Effective Use and Application of Winter Roadway Maintenance Material Enhancers

FINAL REPORT

October 16, 2015

By Erica R. McKenzie, Huichun Zhang, Benoit Van Aken, Bechara Abboud
Temple University

COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF TRANSPORTATION

CONTRACT # 4400011166
WORK ORDER # TEM 003

Technical Report Documentation Page

<table>
<tr><td>1. Report No.

FHWA-PA-2015-009-TEM WO 3</td><td>2. Government Accession No.</td><td>3. Recipient's Catalog No.</td></tr>
<tr><td colspan="2" rowspan="2">4. Title and Subtitle

Effective Use and Application of Winter Roadway Maintenance Material Enhancers</td><td>5. Report Date 10/16/2015</td></tr>
<tr><td>6. Performing Organization Code</td></tr>
<tr><td colspan="2">7. Author(s)

Erica R McKenzie, Huichun (Judy) Zhang, Benoit Van Aken, Bechara Abboud</td><td>8. Performing Organization Report No.</td></tr>
<tr><td colspan="2" rowspan="2">9. Performing Organization Name and Address

Department of Civil and Environmental Engineering
Temple University
Philadelphia, PA, 19122</td><td>10. Work Unit No. (TRAIS)</td></tr>
<tr><td>11. Contract or Grant No.
4400011166, TEM WO 3</td></tr>
<tr><td colspan="2" rowspan="2">12. Sponsoring Agency Name and Address

The Pennsylvania Department of Transportation
Bureau of Planning and Research
Commonwealth Keystone Building
400 North Street, 6th Floor
Harrisburg, PA 17120-0064</td><td>13. Type of Report and Period Covered

Final Report 4/17/2015 – 10/16/2015</td></tr>
<tr><td>14. Sponsoring Agency Code</td></tr>
<tr><td colspan="3">15. Supplementary Notes

Technical advisor: William Davenport | Roadway Programs Manager
Bureau of Maintenance and Operations
Winter Section
400 North Street – 6th Floor
Harrisburg PA 17120
Phone: (717) 787-1199 | Fax: (717) 705-5520
wildavenpo@pa.gov</td></tr>
<tr><td colspan="3">16. Abstract

A study was conducted to evaluate the product performance and potential environmental effects of five (5) winter maintenance additives: salt – reference (as brine or rock salt), AquaSalina, BEET HEET, GreenBlast, and Magic Minus Zero. Product performance was prioritized for the overall product evaluation as direct negative environmental impacts are expected to be minimal (based on project chemical analysis and toxicity testing) and to not exceed relevant water quality criteria; however, this may not apply to very small watersheds (minimal dilution) or watersheds that are known to have existing water quality issues. The top three performers, based on product performance, were as follows: 1) AquaSalina, 2) GreenBlast, 3) Magic Minus Zero. When product cost was included, the top three value products were: 1) Magic Minus Zero, 2) AquaSalina, and 3) GreenBlast.</td></tr>
<tr><td colspan="2">17. Key Words

Deicing, anti-icing, performance, melt, chemical analysis, nutrients, metals, corrosion, toxicity</td><td>18. Distribution Statement
No restrictions. This document is available from the National Technical Information Service, Springfield, VA 22161</td></tr>
<tr><td>19. Security Classif. (of this report)

Unclassified</td><td>20. Security Classif. (of this page)

Unclassified</td><td>21. No. of Pages

172

22. Price

N/A</td></tr>
</table>

Form DOT F 1700.7 **(8-72)** **Reproduction of completed page authorized**

Disclaimer: The contents of this report reflect the views of the author(s) who is (are) responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the US Department of Transportation, Federal Highway Administration, or the Commonwealth of Pennsylvania at the time of publication. This report does not constitute a standard, specification or regulation.

Statement of credit: This work was sponsored by the Pennsylvania Department of Transportation and the U.S. Department of Transportation, Federal Highway Administration.

TABLE OF CONTENTS

Executive Summary

A study was conducted to evaluate the product performance and potential environmental effects of five (5) winter maintenance additives: salt – reference (as brine or rock salt), AquaSalina, BEET HEET, GreenBlast, and Magic Minus Zero. The test results were evaluated, along with cost, to determine the top three performers. The results of the laboratory testing are summarized below, and detailed in the attached report; however, field conditions are not readily recreated in the laboratory (e.g., traffic and weather), and field testing would provide more realistic product evaluation.

Overall product ranking

Product performance was prioritized for the overall product evaluation as direct negative environmental impacts are expected to be minimal (based on project chemical analysis and toxicity testing) and **to *not* exceed relevant water quality criteria; however, this may not apply to very small watersheds (minimal dilution) or watersheds that are known to have existing water quality issues**. The top three performers, based on product performance, were as follows: 1) AquaSalina, 2) GreenBlast, 3) Magic Minus Zero. When product cost was included, the top three value products were: 1) Magic Minus Zero, 2) AquaSalina, and 3) GreenBlast.

Product Performance

Two product performance tests were conducted: the modified ice melting test and eutectic curves. When temperature drops to 0°F, deicers should not be used for deicing purposes because they do not effectively deice and there is a risk of them re-freezing. For the two pre-wetting agents, Magic Minus Zero effectively improved the performance of rock salt at both 15 and 25°F; BEET HEET also generally improved the performance of rock salt, but not to the same extent as Magic Minus Zero. For the liquid deicers, AquaSalina has a slightly higher ice melting capacity than salt brine at 15°F, but not at 25°F. GreenBlast did not significantly affect the performance of salt brine at either temperature. Freezing point testing of all deicer solutions indicates that the two liquid deicers, AquaSalina and GreenBlast, have lower freezing points than salt brine of the same concentration, and thus, will have better anti-icing ability than salt brine, while BEET HEET and Magic Minus Zero were similar to rock salt. When evaluating the performance of all deicers based on both deicing and anti-icing, AquaSalina always has the best performance and BEET HEET always has the worst performance. When it comes to deicing, Magic Minus Zero also performs very well, while GreenBlast was second to AquaSalina in anti-freezing performance.

