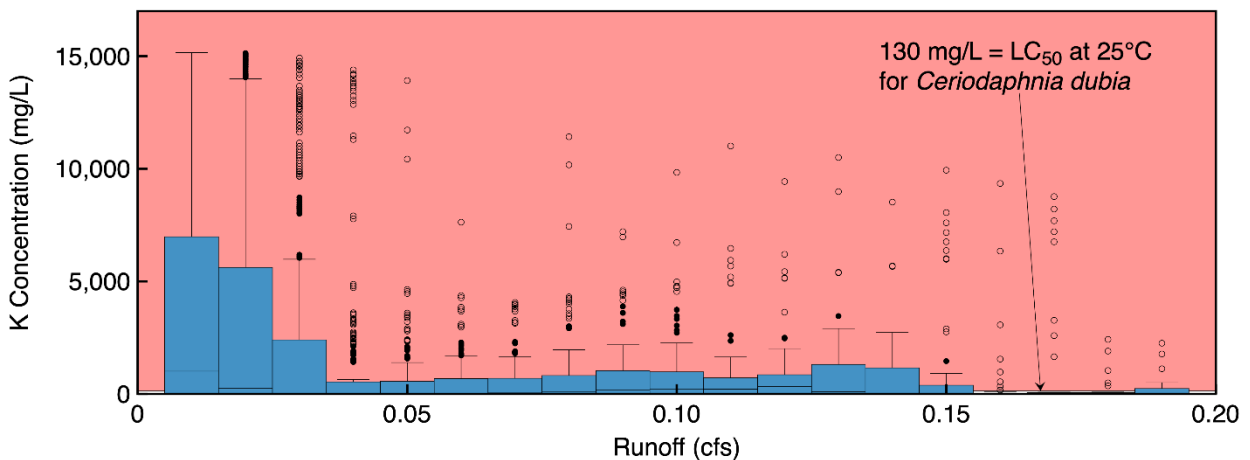
126
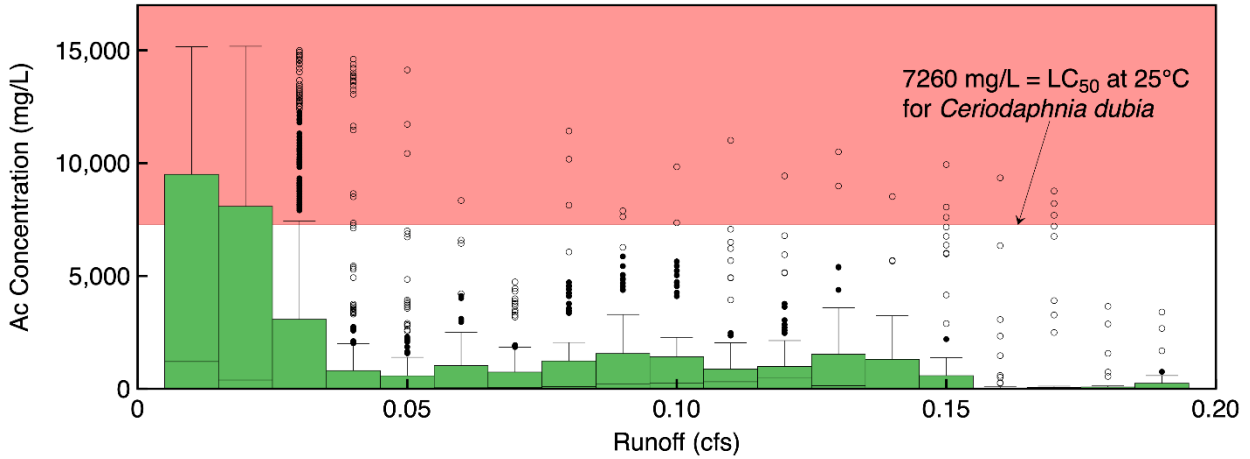
Figure 4.19. Acetate (Ac⁻) concentration statistics for low flow rates (0 – 0.2 cfs) for an individual subcatchment as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the 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 threshold of 7.26 g/L for Ac was assumed and the region of concentration above this value is shaded in light red.
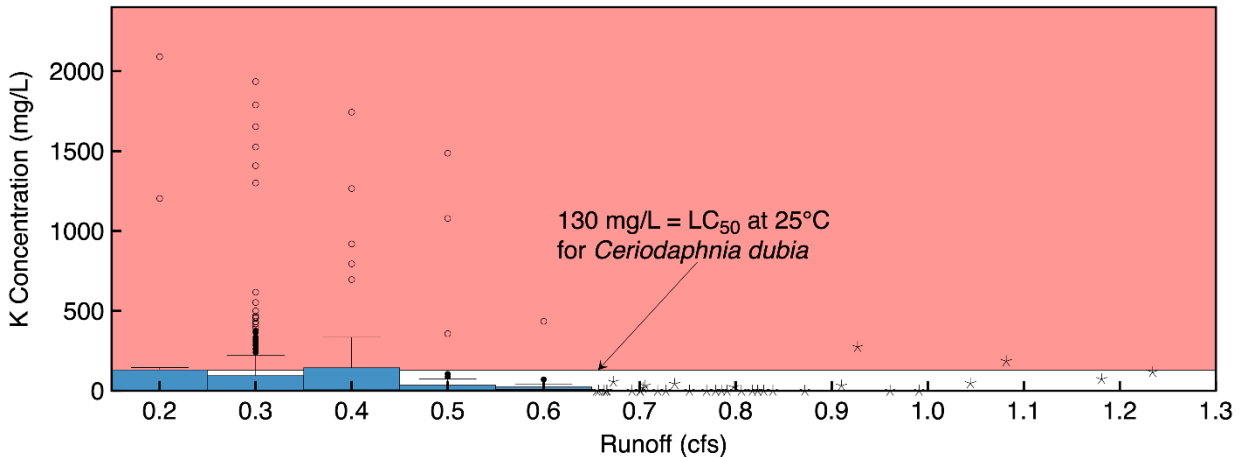

Figure 4.20. Acetate (Ac⁻) concentration statistics for high flow rates (0.2 – 1.3 cfs) for an individual subcatchment as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the whiskers are the 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 (*).

4.3.2.2   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 periods

of October 1, 1991 to April 30, 1992 (1991/92 season); November 1, 1998 to April 30, 1999 (1998/99 season); and November 1, 2006 to April 30, 2007 (2006/07 season):

Case I)   Kac used only on 25% of all connected roadways (this includes highways (MnDOT and other), county roads, and local roads)

Case II)   Kac used on 100% of connected roadways (not including parking lots or other paved areas)

Case III) Kac used on all roadways and parking lots (all paved areas in the watershed except non-roadway impervious surfaces such as sidewalks, trails, driveways, etc.)

The flow rate at the outlet of Miller Creek is substantially larger than outflow from an individual subwatershed as shown in Figure 4.21 for Cases I, II, and III. The flow duration curves for Cases I, II, and III are nearly identical: the maximum of flow rates is between 300 and 320 cfs for all three cases, with 50% of the data less than ~1.7 cfs and 90% of the data less than 35 cfs.
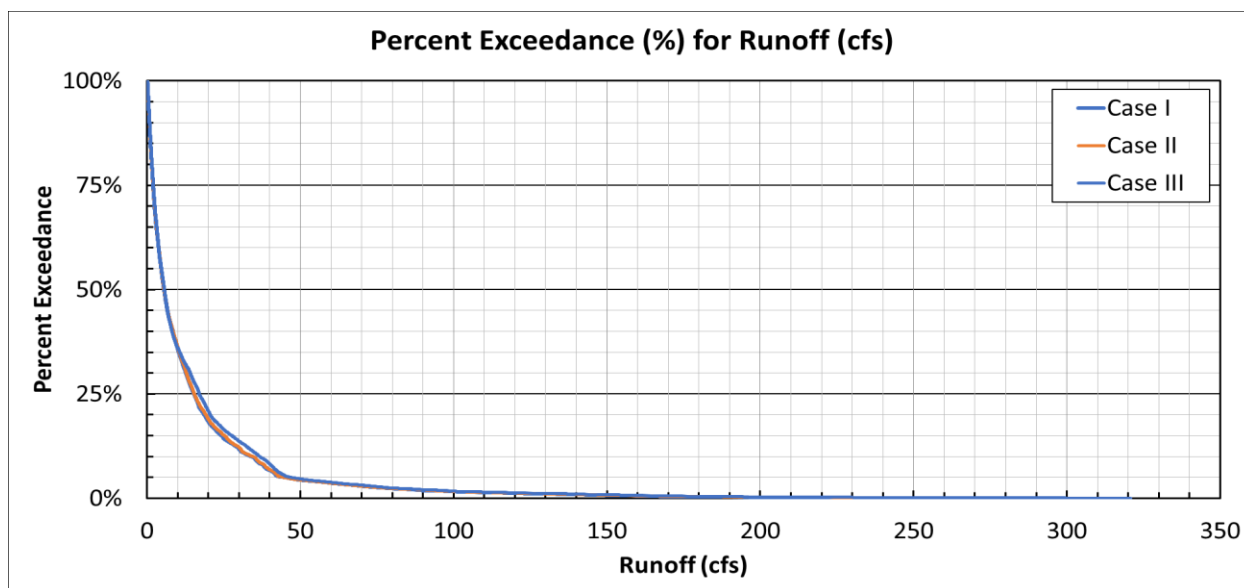
Figure 4.21. Percent exceedance for simulated non-zero outflow data from Miller Creek for Cases I, II, and III for the combined runoff data from the 1991/92, 1998/99, and 2006/07 Winter periods (n = 41,391).