Chemical Analysis and Corrosion Testing

Deicer product chemical analysis and corrosion testing were conducted to identify potential direct environmental and infrastructure effects associated with deicer product use, which include testing pH, nutrient, oxygen demand, metals, and corrosion. Direct environmental effects are expected to be minimal and to *not* exceed relevant environmental water quality criteria. However, this may not apply to very small watersheds (minimal dilution) or watersheds that are known to have existing water quality issues. AquaSalina was the only product found to have a pH outside the regulatory surface water criterion. Oxygen demand from the novel deicer products may result in decreased receiving water body dissolved oxygen concentrations, and the salt deicers (i.e., reference; non-detectable biochemical oxygen demand) may be a prudent choice in watersheds where dissolved oxygen concentration is a concern. Generally, GreenBlast was the least corrosive, while rock salt and BEET HEET were the most corrosive. While there was no clear best performer based on chemical analysis and corrosion testing, overall Magic Minus Zero was determined to be the top performer in this category.

Toxicity Testing

Laboratory toxicity tests were conducted to assess the effects of five deicing materials on model living organisms from different trophic levels, including a green alga (*Selenastrum capricornutum*), an aquatic invertebrate (*Ceriodaphnia dubia*), a fish (fathead minnow, *Pimephales promelas*), an aquatic plant (duckweed, *Lemna minor*), and a terrestrial plant (soybean, *Glycine max*). Results from the toxicity testing consist in various toxicity endpoints, including the lethal or inhibitory concentration 50% (EC50 or IC50) and the non- and lowest-observed-effect concentration (NOEC & LOEC).

The most toxic deicer materials were found to be AquaSalina, based on the overall and plant/alga score, and GreenBlast, based on the animal score. These results may be explained by the relative toxicity of the cationic component of the composing salts. Based on the US EPA *level of concern* for the chronic risk for aquatic organisms, none of the deicers tested in this study seem to pose a significant threat to the environment in low or high exposure scenarios, though AquaSalina and GreenBlast (most toxic deicers identified in this study) may represent a concern for invertebrates (most sensitive aquatic organisms tested) in the highest exposure scenario.

Summary for Overall Product Ranking

Rock salt and salt brine were provided by PennDOT. Magic Minus Zero and BEET HEET, which are pre-wetting agents, were first mixed with rock salt according to the manufacturers' recommendations (i.e., 10 and 5 gallons per ton of rock salt, respectively). GreenBlast, which is a liquid deicer containing 26 - 29% magnesium chloride ($MgCl_2$), was mixed with four volumes of 23.3% salt brine (ratio 1:4), as recommended by the manufacturer. AquaSalina, a liquid deicer containing 22.1% w/w of mixed chloride salts, was used as received. Separate protocols exist for solid and liquid ice melting capacity testing, and products were performance tested in their solid or liquid states. For all other tests, liquid products were required and were prepared by dissolving the rock salt or amended rock salt in Nanopure™ water (18 MΩ-cm).

The chemical analysis data was compared to relevant water quality criteria, and the results suggest that, given typical dilution factors and water quality in the receiving water body, the deicers would likely *not* lead to water quality criteria violations, however, oxygen demand may result in reduced dissolved oxygen concentrations. Toxicity testing data suggest that only AquaSalina and GreenBlast may represent a concern, and only under the most conservative testing and dilution scenario. In general, it can be said that *direct* environmental effects (water quality and toxicity) associated with the five tested deicers are expected to be minimal; indirect effects were not tested in this project. The effects on water quality and toxicity should be carefully reevaluated in small watersheds, where dilution may be minimal, or in sensitive receiving water bodies. Taken together, performance was deemed to be the most important consideration. Therefore, product ranking was assessed for four scenarios as follows:

1. Overall product performance prioritized; chemical analysis/corrosion and toxicity results disregarded
2. Deicing performance prioritized; chemical analysis/corrosion and toxicity results disregarded

3. Anti-freezing product performance prioritized; chemical analysis/corrosion and toxicity results disregarded
4. Overall product performance, chemical analysis/corrosion, and toxicity included with equal weighting

In scenarios 1-3, only product performance is considered. Depending on the relative importance of ice melting and anti-freezing, three different sets of weighting factors were assigned to the ice melting and anti-freezing scores:

1. Deicing and anti-freezing are equally important (referred as "Equal" in Table 1), the final performance score of the deicer will be the average of the two scores for deicing and anti-freezing;
2. Deicing is valued more important than anti-freezing (referred to as "De-icing in Table 1), we assigned a weighting factor of 1.5 and 0.67 to ice-melting and freezing point, respectively, and the final score of the deicer is the weighted average of the two scores for deicing and anti-freezing;
3. Anti-freezing is valued more importantly than deicing (referred to as "Anti-icing in Table 1), we assigned a weighting factor of 0.67 and 1.5 to ice-melting and freezing point, respectively, and the final score is again the weighted average of the two scores for deicing and anti-freezing.

To be consistent with ranking in the other two thematic areas, the lower the final score is, the better the performance. The resultant scores are shown in Table 1.

Table 1. Performance scores and ranking of the deicers in three different scenarios.

	Performance Score			Rank		
	Equal	De-icing	Anti-freezing	Equal	De-icing	Anti-freezing
Rock Salt	1.00	2.17	2.17	4	4	4
Magic Minus Zero	0.79	1.53	1.91	3	2	3
BEET HEET	1.07	2.25	2.41	6	6	6
Salt Brine	1.00	2.17	2.17	4	4	4
GreenBlast	0.66	1.60	1.28	1	3	2
AquaSalina	0.63	1.49	1.23	1	1	1

In Scenario 1 when deicing and anti-freezing are equally weighted, the ranking of the deicers is AquaSalina ≈ GreenBlast > Magic Minus Zero > rock salt ≈ salt brine > BEET HEET.

In Scenario 2 when deicing is more valued, the ranking of the deicers is AquaSalina > Magic Minus Zero > GreenBlast ≈ rock salt ≈ salt brine > BEET HEET.

In Scenario 3 when anti-icing is more valued, the ranking of the deicers is AquaSalina > GreenBlast > Magic Minus Zero > rock salt ≈ salt brine > BEET HEET.

Based on the three performance-emphasis scenarios, AquaSalina was consistently the best performing product, while BEET HEET was consistently the worst performing product. Magic Minus Zero was a strong performer for the deicing scenario (scenario 2) and GreenBlast was a strong performer in the anti-freezing scenario (scenario 3). Note that we assumed rock salt and salt brine have the same performance which is not necessarily the case in the field.