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 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 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 4.22, where flow rates are binned by integer cfs values. As expected, the increase in impermeable areas treated with KAc 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 4.22). For Case I, only the outliers for the lowest flow rate exceed the assumed toxicity threshold of 130 mg/L for K^+ (Figure 4.22). For Case II, the interquartile range of concentration

values at the lowest flow rate exceed the assumed toxicity threshold for the low flows. For Case III, most interquartile ranges exceed the assumed toxicity threshold through the entire range of 0 – 10 cfs flows.
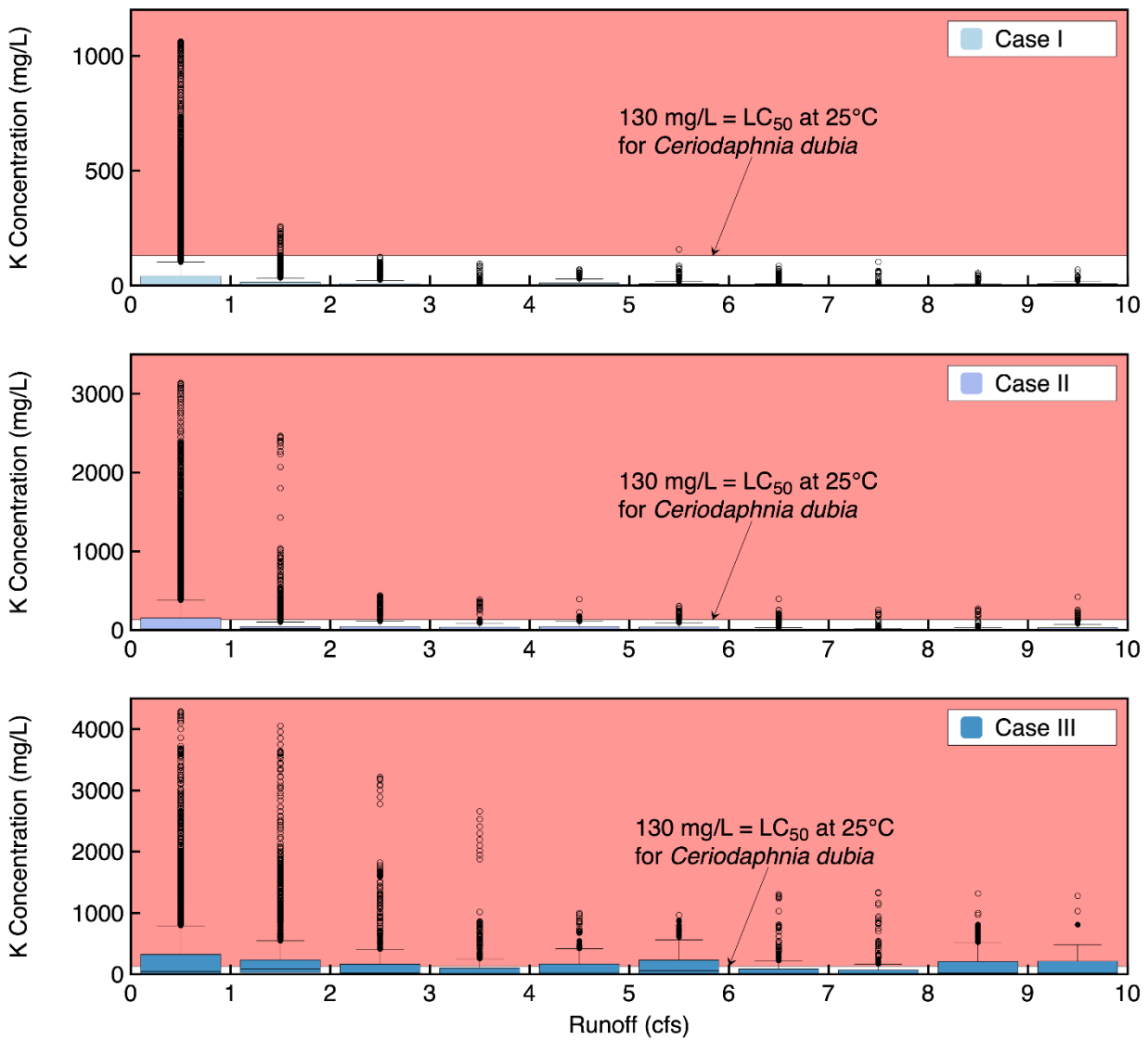
Figure 4.22. Potassium (K$^+$) outflow concentration statistics for low flow rates (0 – 10 cfs) for Case I (top), II (middle), and III (bottom) of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, 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 threshold of 130 mg/L for K was assumed and the region of concentration above this value is shaded in light red.
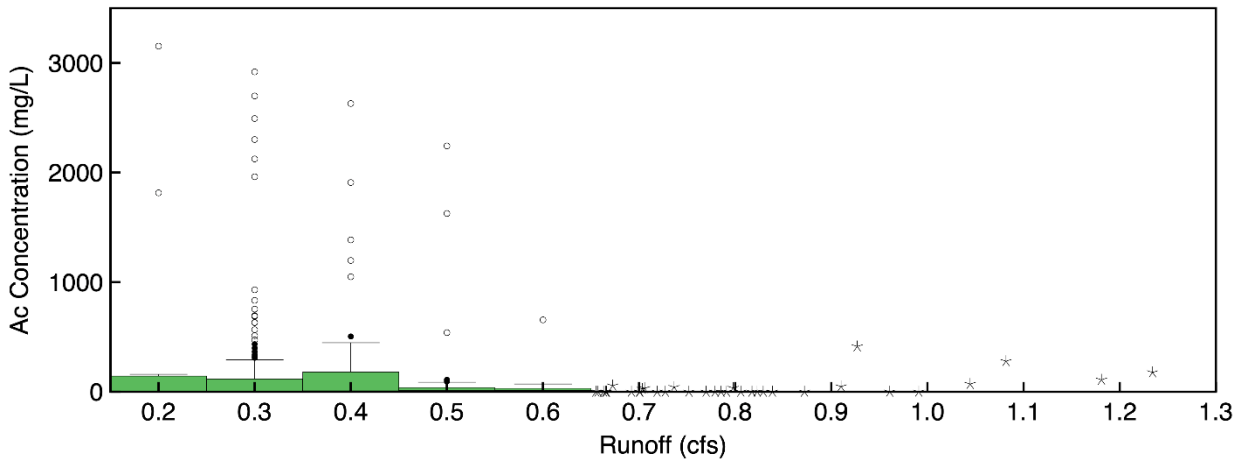
K$^+$ Concentration statistics for Cases I, II, and III for medium flow rates (10 – 45 cfs) are shown in Figure 4.23, where flow rates are binned by integer cfs values. Similar to the low flows, the K$^+$ concentration increases from Case I to Case II and from Case II to Case III. Compared to the low 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 outliers and interquartile ranges exceed the assumed toxicity threshold for medium flow rates in Cases II and III.

Figure 4.23. 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 threshold 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 4.24, where flow rates between 45 and 95 cfs are binned into 10 cfs groups. Flow rates above 95 cfs are shown as individual points. 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, one interquartile range for high flow rates in Case III and some outliers in Case II exceed the assumed toxicity threshold. All values

of K$^+$ concentration in the outflow from Miller Creek for Case I at the high flow rates are below the assumed toxicity threshold of 130 mg/L (Figure 4.24).

Figure 4.24. 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 4.25, where flow rates are binned into integer 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 4.25). The toxicity threshold 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.

Figure 4.25. 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 4.26, where flow rates are binned into integer 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 threshold, 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.
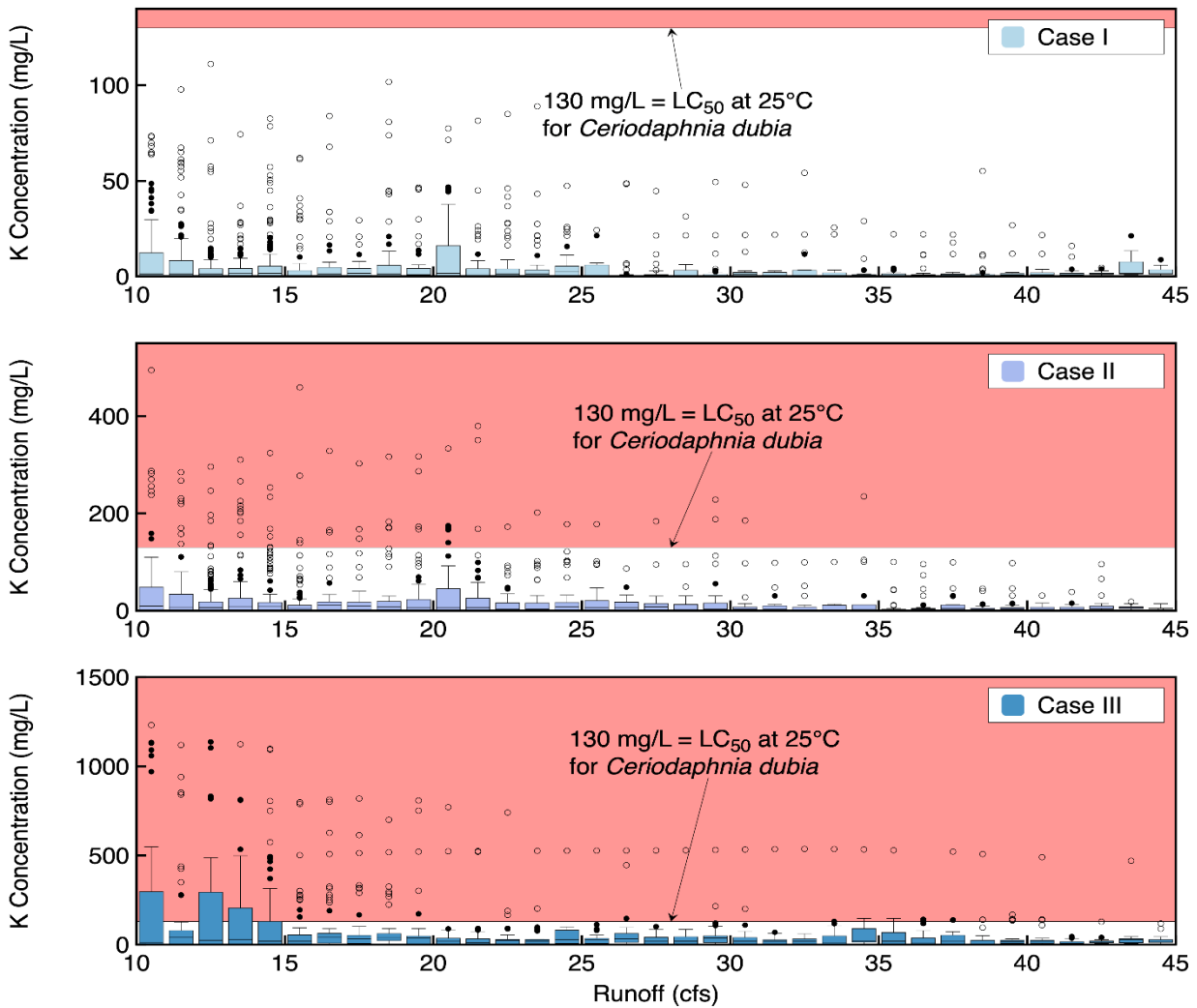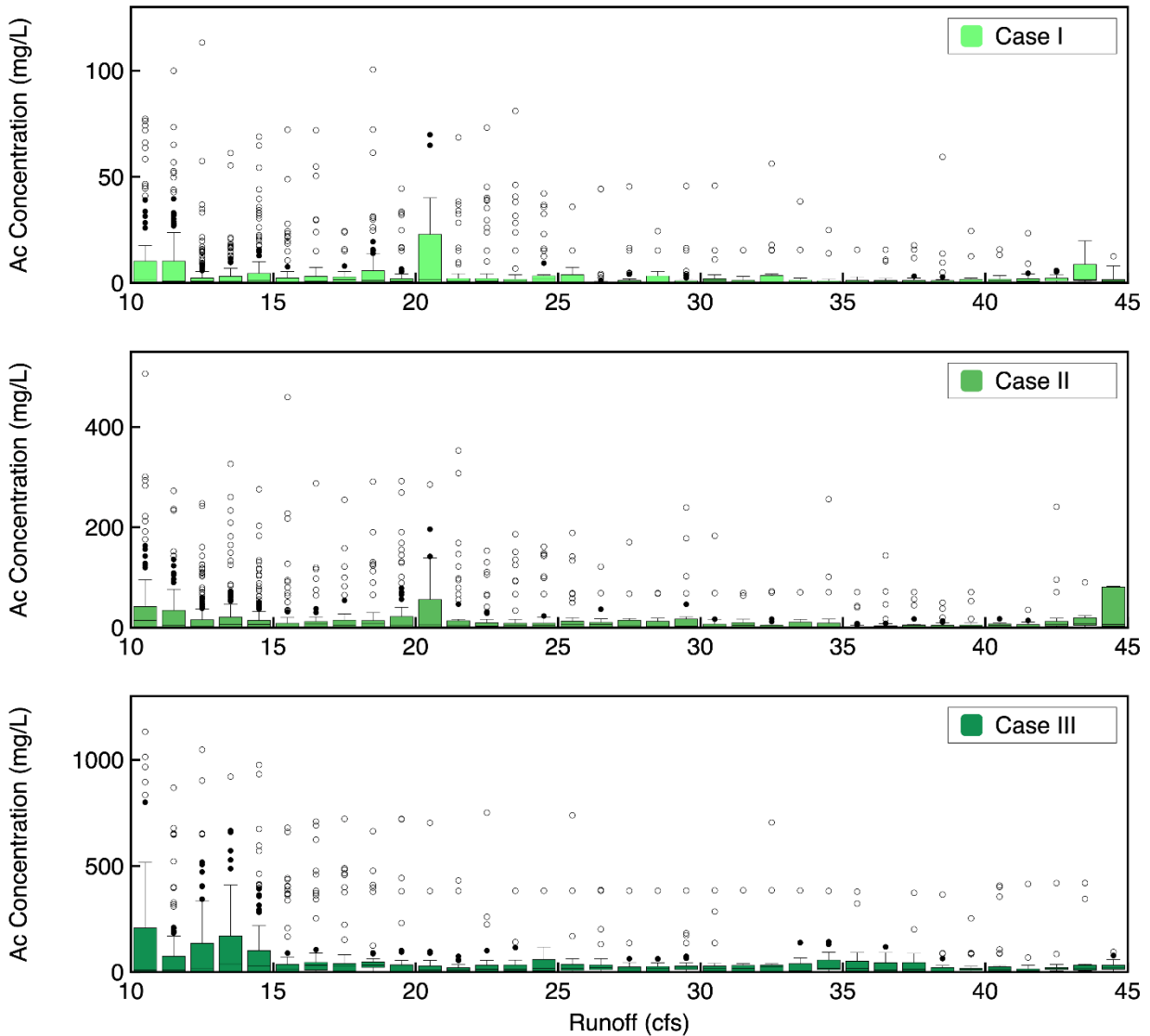
Figure 4.26. Acetate (Ac⁻) outflow concentration statistics for medium flow rates (10 – 45 cfs) for Case I, II, and III of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the 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 4.27, 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 threshold, high