A fourth cumulative product and ranking analysis was conducted to reflect a more sensitive watershed, where water quality and toxicity results are included. For this scenario, a weighted average approach, as shown below, was employed:

$$Score = \beta_{performance} \cdot X_{performance} + \beta_{chem/corrision} \cdot X_{chem/corrision} + \beta_{toxicity} \cdot X_{toxicity}$$

where X_i are the unit scores from the sections (i.e., product performance, chemical analysis and corrosion testing, and toxicity testing) and β_i are the selected weighting factors. Salt brine and rock salt were averaged. The section scores, each discussed in detail in their respective chapters, have been transformed such so that all section scores are presented between 0 and 1, where a lower score is better. The section scores are shown in Table 2, and equal weighting was applied (i.e., all β_i=1/3; average of the three).

Table 2. All-inclusive scenario (i.e., scenario 4) sector scores, cumulative score, ranking. This scenario includes the results of chemical analysis/corrosion and toxicity, as would be appropriate in a sensitive watershed.

	Section score (X_i)			Cumulative	
Product	Performance	Chemical/Corrosion	Toxicity	Score	Rank
Salt	0.87	0.00	0.38	0.42	2
Magic Minus Zero	0.19	0.14	0.88	0.40	1
BEET HEET	1.00	1.00	0.00	0.67	5
GreenBlast	0.11	0.53	1.00	0.55	3
AquaSalina	0.00	0.84	0.85	0.56	4

Under the forth all-inclusive scenario, the product ranking is as follows (best overall shown first): Magic Minus Zero ≈ salt > GreenBlast ≈ AquaSalina> BEET HEET.

Cost is also an important consideration, therefore product value was calculated as follows:

$$Value\ score = \frac{\beta_{performane} \cdot S_{performane}}{C_{fixed}} + \frac{\beta_{chem/corrosion} \cdot S_{adj,chem/corrosion} + \beta_{toxicity} \cdot S_{adj,toxcity}}{C_{adjusted}}$$

Where β_i are the section weighting factors, S_i are the section score (transformed so that a higher score is better), and C_i are cost ($/ln mile). Product performance value calculations were based on measured values and cost/lane×mile for that fixed volume (or mass), while chemical/corrosion and toxicity were adjusted (both sector scores, $S_{adj,i}$, and cost/lane×mile, $C_{adj,i}$) to reflect reductions in product application due to amendment use. The following reductions were assumed for the novel products (based on manufacturer publications): Magic Minus Zero (30%), BEET HEET (39.4%), GreenBlast (0%), and AquaSalina (43.2%, based on a recommended use rate of 50 gal/lane×mile). Baseline condition assumptions reflect 200 lb./lane×mile rock salt or 88 gal/lane×mile salt brine. Substantially different value scores were calculated for liquid and solid formulations, therefore the calculated values were normalized to the appropriate salt reference (i.e., value score ratio); in all cases, higher values scores indicate a higher value product.

Table 3. All-inclusive value assessment and ranking for the four scenarios.

	Performance priority		Deicing priority		Anti-icing priority		Equal weighting of all themes	
	Value score ratio	Rank	Value score ratio	Rank	Value score ratio	Rank	Value score ratio	Rank
Rock Salt	1.00	4	1.00	4	1.00	4	1.00	3
Magic Minus Zero	4.31	1	8.70	1	2.34	1	1.62	2
BEET HEET	0.20	6	0.45	6	0.09	6	1.97	1
Salt Brine	1.00	4	1.00	4	1.00	4	1.00	3
GreenBlast	1.76	3	2.31	3	1.52	3	0.39	6
AquaSalina	1.86	2	2.62	2	1.52	2	0.67	5

Magic Minus Zero and was consistently the top valued product, as a combination of its measured values (e.g., product performance), and the assumption that 30% less rock salt would be required. AquaSalina and GreenBlast were the second and third valued products, for product performance only scenarios. BEET HEET was usually the lowest value, however in scenario 4, where all sections were included, BEET HEET was the top value due primarily to its low toxicity and reduced produce use (39.4% reduction in rock salt use and associated chemical and toxicity scores).

Additional analysis was conducted to more directly evaluate cost associated with product use. Two temperatures were evaluated (15^{o}F and 25^{o}F); the products were not found to be effective at 0^{o}F, therefore this temperature is not further evaluated. Product performance was tested according to standardized methods, which prescribe the mass or volume of liquid deicer to be used in the test. Ice-melting test results were used (g ice melted/g deicer applied; average of all time points) to determine the total amount of ice that would be melted and the cost ($/melted ft^3). Other non-prescribed masses were not tested, so assumptions were made. A second application rate scenario was evaluated using manufacturer recommended application rate (previously described in the cumulative analysis); it was assumed that the manufacturer recommended rate would result in the equivalent amount of ice melted as the salt reference. It should be noted that Cargill did not make any statement regarding changes in application rate. The results of the analyses at two temperatures under the two applications rates are shown in Tables 4 and 5. As expected, cost is noticeably lower at 25^{o}F than at 15^{o}F. Among solid deicer formulations using the laboratory test results, Magic Minus Zero had the lowest cost/melted volume. However, when manufacturer recommended application rates were used (assuming equivalent total ice melted), BEET HEET was the lowest cost product. Among liquid deicers, salt brine was substantially cheaper than the novel formulations ($/melted ft^3 ice) under both application rate scenarios.

Table 4: Product performance and cost at 15 and 25 ^{o}F, based on laboratory ice-melting test results.

	Application rate		15 ^{o}F			25 ^{o}F		
Product	lb./lane-mile	gal/lane-mile	Melt (g ice/g deicer)	Ice melted (ft^3/lane-mile)	Cost ($/melted ft^3)	Melt (g ice/g deicer)	Ice melted (ft^3/lane-mile)	Cost ($/melted ft^3)
Rock Salt	200		1.98	6.33	1.26	4.35	13.94	0.57
Magic Minus Zero	200		2.90	9.29	1.01	5.15	16.50	0.57
BEET HEET	200		2.10	6.73	1.31	4.70	15.06	0.59
Salt Brine		88	0.20	2.35	5.61	1.13	13.23	1.00
GreenBlast		88	0.25	2.94	14.06	1.18	13.82	2.99
AquaSalina		88	0.30	3.53	12.47	1.10	12.94	3.40

Table 5: Product performance and cost at 15 and 25 ^{o}F, based on assumed equivalent performance with manufacturer-recommended application rate reductions.