flow rates in combination with moderate Ac⁻ concentration could produce substantial Ac⁻ load delivered to downstream water bodies.
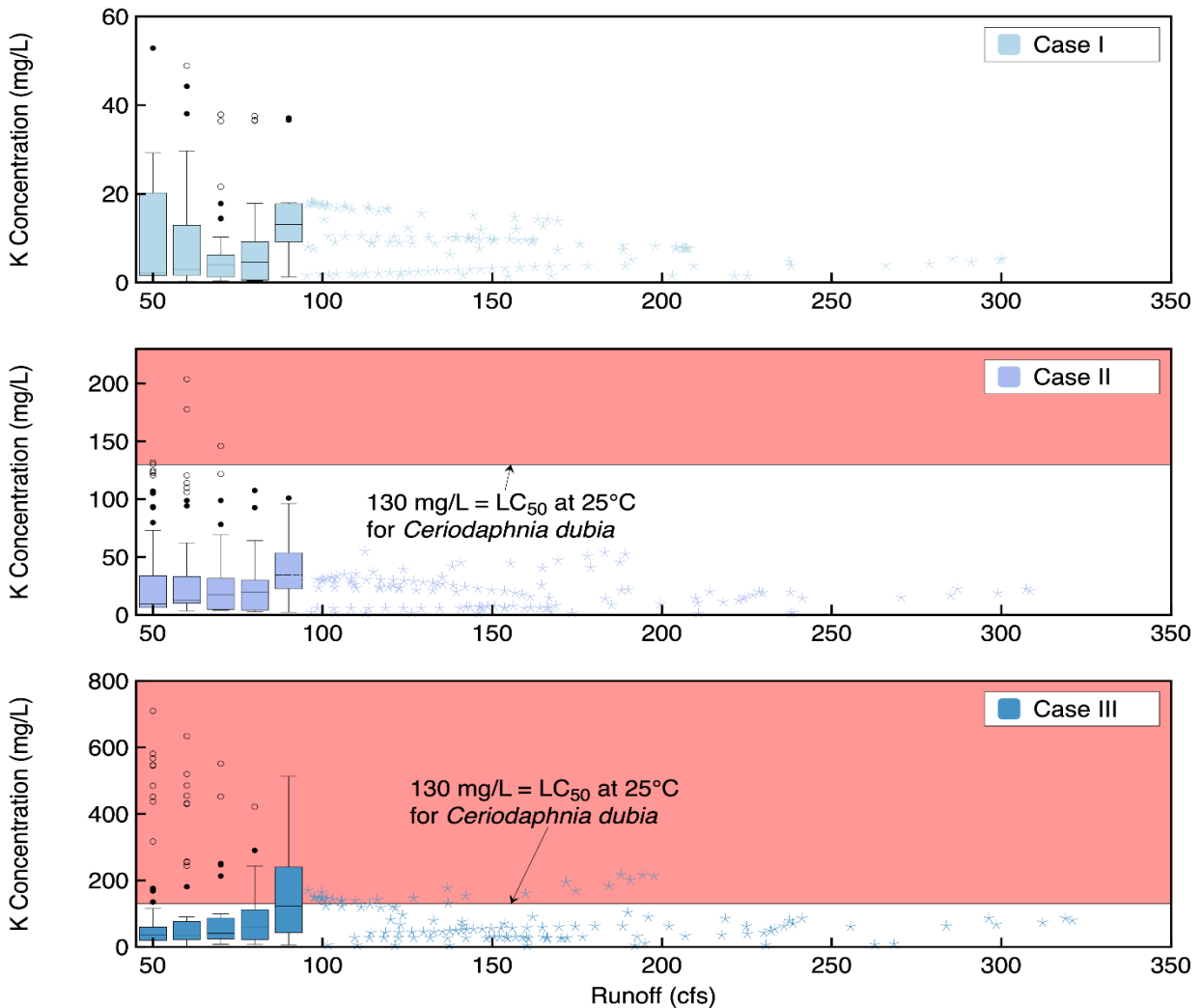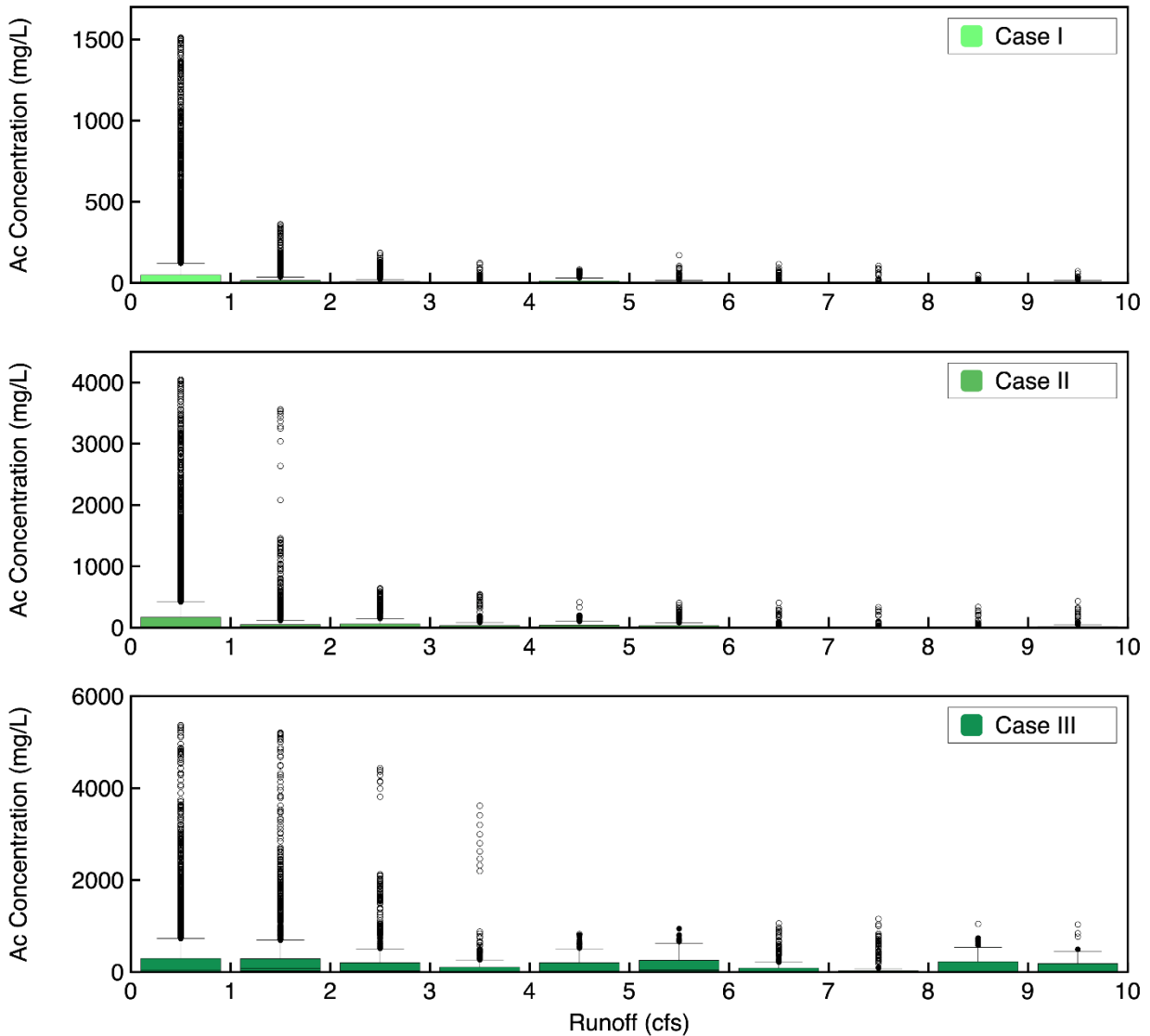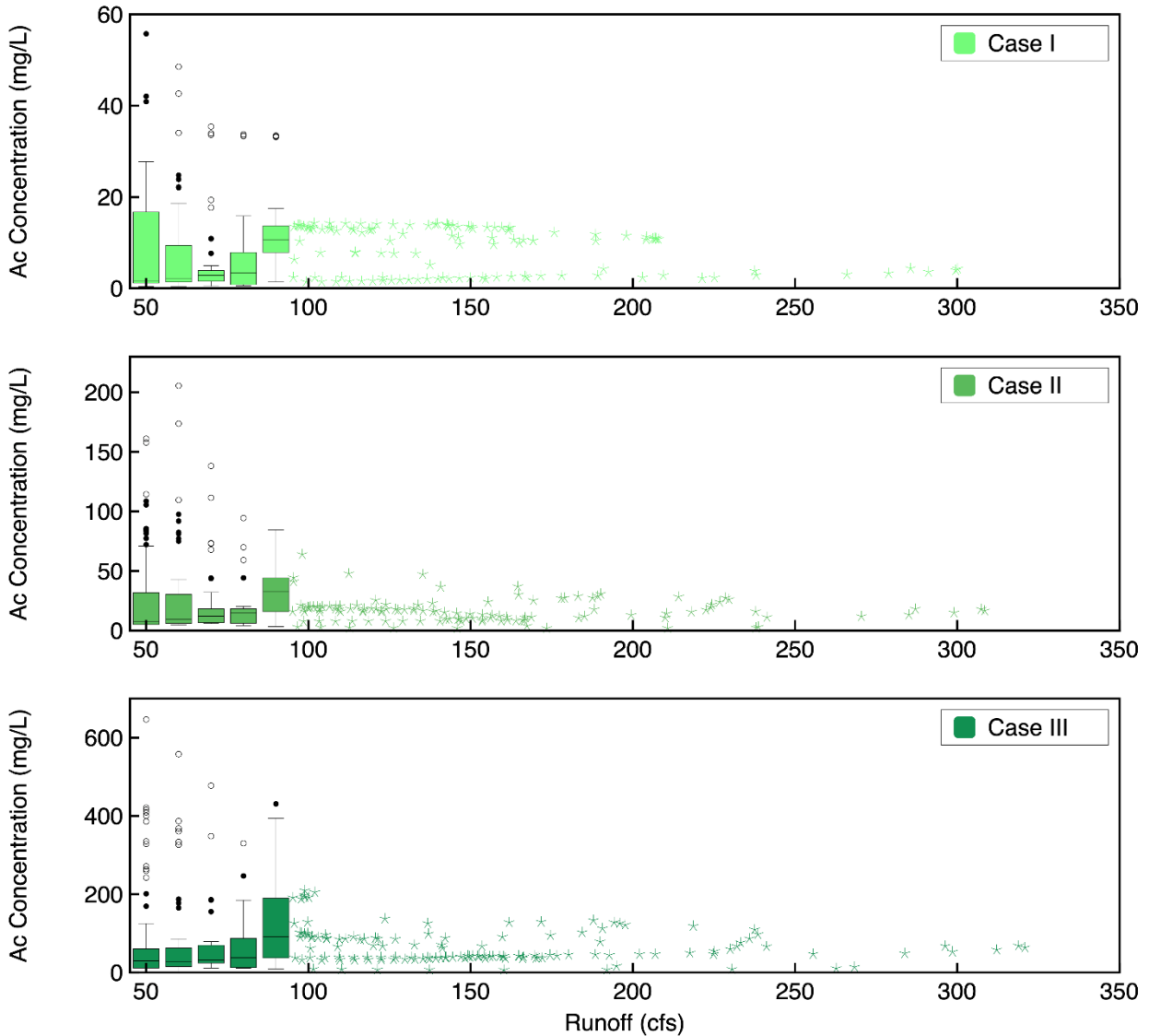
Figure 4.27. Acetate (Ac⁻) outflow concentration statistics for high flow rates (45 – 270 cfs) for Case I, II, and III of Miller Creek as illustrated using box-and-whisker plots in which the center line is the median, the top and bottom of the boxes are the 75th and 25th percentiles, respectively, the 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 (*).