	Application rate		15 ^{o}F			25 ^{o}F		
Product	lb./lane-mile	gal/lane-mile	Melt (g ice/g deicer)	Ice melted (ft^3/lane-mile)	Cost ($/melted ft^3)	Melt (g ice/g deicer)	Ice melted (ft^3/lane-mile)	Cost ($/melted ft^3)
Rock Salt	200		1.98	6.33	1.26	4.35	13.94	0.57
Magic Minus Zero	140		2.82	6.33	1.04	6.21	13.94	0.47
BEET HEET	121.2		3.26	6.33	0.85	7.18	13.94	0.38
Salt Brine		88	0.20	2.35	5.61	1.13	13.23	1.00
GreenBlast		88	0.20	2.35	17.58	1.13	13.23	3.13
AquaSalina		50	0.35	2.35	10.63	1.98	13.23	1.89

Based on the above analyses, the cost of use – for each tested performance and manufacturer claims – are shown in Table 6.

Table 6: Product cost analysis based on test results (as shown in Table 4) and on manufacturer-recommended application rate reduction (as shown in Table 5).

	As tested			Manufacturer claims		
	Application rate			Application rate		
Product	lb./lane-mile	gal/lane-mile	Applied cost ($/ln mile)	lb./lane-mile	gal/lane-mile	Applied cost ($/ln mile)
Rock Salt	200		$8.00	200		$8.00
Magic Minus Zero	200		$9.40	140		$6.58
BEET HEET	200		$8.83	121.2		$5.35
Salt Brine		88	$13.20		88	$13.20
GreenBlast		88	$41.36		88	$41.36
AquaSalina		88	$44.00		50	$25.00

Summary for Task 1.1 – Literature review

In the United States, sodium chloride is prolifically used as a deicing agent, applied either as rock salt or as salt brine. Road-applied salt is washed into adjacent terrestrial and aquatic ecosystems, but it seems that direct toxic effect of deicers on aquatic organisms and humans are unlikely, due to the low inherent toxicity and high dilution rate of these materials in the receiving waters. Only very localized (e.g., roadside soil) or temporary events (e.g., pulse of deicers in streams after winter storm) are likely to result in direct toxic effects on plants and aquatic organisms. However, there is evidence of salt buildup in the environment which could lead to unsuspected, long-term effects.

Deicer use has been associated with some indirect negative environmental impacts. In terrestrial systems, the salt has been observed to change the soil structure, which can lead to a reduction in permeability. Additionally, salt application has caused the release of soil-bound metals due to cation exchange. Deicers have been associated with stimulation of blue-green algae and oxygen depletion in surface waters, as well as disruptions to lake turnover processes (i.e., effects to oxygen exchange).

Summary for Task 2.1 – Deicer Performance Testing

Deicer product performance is an important consideration, both for understanding the environmental conditions (e.g., temperature) for which a product is expected to be effective and for the effectiveness and expected cost associated with using a product. Performance was evaluated using two tests: the ice melting test for the deicing performance, to determine the amount of ice melted at a set temperature for a specified amount of product; and the freezing point test for the anti-icing performance, to determine the eutectic curve of a product (i.e., freezing point as a function of deicer concentration). The key findings are summarized below.

Task 2.1.1 Ice Melting Test

The objective of this sub-task was to test the performance of different types of deicers by evaluating their ability to melt ice at three temperatures (25, 15, and 0 ± 0.5 °F). Six products were tested, three liquids and three solids, in accordance with the request of PennDOT. Rock salt and salt brine were tested as the reference materials for the solid and liquid deicers, respectively. Our results showed that the average volumes of brine collected for rock salt and salt brine are mostly comparable to the reported values (Akin and Shin 2012). The small differences between our observed and the reported values are likely due to the different sources and purity of the rock salts. Also, the small standard deviations in Table 5 in Task 2.1 Report suggest the quality of our data is acceptable.

Tables 6-8 and Figure 5 in Task 2.1 report show the average grams of ice melted per gram of deicer for each product at all three temperatures. At 0°F, little ice was melted for all deicers within 60 minutes. The two pre-wetting agents, i.e., Magic Minus Zero and BEET HEET, did not affect the ice melting capacity of rock salt. For the liquid deicers, the negative values in the ice melting capacities suggest that they will not effectively melt ice at or approaching 0°F. Fortunately, winter temperatures in Pennsylvania rarely drop to this temperature. Additionally, cold and dry snow at ~ 0°F can often be easily removed by plowing.

At 15°F, Magic Minus Zero melted more ice than rock salt at all times (17 – 91% increase). BEET HEET melted more ice at 20 and 40 min (40 – 45% increase), but did not improve the performance of rock salt at 10 and 60 min. All these numbers for BEET HEET are much smaller than the manufacture reported value, that is, 153.2% more ice melted than untreated salt at 15°F.

Among the liquid deicers, AquaSalina has a slightly higher ice melting capacity than salt brine, but not to the extent the manufacture reported: 2.0 vs. 1.4 mL ice melted per mL AquaSalina vs salt brine at 15 °F; GreenBlast melted slightly more ice than salt brine at 10 and 20 min, but did not affect the performance of salt brine at 40 and 60 min. There is no reported value for ice melting capacities of Magic Minus Zero and GreenBlast.

At 25°F, both Magic Minus Zero and BEET HEET increased the ice melting ability of rock salt by 13% and 16%, respectively, at 60 min. For comparison, the manufacture of BEET HEET reported 65.1% more ice melted than untreated rock salt. There is no reported ice melting values for all other products at 25°F. Magic Minus Zero outperformed BEET HEET at short durations (10 and 20 min), but both pre-wetting agents performed comparably at longer durations (40 and 60 min). For the liquid deicers, no significant difference was observed among the ice melting capacity of the three products except at 60 min, where both AquaSalina and GreenBlast increased the ice melting capacity of salt brine by 7%.

At 15 and 25°F, the solid deicers melted much more ice than the liquid deicers. This finding is consistent with the literature (Akin and Shi 2012) and can be mostly explained by the fact that more chlorides were applied from the solid deicers than from the liquid deicers during the tests. Based on deicer dry weight, liquid deicers are more effective because it allows direct deicing while solid deicers need to dissolve first (which takes energy) before they can deice. Note that there are additional costs associated with salt brine preparation from rock salt; therefore, a more accurate comparison between solid and liquid deicers should take cost, handling, performance, and other relevant factors into consideration.

Task 2.1.2 Freezing Point Test

The objective of this sub-task was to obtain the eutectic curves for different types of deicers by examining the freezing points of the deicer solutions at different concentrations. The experiments were conducted according to the American Society for Testing Materials (ASTM) "Standard Test Method for Freezing Point of Aqueous Engine Coolants" (ASTM D1177 – 12).

Eutectic curves provide valuable information on the anti-icing performance of the deicer products. The freezing point of deicer solutions decreases with increase in deicer concentration until it reaches a point (i.e., eutectic point, the minimum freezing temperature) where further increase in deicer concentration yields higher freezing points. Above the eutectic curves, the deicers exist as solution, while below the curves, the deicers exist as solid. During field application, deicer solutions will be continuously diluted with water from either the melting of ice/snow or falling rain/freezing rain. With decreasing deicer concentration upon dilution, the freezing point of the solution increases such that there is a risk of solution refreezing when its freezing point reaches the pavement temperature (FHA 1996). The lower the freezing point, the less likely the solution refreezes, thus resulting in better anti-icing ability.

The eutectic curves of all deicers are shown in Figure 8 in Task 2.1 Report and the observed freezing points are summarized in Table 9. Based on the results, all deicer solutions have comparable freezing points when the salt concentration is less than about 5%. BEET HEET has almost the same eutectic curve as rock salt, indicating it does not affect the anti-icing ability of rock salt. Magic Minus Zero has a freezing point 1.3 – 3.0 °F lower than the rock salt solution at concentrations between 11.5% and 30%. For the liquid deicers, both GreenBlast and AquaSalina have lower freezing points than the salt brine of the concentration between 11.5% and 23.3%. Within this range, the freezing point of GreenBlast solutions is about 2.0 – 3.0 °F lower than that of salt brine. The difference is most significant at about 20% where the freezing point of GreenBlast is 11.8 °F less, suggesting it having a much better anti-icing ability than salt brine. At 11.5%, the freezing point of AquaSalina is about 2.5°F lower than that of salt brine. At higher concentrations, the difference between the two solutions is even more significant. These results suggest that the liquid deicers tend to freeze at lower temperatures than salt brine, enabling better anti-icing ability.

To better predict the freezing points of the deicer solutions at different concentrations, we fit the points between no deicer and the eutectic point for each curve into the quadratic equation:

Rock salt: $Freezing\ Point = 31.4897 - 0.7998 \times C - 0.0351 \times C^2$ $R^2 = 0.998$

Magic Minus Zero: $Freezing\ Point = 32.3606 - 1.2744 \times C - 0.0140 \times C^2$ $R^2 = 0.998$

BEET HEET: $Freezing\ Point = 31.4402 - 0.5763 \times C - 0.0408 \times C^2$ $R^2 = 0.994$

Salt brine: $Freezing\ Point = 31.7050 - 0.8349 \times C - 0.0364 \times C^2$ $R^2 = 0.999$

GreenBlast: $Freezing\ Point = 31.1067 - 0.2576 \times C - 0.0898 \times C^2$ $R^2 = 0.987$

AquaSalina: $Freezing\ Point = 31.9059 - 0.9957 \times C - 0.0499 \times C^2$ $R^2 = 0.999$

where *C* stands for the deicer concentration in weight %. With these equations, we are able to quickly estimate freezing points at any given concentration for all the deicer products.

Summary for Task 3.1 – Chemical Analysis and Corrosion Testing

Chemical analysis was conducted over four thematic areas: pH, nutrients, oxygen demand, and metals. Three of the novel formulations – Magic Minus Zero, BEET HEET, and GreenBlast – were amendments to the salt reference, therefore were expected to have equal or greater nutrient and metal concentrations than the salt reference. AquaSalina was analyzed as distributed (i.e., is not a salt amendment), and therefore, there was no expected relationship between AquaSalina and the salt reference. Corrosion testing was also conducted. The results of these analyses are presented below.

- The salt reference, Magic Minus Zero, BEET HEET, and GreenBlast all had circumneutral pH values (pH 7 to 9) that were within the Pennsylvania Department of Environmental Protection (DEP0 and U.S. Environmental Protection Agency (EPA) water quality criterion. AquaSalina was moderately acidic (pH 3.78). In the environment, pH play a significant role in many biological and abiotic functions, and the effect of roadway runoff pH on the receiving water body will depend on water quality; substantial changes to receiving water body pH due to deicer use are *not* expected.
- Phosphorus, ammonia, nitrite, and total nitrogen results suggested that deicer application would *not* lead to water quality criteria exceedance for any of the conventional or novel formulations. Generally, the salt reference was found to have lower nutrient concentration than were the novel deicing formulations, which is consistent with expectations. Among the novel deicing formulations, GreenBlast was least likely to have negative environmental effects based on measured nutrient concentrations. Nitrate and organic nitrogen were also analyzed, but due to analytical challenges were deemed to not be usable.
- Biochemical and chemical oxygen demand were measured, and the novel deicing formulations were found to have significantly greater oxygen demand than the salt reference. Among the novel formulations, Magic Minus Zero exerted the lowest oxygen demand. Oxygen demand among the novel deicing formulations may be point of concern for sensitive watershed.