4.4   SUMMARY OF ENVIRONMENTAL IMPACTS

The anti-icer concentration statistics for the Miller Creek outlet are summarized in Table 4.2. It is apparent from the difference in toxicity threshold between Potassium (130 mg/L) and Acetate (7260 mg/L) that potassium has more environmental impacts if the concentration of K^+ and Ac^- are similar in magnitude. For K^+, the mean concentration exceeds the toxicity threshold for Cases II and III, suggesting that less than 100% of the roadways can be treated with Kac without exceeding the toxicity threshold. This is consistent with the data shown in Figures 4.22 – 4.24. The 90th percentile and max K^+

concentrations exceed the toxicity threshold 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 threshold 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 4.25 – 4.27. 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 at. 2004), and the most likely impact would be in the downstream water body.

Table 4.2. Summary of Scenario Cases and Simulated Anti-icer Concentrations at the Miller Creek outlet. Anti-icer concentration statistics from October 1, 1991 to April 30, 1992 (1991/92 season); November 1, 1998 to April 30, 1999 (1998/99 season); and November 1, 2006 to April 30, 2007 (2006/07 season). All concentrations are mg/L. Values in bold italics exceed the assumed toxicity threshold.

	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 threshold	130	130	130
Mean K$^+$ Concentration	37.2	115.5	***227.2***
90th Percentile K$^+$ Concentration	73.9	***267.9***	***701.5***
Max K$^+$ Concentration	***1062***	***3136***	***4289***
Acetate (Ac$^-$)			
Assumed Ac$^-$ Toxicity threshold	7260	7260	7260
Mean Ac$^-$ Concentration	45.3	137.1	231.2
90th Percentile Ac$^-$ Concentration	88.07	311.8	663.8
Max Ac$^-$ Concentration	1512	4050	5371.8

Time series of flow rate, K$^+$ concentration, and Ac$^-$ concentration for Case II are shown in Figure 4.28. 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 threshold (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 threshold was exceeded. Some events exceeded the toxicity threshold by more than 10x. By contrast, the toxicity threshold for Acetate is above the range for Figure 4.28 and thus is not exceeded during this simulated winter.
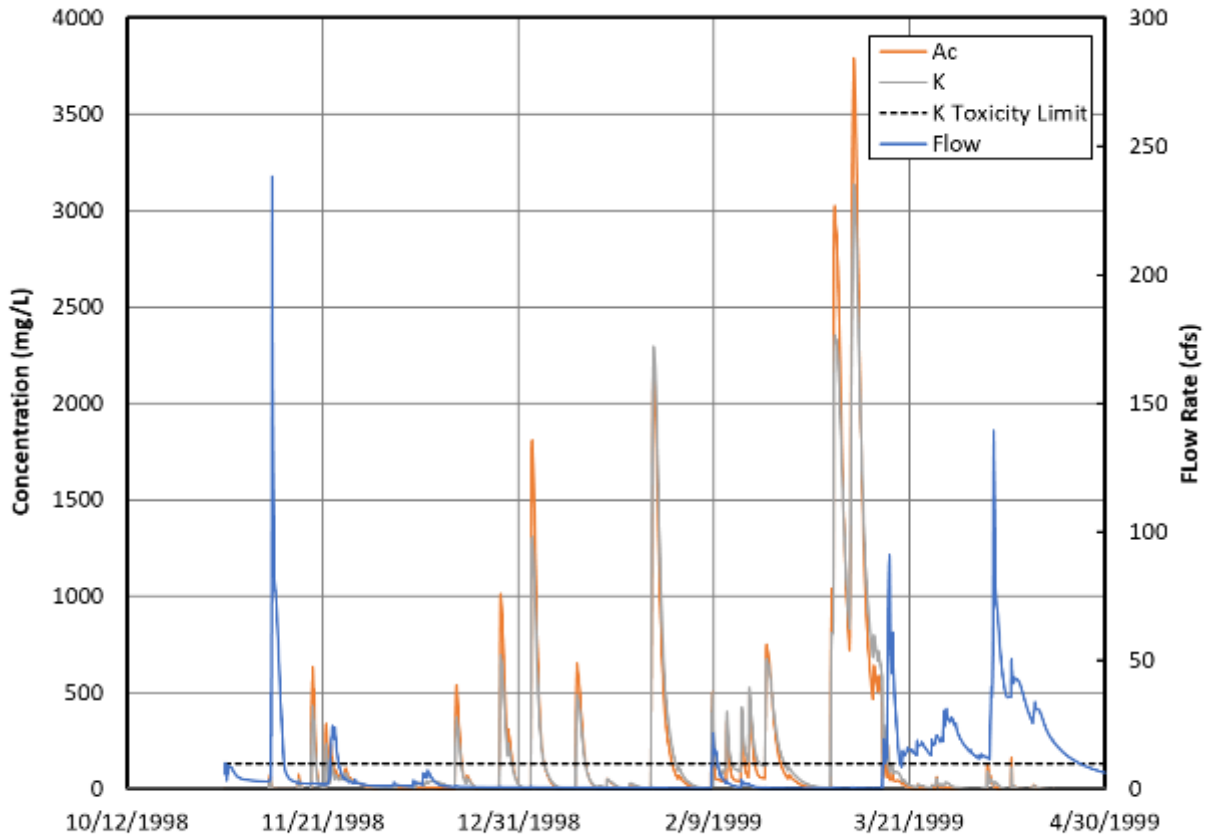
Figure 4.28. Simulated flow rate and K⁺ and Ac⁻ concentration at the outlet of Miller Creek for Case II (Kac applied to all roadways) for the 1998/99 season.

The time series of K⁺ concentration for the three cases for the 1998/99 season are shown in Figure 4.29. 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 threshold, 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 threshold between events, resulting in extended periods of time when the toxicity threshold was exceeded. The environmental impacts of such conditions are substantial.
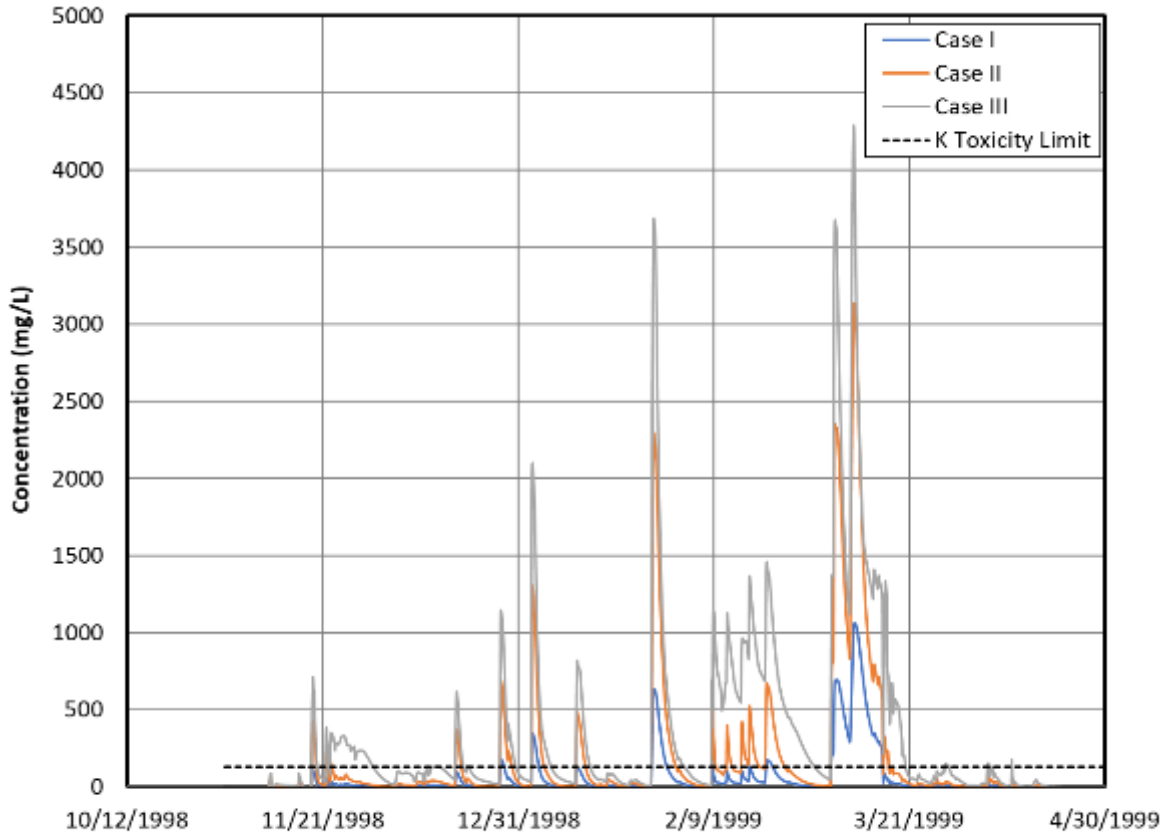
Figure 4.29. Simulated K⁺ concentration at the outlet of Miller Creek for Cases I, II, and III for the 1998/99 season.

4.5   CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

This report summarizes the impact of KAc road applications under a variety of settings as described above. The report makes recommendations regarding when KAc application may be considered a non-threat to biota in receiving water bodies and when it should be considered a threat and, therefore, when road application should be avoided.

The K⁺ concentrations due to KAc application as an anti-icer to 25% of the roads (only) 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. This impact is acute concentration-based, not chronic, so it only takes a single event above the toxicity threshold to potentially kill 50% of the biota. The final concentration depends on the watershed and climate conditions, so extreme caution is warranted to avoid environmental and ecological impacts. We recommend that KAc only be used in the most precarious winter driving safety locations on days where the temperature is below the level that other anti-icers function, but not over all watershed roads or for all storms. KAc is not recommended for application on parking lots due to the susceptibility for over-application. 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 chapter focus on estimating concentrations of KAc 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 chapter 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 (French et al. 2001). 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 report are based on an analysis of the Miller Creek watershed in Duluth, Minnesota. Other watersheds with similar climate conditions, watershed response to precipitation, and application rates of de-icers 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.

5   References

Alatyppö, V., & Valtonen, J. (2007). Experiences on the effects of deicing chemicals on bituminous airfield runways in rinland. In *Proceedings of the 2007 FAA Worldwide Airport Technology Transfer Conference*, pp.16–18.

Albright, M. (2009). Changes in water quality in an urban stream following the use of organically derived deicing products. *Lake and Reservoir Management*, *18*(3), 119–124.

Almodares, A., Hadi, M. R., & Dosti, B. (2007). Effects of salt stress on germination percentage and seedling growth in sweet sorghum cultivars. Journal of Biological Sciences, 7(8), 1492–1495.

Amrhein, C., Strong, J. E, & Mosher, P.A. (1992). Effect of deicing salts on metal and organic matter mobilization in roadside soils. *Environmental Science and Technology*, *26*(4), 703–709.

Apeagyei, A. K., Struble, L. J., & Buttlar, W. (2008). Investigation of alkali-silica reaction in asphalt mixtures. *Advanced Testing and Characterisation of Bituminous Materials*, *1-2,* 463–475.

Balachandran, C., Olek, J., Rangaraju, P. R., & Diamond, S. (2011). Role of potassium acetate deicer in accelerating alkali–silica reaction in concrete pavements: Relationship between laboratory and field studies. *Transportation Research Record, 2240*(1), 70–79.

Baltrenas, P., & Kazlauskiene, A. (2009). Sustainable ecological development reducing negative effects of road maintenance salt. *Technological and Economic Development of Economy*, *15*(1), 178–188.

Bang, S. S., & Johnston, D. (1998). Environmental effects of sodium acetate/formate deicer, Ice Shear ™. *Arch. Environ. Contam. Toxicol.*, *35*(4), 580–587.

Bang, S. S., & Roseland, J. A., (1989). *Biological effect of South Dakota Deicer Number 2 on environment.* Final report submitted to South Dakota Department of Transportation.

Bark, A. R., Fu, G. Y., Hedeen, D. (2020) Water quality impacts of bridge stormwater runoff from scupper drains on receiving waters: A review. Science of Total Environment, 726, 138068

Bates, T. J., Van Dam, T. J., Gress, D. Peterson, K., & Sutter, L. (2007). Comparison of field and laboratory concrete exposed to potassium acetate runway deicer. In A. M. Amde, G. Sabnis, & J. S. Y. Tan (Eds.), *Recent advances in concrete yechnology* (pp. 389–402). Lancaster, PA: DEStech Publications, Inc.