- Metals analysis resulted in quantification of the following metals: chromium, nickel, zinc, copper, arsenic, silver, cadmium, and lead. Measured metals concentrations are *not* expected to be a concern, though metals criteria are dependent on water quality parameters including hardness. Generally, the salt brine reference contained the lowest metals concentrations; among novel formulations, AquaSalina and Magic Minus Zero contained the lowest metals concentrations. Mercury was also analyzed, but was deemed to not be detectable (i.e., below the detection limit, though mercury detection limits were substantially higher than other analyzed elements).
- Corrosion results were variable between tests. Generally, rock salt was the most corrosive along with BEET HEET, while GreenBlast was the least corrosive.
- Chemical analysis and corrosion overall ranking was conducted based on the thematic groups; a z-score approach was used, and is detailed in Task 3.1. In the absence of another rationale, each of the five themes (pH, nutrients, oxygen demand, metals, and corrosion) was equally weighted. The overall chemical analysis and corrosion testing results were as follows (best performance first): salt brine, Magic Minus Zero, rock salt, GreenBlast, BEET HEET, and AquaSalina.

Summary for Task 4.1 – Toxicity Testing

1. Introduction:

The release of deicing materials in the environment adversely impacts living organisms. Laboratory toxicity testing was conducted to assess the direct effects of five deicing materials on living organisms. Because deicer salts mostly impact the aquatic environment, the study used a majority of model aquatic species from different trophic levels, including a green alga, an aquatic invertebrate (daphind), a fish (fathead minnow, larval and embryonic stage), and an aquatic plant (duckweed). In addition, because deicer salts are known to impact terrestrial vegetation, a model terrestrial plant, soybean, was included in the study.

2. Toxicity Tests:

All assays used in this study are standardized toxicity tests that were conducted following published US EPA guidelines. Procedures involving vertebrate animals were formally approved by the Temple University Institutional Animal Care & Use Committee (IACUC) to be compliant with the Federal Animal Welfare Act.

The following tests were conducted:

- Freshwater alga, *Selenastrum capricornutum*, algal growth assay.
- Aquatic daphnid, *Ceriodaphnia dubia*, survival and reproductive assays.
- Fathead minnow, *Pimephales promelas*, larval toxicity test.
- Fathead minnow, *Pimephales promelas*, embryo-larval survival and teratogenicity test.
- Duckweed, *Lemna minor*, aquatic plant toxicity test using *Lemna* spp.
- Soybean, *Glycine max*, germination and root elongation tests.

3. Deicer Materials:

Because in the proposed toxicity tests, the test organisms – all aquatic except the terrestrial plant soybean – are exposed to toxicants via the liquid medium, the deicers were tested in their liquid form. Five concentrations and a control were used for each deicer in each test. The highest concentration tested was obtained by diluting the liquid form of the deicers 5 to 40 times, depending on the sensitivity of the test organism. The lower test solutions were then prepared by diluting sequentially the highest concentration by a factor 2.

4. Data Processing:

Results from toxicity testing are expressed as the toxicity endpoints, inhibitory concentration 50% (IC50) or lethal concentration 50% (LC50) – which were calculated using point estimation methods – and lowest-observed-effect level (LOEC) and non-observed-effect level (NOEC) – which were estimated using hypothesis testing. The endpoints were expressed as mass of salt (NaCl, $CaCl_2$, and/or $MgCl_2$) per volume of diluent (g salt/L) and as mass of deicer material – liquid form – per volume of diluent (g liquid product/L). Toxicity data were analyzed following statistical procedures recommended in the US EPA guidelines, when applicable, or equivalent procedures.

5. Summary of Toxicity Test Results:

The toxicity testing results (i.e., NOEC, LOEC, IC50, and LC50) for the five deicer materials obtained using the different tests were compiled to establish a ranking of the deicers based on their relative toxicity and to assess the associated environmental risk.

The toxicity endpoints were normalized by reference to the salt brine. For each material, a *toxicity score* was calculated using a weighted average of the normalized toxicity endpoints – referred to as *overall score*. In the absence of further rationale, the same weighting factor was used for all endpoints. Specific scores were also calculated for the plant and algal tests – referred to as *plant/algal score* – and animal tests –referred to as *animal score*. These score were then calculated for all endpoints (NOEC, LOEC, and IC/LC50) and for the IC/LC50 only. The deicers were then ranked based on their relative toxicity score (Table 4).

Table 4: Ranking of the five deicers based on the toxicity endpoints: 1 = most toxic, 5 = least toxic. Ranks were calculated based on the normalized toxicity endpoints. The red highlight depicts the most toxic deicers.

Deicer	Overall Score				Plant/Algal Score				Animal Score			
	NOEC, LOEC, IC/LC50	Rank	IC/LC50	Rank	NOEC, LOEC, IC/LC50	Rank	IC/LC50	Rank	NOEC, LOEC, IC/LC50	Rank	IC/LC50	Rank
Brine	1.00	2.5	1.00	4.0	1.00	2.0	1.00	3.0	1.00	3.0	1.00	2.0
Aquasalina	1.16	5.0	0.96	2.5	0.97	1.0	0.75	1.0	1.34	5.0	1.18	5.0
Beet Heet	1.13	4.0	1.08	5.0	1.25	5.0	1.14	5.0	1.01	4.0	1.03	3.0
GreenBlast	0.90	1.0	0.93	1.0	1.14	4.0	1.03	4.0	0.67	1.0	0.84	1.0
Magic Minus 0	1.00	2.5	0.96	2.5	1.03	3.0	0.83	2.0	0.96	2.0	1.09	4.0

Based on the overall score and animal score, the most toxic deicer is GreenBlast. Based on the Plant/algal score, the most toxic deicer is AquaSalina. This observation may be explained by the presence of more toxic salt components in these two deicers (AquaSalina contains $MgCl_2$ and KCl and GreenBlast contains $MgCl_2$).

An environmental risk assessment was then conducted based on the lowest NOEC and LC/IC50 for aquatic organisms and three environmental exposure scenarios: 'low' exposure (25 mg salt/L), 'high' exposure (165 salt/L), and exposure to a 500-time dilution of the deicers (470 mg salt/L). In short, we used the *risk quotient* method, which compares toxicity thresholds (i.e., endpoints) with predicted environmental concentrations. Based on the results, none of the deicers tested seem to pose a significant threat to the environment at the concentration of 25 or 165 salt/L. Only AquaSalina and GreenBlast – the most toxic deicers identified in this study – may represent a concern for invertebrates – the most sensitive aquatic organisms tested – in the highest exposure scenario (dilution 500 times).

Background:

On average, 18 million tons of salt (sodium chloride - NaCl) are used annually in U.S. for deicing paved surfaces. The use of rock salt on U.S. roads has dramatically increased in the last 65 years (Figure 1). After spreading on pavement, the salt dissolves and is washed into adjacent terrestrial and aquatic ecosystems, resulting in increased concentration of composing ions (e.g., chloride – Cl^-, sodium – Na^+, calcium – Ca^{2+}, magnesium – Mg^{2+}) in surface water, groundwater, and soil (Jackson and Jobbagy, 2005). The salinity increase results in a range of potentially negative impacts on the environment and human health.

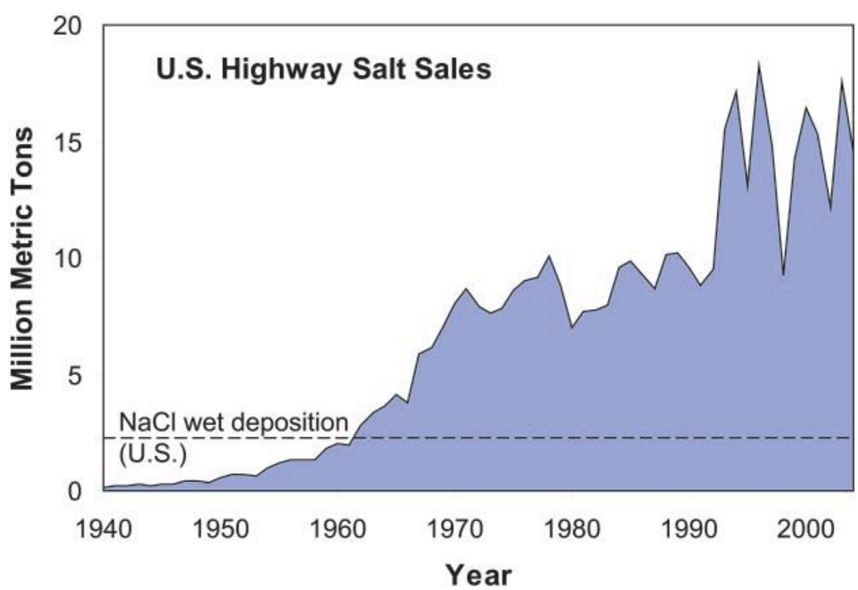

Figure 1: Sales of rock salt for deicing use in the U.S. from 1940 to 2004. The dashed line represents an estimate of the annual wet deposition of NaCl in the U.S. primarily from sea salt (Jackson and Jobbagy, 2005).

Deicer materials and performance evaluation:

Chloride-based salts are the most common materials used for winter road maintenance applications. Sodium chloride (NaCl), which can be used either as rock salt (de-icing) or salt brine (anti-icing), is the most widely used chemical due to its abundance and low cost. Calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) have better ice-melting performance at cold temperatures (the effective application temperatures for $CaCl_2$, $MgCl_2$, and NaCl are -25 °C, -15 °C, and -10 °C, respectively), but are more expensive than NaCl. Granular $CaCl_2$ can be combined with salt to increase its effectiveness in cold conditions. Acetates, such as potassium acetate (KAc) and calcium magnesium acetate (CMA), are more effective, less corrosive, and less environmentally damaging as chloride-based salts, but they are generally much more expensive. A variety of agriculturally-based chemicals (e.g., molasses, plant residues) are available today to be used either alone or as additives for other deicer materials. Agriculturally-based additives provide improved performance, reduce deicer corrosive action, and improved longevity compared to standard salt deicers, but they are also expensive. Although little information is available about the environmental impacts of acetate and agriculturally-based additives, they are suspected to increase the biochemical oxygen demand (BOD), contributing to oxygen depletion in surface water (Shi et al., 2013).

Deicers have been mainly used for two distinct snow and ice control purposes: deicing and anti-icing. Deicing performance tests are mainly conducted to evaluate the ability of deicers to remove ice once it has formed. Anti-icing performance tests, on the other hand, are conducted to measure a product's ability to prevent the formation or development of bonded snow and ice.

In 1992, the Strategic Highway Research Programs (SHRP) sponsored the development of the Handbook of Test Methods for Evaluating Chemical Deicers (SHRP-H-332) that created the three most widely used deicing performance tests (solid and liquid deicers): ice melting tests (SHRP H-205.1 and H-205.2, respectively), ice penetration tests (SHRP H-205.3 and H-205.4, respectively), and ice undercutting tests (SHRP H-205.5 and H-205.6, respectively; Akin and Shi, 2012L; Muthumani et al, 2014). These tests were adopted by Pacific Northwest Snowfighters (PNS) in 2010 in its two sponsored projects (Projects 0092-10-17/CR09-01 and 0092-08-32/CR07-02). A recent study critically reviewed the three tests and recommended only the ice melting test as a reliable laboratory testing method for deicing performance (Akin and Shi, 2012). The ice penetration test was not recommended for the following three reasons: (1) this test provides information that is very similar to that of the ice melting test (with much more noise), and is thus redundant; (2) due to the inherent variability associated with the test design, the ice penetration results are highly variable; and (3) this test method has particularly large errors for solid deicers.

For the original SHRP ice melting test, 4.170 g of solid deicers or 3.8 ml of liquid deicers should be applied over a standard, smooth ice surface at a fixed temperature – typically ranging from 0 to 30 °F. After a pre-determined duration (e.g., 10, 20, 30, 45, and 60 min), the liquid volume is measured, and then the liquid is returning to the ice sample. The obtained liquid volume is then converted to the amount of water melted per g of deicer, which is used to quantify the ice melting capacity of the deicer. Recently, Akin and Shi (2012) modified the original ice melting test in two aspects: (1) using commercially available disposable Petri dishes (100 mm × 15 mm) instead of a custom-built Plexiglass apparatus (229 mm × 3.2 mm) to prepare ice samples and (2) conducting four tests simultaneous, three replicates for the test deicer and one for salt brine as a control. Accordingly, the deicer application rate has been modified to 1.0 g for solid deicers or 0.9 ml for liquid deicers. Consistent results have been reported using the modified test. This modified ice melting test was developed and recommended by a recent PNS sponsored project (0092-08-32/CR07-02).