Bewley, J.D.; Black, M. Seeds.Physiology of Development and Germination, 2nd ed.; Springer Science & Business Media: Berlin, Germany, 1994; p. 421

Boice, P. (1986). CMA: An alternative to road salt? *Environment*, *28*(1), 5–6.

Brenner, Mark V., & Horner, R. R. (1992). Effects of calcium magnesium acetate (CMA) on dissolved oxygen in natural waters. *Resources, Conservation and Recycling, 7,* 239–265.

Brown, T. E., LeMay, H. E. Bursten, B. E., Murphy, C., Woodward, P. & Stoltzfus M. E. (2018) Chemistry. In The central science (14th ed., Chapter 4.1-4.3). New York, NY: Pearson

Bryson, G. M., & Barker, A.V. (2002). Sodium accumulation in soils and plants along Massachusetts roadsides. Communications in Soil Science and Plant Analysis, 33(1-2), 67–78.

Bulich, A. A. (1982). A practical and reliable method for monitoring the toxicity of aquatic samples. *Process Biochem*, 17 (March/April), 45–47.

Burkett, A, & Gurr, N. (2004). Icy road management with calcium magnesium acetate to meet environmental and customer expectations in New Zealand. *Transportation Research Circular* (Number E-C063), Sixth International Symposium on Snow Removal and Ice Control Technology, Spokane, WA.

Buteau, G. H., Cushman, J. R., Griffis, L. C., Rogers, B. C, Duke, J. T., & Cooper, P.N. (1992). The effects of exposure Chevron Ice-B-Gone deicer in laboratory animals and human volunteers. *Resource, Conservation, and Recycling*, *7,* 133–138.

Chachar, Q. I., Solangi, A. G, & Verhoef, A. (2008). Influence of sodium chloride on seed germination and seedling root growth of cotton (Gossypium hirsutum L.). Pakistan Journal of Botany, 40(1), 183.

Chappelow, C. C., McElroy, A. D., Blackburn, R. R., Darwin, D., & de Noyelles, F. G. (1992). *Handbook of test methods for evaluating chemical de-icers*. Kansas City, MO: Midwest Research Institute.

Cheng, K. C., & Guthrie, T. F. (1998). *Liquid road deicing environment impact* (File number 498-0670). Kamloops, BC: Insurance Corporation of British Columbia.

Civil Engineering Research Foundation. (1999). *Summary of evaluation findings for the testing of Ice Ban* (Technical evaluation report). CERF Report #40410, American Society of Civil Engineers, Reston, VA, 978-0-7844-0410-2 (ISBN-13

Corsi, S. R., Geis, S. W., Bowman, G., Failey, G. G., & Rutter, T. D. (2009). Aquatic toxicity of airfield-pavement de-icer materials and implications for airport runoff. Environmental Science & Technology, 43(1), 40–46.

Corsi, S. R., Graczyk, D. J., Geis, S. W., Booth, N. L., & Richards, K. D. (2010). A fresh look at road salt: Aquatic toxicity and water-quality impacts on local, regional, and national scales. Environmental Science & Technology, 44(19), 7376–7382.

Corsi, S. R., Mericas, D., &. Bowman, G. T. (2012). Oxygen demand of aircraft and airfield pavement de-icers and alternative freezing point depressants. *Water, Air & Soil Pollution*, *223*(5), 2447–2461.

Cramer, G. R., Läuchli, A., & Polito, V. S. (1985). Displacement of Ca2+ by Na+ from the plasmalemma of root cells: A primary response to salt stress? Plant Physiology, 79(1), 207–211.

Davis, G., Krannitz, S, & Goldstein, M. (1993). *A reconnaissance study of roadside tree injury and decline at 17 sites in interior B.C.* Victoria, BD: Roadside Tree Injury Committee.

Defourny, C. (2000). Environmental risk assessment of deicing salts. *Proceedings of the 8th World Salt Symposium, 2,* 767–770.

D'Itri, F. M. (1992). *Chemical de-icers and the environment*. Chelsea, MI: Lewis Publishers.

Dougherty, C. K., & Smith, G. R. (2006). Acute effects of road de-icers on the tadpoles of three anurans. *Applied Herpetology*, *3*(2), 87–93.

Dudley, M. M., Jacobi, W. R., & Brown, C. S. (2014). Roadway deicer effects on the germination of native grasses and forbs. Water, Air, & Soil Pollution, 225(6), 1–12.

Dunn, S. A., & Schenk, R. U. (1980). *Alternative highway deicing chemicals*. Madison, WI: Bjorksten Research Laboratories, Inc.

Ellis, J. B., Revitt, D. M., & Llewellyn, N. (1997). Transport and the environment: Effects of organic pollutants on water quality. *Water and Environment Journal, 11*(3), 170–177.

Erickson, A. J., Weiss, P. T. & Gulliver, J. S. (2013) *Optimizing stormwater treatment practices: A handbook of assessment and maintenance* (ISBN 978-1-4614-4623-1). New York: Springer Publishing.

Erickson, T., Herb, W. & Stefan, H. G. (2009). *Streamflow modeling of Miller Creek, Duluth, Minnesota* (St. Anthony Falls Laboratory, Project Report No. 536). St. Paul, MN: Minnesota Pollution Control Agency.

Fay, L., & Akin, M. (2018). *Investigation of alternative de-icers for snow and ice control.* Fairbanks, AK: Center for Environmentally Sustainable Transportation in Cold Climates, University of Alaska Fairbanks.

Fay, L., & Muthumani, M. (2017). *Field usage of alternative de-icers for snow and ice control.* western Transportation Institute, Montana State University, Boseman, MT.

Fay, L., & Shi, X. (2011). Laboratory investigation of performance and impacts of snow and ice control chemicals for winter road service. *Journal of Cold Regions Engineering* (ASCE), *25*(3), 89–114.

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

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*. St. Paul, MN: MnDOT.

Findlay, S. E. G., & Kelly, V. R. (2011). Emerging indirect and long-term road salt effects on ecosystems. *Annals of the New York Acadamy of Sciences*, *Vol 1223 (1),* 58-68.

Fischel, M. (2001). *Evaluation of selected de-icers based on a review of the literature* (Report No. CDOT-DTD-R-2001-15). Denver, CO: Colorado Department of Transportation.

Fitch, M., Smith, J. A., & Clarens, A. F. (2013). Environmental cife-cycle assessment of winter maintenance treatments for roadways. *Journal of Transportation Engineering*, *139*(2),138–146.

Fortin, C., Tjaden, L., & Mulhern, N. (2014). *Chloride free snow and ice control material* (Transportation research synthesis 1411). St. Paul, MN: MnDOT.

French, H. K., Van der Zee, S. E. A. T. M., & Leijnse, A. (2001). Transport and degradation of propyleneglycol and potassium acetate in the unsaturated zone. *Journal of Contaminant Hydrology*, *49*(1), 23–48.

Fritzsche, C. J. (1992). Calcium magnesium acetate deicer. *Water Environment & Technology*, *4,* 44–51.

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

Gerasimov, A., Chugunova, M., & Polyak, Y. (2021). Changes in salinity and toxicity of soil contaminated with ee-icing agents during growing season. Environmental Research, Engineering and Management, 77(2), 53–62.

Goldman, C. R., & Lubnow, F. S. (1992). Seasonal influence of calcium magnesium acetate on microbial processes in 10 northern Californian lakes. *Resources, Conservation and Recycling*, *7*(1-3), 51–67.

Granato, G. E., Church, P. E., &. Stone, V. J. (1995). Mobilization of major and trace constituents of highway runoff in groundwater potentially caused by deicing chemical migration. *Transportation Research Record, 1483,* 91-104.

Hall, R., Hofstra, G., & Lumis, G. P. (1972). Effects of deicing salt on eastern white pine: Foliar injury, growth suppression and seasonal changes in foliar concentrations of sodium and chloride. Canadian Journal of Forest Resources, 2, 244–249.

Hanslin, H. M. (2011). Short-term effects of alternative de-icing chemicals on tree sapling performance. *Urban Forestry and Urban Greening*, *10*(1), 53–59.

Harless, M. L., Huckins, C. J., Grant, J. B., & Pypker, T. G. (2011). Effects of six chemical de-icers on larval wood frogs (Rana Sylvatica). *Environmental Toxicology and Chemistry*, *30*(7), 1637–1641.

Harris, J. C., Gibson, J. R., & Street, D. (1965). *Chemical means for prevention of accumulation of ice, snow, and slush on runways*. Washington, DC: Federal Aviation Association.

Hartl, W., & Erhart, E. (2002). Effects of potassium carbonate as an alternative road de-icer to sodium chloride on soil chemical properties. Annals of Applied Biology, 140(3), 271–277.

Hassan, Y., Abd El Halim, A. O., Razaqpur A. G., Bekheet W., & Farha, M. H. (2002). Effects of runway de-icers on pavement materials and mixes: Comparison with road salt *Journal of Transportation Engineering*, *128*(4), 385–391.

Hellstén, P. & Nystén, T. (2003). Migration of alternative de-icers in unsaturated zone of aquifers – in vitro study. *Water Science and Technology*, 4*8*(9), 45–50.

Hellstén, P. P., Kivimäki, A. L., Miettinen, I. T., Salminen, J. M., & Nystén, T. H. (2005). Degradation of potassium formate in the unsaturated zone of a sandy aquifer. *Journal of Environmental Quality*, *34*(5), 1665–1671.

Herb, W. (2021). *Analysis of stormwater runoff best management practices in Miller Creek, Duluth, MN* (St. Anthony Falls Project Report 596). Minneapolis, MN: Minnesota Sea Grant.

Herb, W., Johnson, L., & Gulliver, J. (2020). *Detailed hydrology for stormwater BMPs* (St. Anthony Falls Project Report 592). Minneapolis, MN: Minnesota's Lake Superior Coastal Program.

Heugens, E. H. W., Jager, T., Creyghton, R., Kraak, M. H. S., Hendriks, A. J., Van Straalen, N. M., & Admiraal, W. (2003). Temperature-dependent effects of cadmium on Daphnia magna: Accumulation versus sensitivity. Environmental Science and Technology, 37(10), 2145–2151

Hocking, M. B. (2005). 4-water quality measurement. In MB Hocking, Handbook of chemical technology and pollution control (3rd ed., pp. 105-135). San Diego, CA: Elsevier Inc.

Hordijk, C. A., Kammiga, H., & Cappenberg, T. E. (1994) Kinetic studies of acetate in freshwater sediments: Use of stable isotopic tracers, Geochimica et Cosmochimica Acta, 58 (2), 683–694

Horner, R. R. (1988). *Environmental monitoring and evaluation of calcium magnesium acetate (CMA)* (National Cooperative Highway Research Program report, 305). Trnasportation Research Board, Washingtom, D.C.

Horner, R. R., & Brenner, M. V. (1992). Environmental evaluation of calcium magnesium acetate for highway deicing applications. Resources, Conservation and Recycling, 7(1-3), 213–237.

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

Huisman, J. L., Weber, N., & Gujer, W. (2004). Reaeration with tracers. *Water Research, 38,* 1089–1100.

Ihs, A., & Gustafson, K. (1996). *Calcium magnesium acetate (CMA) an alternative deicing agent: A literature review*. Statens väg- och transportforskningsinstitut. Linköping, Sweden: Swedish Road and Transportation Institute.

Jain, K. R. (2018). *Effects of alternative road salts on soil leachate quality* (Master's thesis), Pennsylvania State University, State College, PA.

Jani, J., Yang, Y. Y., Lusk, M. G., & Toor, G. S. (2020). Composition of nitrogen in urban residential stormwater runoff: Concentrations, loads, and source characterization of nitrate and organic nitrogen. PloS one, 15(2), e0229715.

Jin, F., Zhang, G., Jin, Y., Watanabe, Y., Kishita, A., & Enomoto, H. (2010). A new process for producing calcium acetate from vegetable wastes for use as an environmentally friendly deicer. *Bioresource Technology*, *101*(19), 7299–7306.

Johnston, D. P. & Huft, D. L. (1992). Sodium salts of carboxylic acids as alternative de-icers, *Transportation Research Record, 1387,* 67-70.

Joutti, A., Schultz, E., Pessala, P., Nysten, T., & Hellsten, P. (2003). Ecotoxicity of alternative de-icers. *Journal of Soils and Sediments*, *3*(4), 269–272.

Jungwirth, S., Cao, L., & Shi, X. (2014). *Developing locally sourced brine additive* (Report: INE/AUTC 14.09). Boseman, MT: Western Transportation Institute, Montana State University.

Kahl, S. (2002). *Agricultural by-products for anti-icing and deicing use in Michigan*. Lansing, MI: Michigan Department of Transportion.

Kaushal, S. S., Likens, G. E., Pace, M. L., Utz, R. M., Haq, S., Gorman, J., & Grese, M. (2018). Freshwater salinization syndrome on a continental scale. Proceedings of the National Academy of Sciences, 115(4), e574-e583.

Kiaghadi, A., & Rifai, H. S. (2019). Natural attenuation of indicator bacteria in coastal streams and estuarine environments. Science of the Total Environment, 677(6) 230–240

Kim, J. Park, J., Kim, P., Lee, C., Choi, K., & Choi, K. (2010). Implication of global environmental changes on chemical toxicity-effect of water temperature, pH, ultraviolet B irradiation on acute toxicity of several pharmaceuticals in Daphnia magna. Ecotoxicology, 19, 662–669.

Koch, G. H., Brongers, M. P., Thompson, N. G., Virmani, Y. P., & Payer, J. H. (2002). Corrosion cost and preventive strategies in the United States (No. FHWA-RD-01-156, R315-01). Washington, DC: U.S. Federal Highway Administration.

LaPerriere, J. D, & Rea, C. L. (1989). Effects of calcium magnesium acetate de-icer on small ponds in interior Alaska. Lake and Reservoir Management, 5(2), 49–57.

Laurinavičius, A., Mažeika, R., Vaiškūnaitė, R., Brimus, G., &. Milašius, S. (2011). Possibilities for the use of chemicals materials alternative to chlorides for decreasing road slipperiness in vinter. *The Baltic Journal of Road and Bridge Engineering*, *6*(4), 274–282.

Lee, B. D., Choi, Y. S., Kim, Y. G., Kim, S., & Yang, E. (2017). A comparison study of performance and environmental impacts of chloride-based de-icers and eco-label certified de-icers in South Korea. *Cold Regions Science and Technology*, *143,* 43–51.

Lee, H., Cody, R. D., Cody, A. M., &. Spry, P. G. (2000). Effects of various deicing chemicals on pavement concrete deterioration. In *Mid-Continent Transportation Symposium Proceedings*, Ames, IA, May 15 – 16.

Levelton Consultants Limited. (2008). *Guidelines for the selection of snow and ice control materials to mitigate environmental impacts*. Washington, DC: Transportation Research Board.

Lindstrom, R. (2006). A system for modelling groundwater contamination in water supply areas: Chloride contamination from road de-icing as an example. *Nordic Hydrology*, *37*(1), 41–51.

Lundmark, A., & Olofsson, B. (2007). Chloride deposition and distribution in soils along a deiced highway–assessment using different methods of measurement. Water, Air, and Soil Pollution, 182(1), 173–185.

Mallela, J., Hein, D., Kalberer, E., Farrar, M., & Bonaquist, R. (2010). *Effect of deicing and anti-icing chemicals on HMA airfield runways.* 2010 FAA Worldwide Airport Technology Transfer Conference, Atlantic City New Jersey, April 20 – 22.

Masova, T., & Herben, T. (2018). Root:shoot ratio in developing seedlings: How seedlings change their allocation in response to seed mass and ambient nutrient supply. Ecological Evolution, 8(14), 7143–7150.

McCullouch, B. (2010). *Snow and ice removal and anti-icing synthesis study* (SPR-2454, summary report). West Lafayette, IN: Purdue University.

McFarland, B., & O'Reilly, K. (1992). Environmental impacts and toxicological characteristics of calcium magnesium acetate (CMA). In *Chemical de-icers and the dnvironment.* Boca Raton, FL: Lewis Publishers, Inc.

McKenney, C. T. (2015). *Using chemical admixtures to increase the effectiveness of snow/ice removal*. Little Rock, AR: Arkansas State Highway and Transportation Dept.

MDOT and Tetra Tech. (2006). *Emerging technologies in winter road maintenance.* St. Paul, MN: MnDOT.

Meriano, M., Eyles, N., & Howard, K. W. (2009). Hydrogeological impacts of road salt from Canada's busiest highway on a Lake Ontario watershed (Frenchman's Bay) and lagoon, City of Pickering. *Journal of Contaminant Hydrology, 107*(1-2), 66–81.

MnDOT. (2019). *Maintaining Minnesota's highways*. Retrieved from https://www.dot.state.mn.us/maintenance/faq.html

Mount, D. R., Erickson, R. J., Highland, T. L., Hockett, J. R., Hoff, D. J., Jenson, C. T., Norberg King, T. J., Peterson, K. N., Polaske, Z. M., & Wisniewski, S. (2016). The acute toxicity of major ion salts to Ceriodaphnia dubia: I. Influence of background water chemistry. Environmental Toxicology and Chemistry, 35(12), 3039–3057.

MPCA (2018). Environmental impacts of road salt and other de-icing chemicals. In Minnesota stormwater manual. Minnesota Pollution Control Agency, St. Paul, MN

Mussato, B. & Guthrie, T. (2000). *Anti-icers – Chemical analysis and toxicity test results*. Kamloops, BC: Insurance Corporation of British Columbia.

Mussato, B., and T. Guthrie. 2000. Anti-icers – Chemical Analysis and Toxicity Test Results. Levelton Engineering Ltd., Richmond, B.C. Prepared for the Insurance Corporation of British Columbia, File number 498-0954.

Muthumani, A., Fay, L., Bergner, D., & Shi, X. (2015). *Understanding the effectiveness of non-chloride liquid agricultural by-poducts and solid complex chloride/mineral products* (Clear Roads Pooled Fund Contract 99006). St. Paul, MN: MnDOT.

Muthumani, M., Fay, L., Akina, M., Wang, S., Gong, J., & Shi, X. (2014). Correlating lab and field tests for evaluation of deicing and anti-icing chemicals: A review of potential approaches. *Cold Regions Science and Technology*, *97,* 21–32.

Nazari, M. H., Havens, E. A., Muthumani, A., & Shi, X. (2016). *Bio-based renewable additives for anti-icing applications (Phase I)*. Fairbanks, AK: Center for Environmentally Sustainable Transportation in Cold Climates, University of Alaska Fairbanks.

Neumann, P. M., Azaizeh, H., & Leon, D. (1994). Hardening of root cell walls: A growth inhibitory response to salinity stress. Plant, Cell & Environment, 17(3), 303–309.

Nolan, D. (1994). *A comparison of the effects of urea, potassium acetate, calcium magnesium acetate and sodium formate runway de-icers on the environment* (Report TP12285E). Ottawa: Transport Canada.

Novotny, E. V., & Stefan, H. G. (2010). Projections of chloride concentrations in urban lakes receiving road de-icing salt. *Water, Air, and Soil Pollution, 211*(1-4), 261–271.

Pan, T., He, X., & Shi, X. (2008). Laboratory investigation of acetate-based deicing/anti-icing agents deteriorating airfield asphalt concrete. *Asph. Paving Technol.-Proc.*, *77,* 773.

Pedersen, L. B., Randrup, T. B., & Ingerslev, M. (2000). Effects of road distance and protective measures on deicing NaCl deposition and soil solution chemistry in planted median strips. Journal of Arboriculture, 26(5), 238–245.

Perera, N., Gharabaghi, B., & Howard, K. (2013). Groundwater chloride response in the Highland Creek watershed due to road salt application: An e-assessment after 20 years. *Journal of Hydrology, 479,* 159–168.

Pilgrim, K. M. (2013). Determining the aquatic toxicity of deicing materials (Clear Roads Pooled Fund). St. Paul, MN: MnDOT.

Pinhal, S., Ropers, D., Geiselmann, J., & de Jong, H. (2019). Acetate metabolism and the inhibition of bacterial growth by acetate. Journal of Bacteriology, 201(13), e00147-19.

Pitt, R., Maestre, A., & Morquecho, R. (2004, February). The national stormwater quality database (NSQD, version 1.1). In 1st Annual Stormwater Management Research Symposium Proceedings, pp. 13–51.

Rabideau, A. J., Weber, S., & Matsumoto, M. R. (1987). Impact of calcium magnesium acetate road deicer on POTW operation. *Journal of Water Resources Planning and Management*, *113*(2), 311–315.

Ramakrishna, D., & Viraraghavan, T. (2005). Environmental impact of chemical de-icers – A review, *Water, Air, and Soil Pollution*, *66*(1-4), 49–63.

Rangaraju, P. R., & Desai, J. (2009). Effectiveness of fly ash and slag in mitigating alkali–silica reaction induced by deicing chemicals, *Journal of Materials in Civil Engineering*, *21*(1), 19–31.

Rangaraju, P. R., & Olek, J. (2007). *Potential for ASR in concrete in presence of airfield deicing shemicals* (Research report IPRF-01-G-002-03-9). Skokie, IL: Innovative Pavement Research Foundation.

Rangaraju, P. R., Sompura, K. R., & Olek, J. (2007). Modified ASTM C 1293 test method to investigate potential of potassium acetate deicer solution to cause alkali–silica reaction. *Transportation Research Record, 2020,* 50–60.

Rasa, K., Peltovuori, T., &. Hartikainen, H. (2006). Effects of de-icing chemicals sodium chloride and potassium formate on cadmium solubility in a coarse mineral soil. *Science of The Total Environment*, *366*(2–3), 819–825.

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

Rhodan, M., & Sanburn, J. (2014). How beet juice is helping keep roads safe this winter, *Time* Newsfeed, February 14, 2014. Retrieved from http://time.com/5761/salt-shortage-triggers-beet-juice-cheese-brine-alternatives/

Robidoux, P. Y., & Delisle, C. E. (2001). Ecotoxicological evaluation of three de-icers (NaCl, NaFo, CMA): Effect on terrestrial organisms. *Ecotoxicology and Environmental Safety, 48*, 128–139.

Roosevelt, D.S., & Fitch, G. M. (2000). *Evaluation of an Ice Ban ® product as a prewetting agent for snow removal and ice control operations*. Charlottesville, VA: Virginia Transportation Research Council.

Scarsbrook, M. R., Wilcock, R. J., Rutherford, J .C, Hawken, J. L., & Henderson, R. (1996). *Effects of calcium magnesium acetate (CMA) on dissolved oxygen levels in desert road streams: A modeling study* (Consultancy Report WOR70208/01). Hamilton, New Zealand: Transit New Zealand, NIWA.

Schuler, M. S., & Relyea, R. A. (2018). A review of the combined threats of road salts and heavy metals to freshwater systems. BioScience, 68(5), 327–335.

Schuler, M. S., Hintz, W. D., Jones, D. K., Lind, L. A., Mattes, B. M., Stoler, A. B., Sudol, K. A., & Relyea, R. A. (2017). How common road salts and organic additives alter freshwater food webs: In search of safer alternatives. *Journal of Applied Ecology*, *54*(5), 1353–1361.

Schulte, E. E., & Kelling, K. A. (2004). Understanding plant nutrients: Soil and applied calcium, (A2523). Retrieved from http://www.soils.wisc.edu/extension/pubs/A2523.pdf. Soil and applied magnesium (A2524). Retrieved from http://www.soils.wisc.edu/extension/pubs/A2524.pdf. Soil and applied potassium (A2521). Retrieved from http://www.soils.wisc.edu/extension/pubs/A2521.pdf

Shi, X., & Fu, L. (ed.). (2018). *Sustainable winter road operations.* Oxford, UK: Wiley Blackwell.

Shi, X., Akin, M., Pan, T., Fay, L., Liu, Y., & Yang, Z. (2009b). Deicer impacts on pavement materials: Introduction and recent developments. *Open Civil Engineering Journal*, *3,* 16–27.

Shi, X., Fay, L., Gallaway, C., Volkening, K., Peterson, M. M., Pan, T., Creighton, A., Lawlor, C., Mumma, S., Liu, Y., & Nguyen, T. A. (2009a). *Evaluation of alternative anti-icing and deicing compounds using sodium chloride and magnesium chloride as baseline de-icers — Phase I* (Report CDOT-2009-1). Denver, CO: Colorado Department of Transportation Applied Research and Innovation Branch.

Shitole, S. M., & Dhumal, K.N. (2012). Effect of water stress by polyethylene glycol 6000 and sodium chloride on seed germination and seedling growth of Cassia angustifolia. International Journal of Pharmaceutical Sciences and Research, 3(2), 528.

Silva, J. M. S. (2012). *Effects of aggregate microfines and potassium acetate interactions on concrete performance*, Master's thesis, University of Wisconsin-Madison, Madison, WI.

Silva, J. M. S., Cramer, S. M., Anderson, M. A., Tejedor, M. I., & Munoz, J. F. (2014a). Physical responses to interaction of deicer and natural microfines. *ACI Materials Journal*, *11*(4), 363–371.

Silva, J. M. S., Cramer, S. M., Anderson, M. A., Tejedor, M. I., & Munoz, J. F. (2014b). Concrete microstructural responses to the interaction of natural microfines and potassium acetate-based deicer. *Cement and Concrete Research*, *55,* 69–78.

Sonon. L. S., Kissel, D. E., & Saha, U. (2017). Cation exchange capacity and base saturation. UGA Cooperative Extension Circular 1040. Athens, GA: UGA Cooperative Extension.

Stevenson, I. L., & Katznelson, H. (1958). The oxidation of ethanol and acetate in soils. *Canadian Journal of Microbiology*, *4*, 73–79.

Sulej, A. M., Polkowska, Z., & Namieśnik, J. (2012). Pollutants in airport runoff waters. *Critical Reviews in Environmental Science and Technology*, *42*(16), 1691–1734.

Switzenbaum, M. S., Veltman, S., Mericas, D., Wagoner, B., & Schoenberg, T. (2001). Best management practices for airport deicing stormwater. Chemosphere, 43(8), 1051–1062.

Tanner, D. Q., & Wood, T. M. (1999). *The effects of calcium magnesium acetate (CMA) deicing material on the water quality of bear creek, Clackamas County, Oregon* (Water resources investigations report 00-4092). Portland, OR: U.S. Geological Survey.

Tester, M., & Davenport, R. (2003). Na+ tolerance and Na+ transport in higher plants. Annals of Botany, 91(5), 503–527.

Transportation Research Board. (1991). *Highway deicing: Comparing salt and calcium magnesium acetate* (Special Report 235). Washington, DC: National Research Council.

Tsang, C., Shehata, M. H., & Lotfy, A. (2016). Optimizing a test method to evaluate resistance of pervious concrete to cycles of freezing and thawing in the presence of different deicing salts. *Materials*, *9*(11), 878. doi:10.3390/ma9110878

U.S. Environmental Protection Agency. (2000). Preliminary data summary: Airport deicing operations (revised) (Report EPA-821-R-00-016). Washington, DC: EPA.

U.S. Environmental Protection Agency. (2003). Guidelines establishing test procedures for the analysis of pollutants; analytical methods for biological pollutants in ambient water; final rule. Federal Register, 68, 43272– 43283.

U.S. Environmental Protection Agency. (2005). National management measures to control nonpoint source pollution from urban areas (EPA-841-B-05-004). Washington, DC: EPA.

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

U.S. Environmental Protection Agency. (2020). Water quality criteria. Retrieved from www.epa.gov/wqc

Van de Perre, D., Janssen, C. R., & De Schamphelaere, K. A. C. (2018). Combined effects of interspecies interaction, temperature, and zinc on Daphnia longispina population dynamics. Environmental Toxicology, 37(6), 1667–1678.

Wåhlin, J., & Klein-Paste, A. (2017). The effect of mass diffusion on the rate of chemical ice melting using aqueous solutions. *Cold Regions Science and Technology*, *139*, 11–21.

Western Transportation Institute. (2017). *Field usage of alternative de-icers for snow and ice control* (Transportation research synthesis 1706). St. Paul, MN: Local Road Research Board, MnDOT.

Winters, G. R., Gidley, J., & Hunt, H. (1984). *Environmental evaluation of calcium-magnesium acetate (CMA)* (FHWA-RD-84-094). Washington, DC: Office of Research and Development, Materials Division.

Xie, N., Muthumani, A., Dang, Y., & Shi, X. (2015). Deicer impacts on concrete bridge decks: A comparative study of field cores from potassium acetate and sodium chloride environments. presented at the International Symposium on Systematic Approaches to Environmental Sustainability in Transportation, Fairbanks, Alaska, August 2-5.

Xie, N., Shi, X., & Zhang, Y. (2017). Impacts of potassium acetate and sodium-chloride de-icers on concrete. *Journal of Materials in Civil Engineering*, *29*(3), 04016229.

Zhuang, G.-C., Peña-Montenegro, T. D., Montgomery, A., Montoya, J. P., & Joye, S. B. (2019). Significance of acetate as a microbial carbon and energy source in the water column of Gulf of Mexico: Implications for marine carbon cycling. Global Biogeochemical Cycles, 32(2), 223–235