The ice melting test provides information mainly on deicing performance rather than on anti-icing performance. The most widely used test for anti-icing performance is the standard freezing point test (ASTM D1177) which has been adapted to provide the freezing points of deicer solutions of different concentrations (Ketchum et al., 1996). As exemplified in Figure 2, deicer solutions of different concentrations have different freezing points. For sodium chloride, the solution's freezing point decreases with increasing salt concentration until it reaches 23%, after that, the trend is reversed and the freezing point increases with increasing salt concentration. Sodium chloride's eutectic point is thus 23% (i.e. the composition of a solution with the lowest freezing point), which freezes at about -21 °C (-6 °F). The solid curves in Figure 2 represent how freezing points of various salt solutions change as a function of salt concentration and are called eutectic curves. Similarly, based on Figure 2, the eutectic composition of the calcium chloride ($CaCl_2$)-water system is about 30% $CaCl_2$ with a freezing point of -51 °C (-60 °F). The lower freezing point of 30% $CaCl_2$ solution means it may have a better anti-icing performance than 23% NaCl.

During anti-icing treatments, brine solutions should be prepared as close as possible, but less than, the eutectic composition. With the dilution of a brine solution after application, its freezing point increases until it reaches a point when the solution refreezes (Figure 1). For example, the refreeze concentrations of NaCl and $CaCl_2$ at -10 °C (14 °F) are about 13.5% and 12.5%, respectively. This means that $CaCl_2$ brines can be diluted more than NaCl before refreezing. Based on these literature data, conducting freezing point tests to obtain eutectic curves of deicer solutions at different concentrations will provide important information regarding product anti-icing performance.

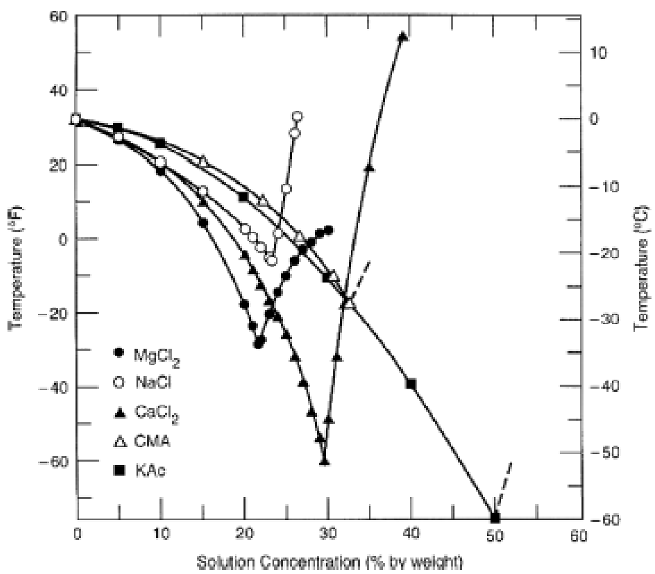

Figure 2. Eutectic temperature and eutectic concentration of five chemicals (Ketchum et al., 1996).

Other than the above tests, there are a number of other laboratory test methods developed to examine deicer performance but remain non-standardized (Akin and Shi, 2012). Examples include ice shearing, de-bonding, or scraping tests (Ashworth et al., 1989; Adams et al. 1992, Kirchner et al., 1992; Bernardin et al., 1996), and differential scanning calorimetry thermogram test (Akin and Shi, 2012). Moreover, a number of laboratory tests are available to measure friction between vehicle tires and a road surface using various devices such as drag sled, In Road Friction Sensor, Scraper and Friction System, Simple Skid Friction Measurement Device, Bench-top Tribometer, British Pendulum Tester, Handheld Tribometer, and Dynamic Friction Tester

(Muthumani et al., 2014). Measurement of friction is important to evaluate if the application of a deicer has any negative effect on road safety, therefore, future work is warranted to conduct friction tests at either the lab scale or the field scale.

Deicer water quality, soil quality, and corrosion effects:

Two reviews – "Environmental impacts of chemical deicers – a review" (Ramiakrishna and Viraraghavan, 2005) and "Road salts in urban stormwater: an emerging issue in stormwater management in cold climates" (Marsalek, 2003) – are commonly cited as summaries (state of the science) on environmental impacts of deicers. "Corrosion of deicers to metals in transportation infrastructure: introduction and recent developments" (Shi, 2009) is an infrastructure corrosion review. Additional studies supplemental information.

After being applied to the roadway, the chemical deicers can be transported to the environment via several pathways including spray onto nearby soil and vegetation, snow removal to a remote site, overland flow (particularly in areas of low permeability), infiltration into the soil column down to the water table, and transport in a water body (i.e., surface water streams and lakes, as well as groundwater). The salt can affect soils, surface and groundwater, biota, and infrastructure (Marsalek, 2003). Roadway runoff transport can be influenced by human factors (e.g., road drainage system, urbanization extent) as well as natural factors (e.g., topography, precipitation, temperature, and discharge of local surface and groundwater resources; Ramiakrishna and Viraraghavan, 2005). Depending on the nature of the site, it is estimated that 10 to 60% (on average 45%) of NaCl applied on highway infiltrates and enters the shallow subsurface (Environment Canada, 2000). The soil zone affected by deicer salts is generally very narrow (e.g., less than 10 m; NRC, 1991), but can affect the local soil structure. Elevated sodium concentrations can affect soil dispersion, which ultimately can decrease soil infiltration (decrease permeability), decrease aeration, and increase surface runoff (Marsalek, 2003; Ramiakrishna and Viraraghavan, 2005). Kakururu and Clark (2015) found that salt application resulted in 19.1% permeability loss.

Salt-based deicers have been observed to impact groundwater taste (organoleptic character). The nominal sodium and chloride concentration can be increased, sometimes in excess of the drinking water recommendation and thus increase drinking water treatment cost, though this is generally only a concern for drinking water wells in close proximity to the application site (e.g., within 30 m down gradient of roadways; NRC, 1991; Marsalek, 2003; Ramiakrishna and Viraraghavan, 2005). Sodium, as well as calcium and magnesium, can participate in cation exchange within the soil matrix, which can result in slower transport through the soil column and in groundwater (Lofgren, 2001; Ramiakrishna and Viraraghavan, 2005).

Chloride concentrations in surface freshwater generally range from 0 to 100 mg/L, with most concentrations lower than 20 mg/L. The primary effect of salt application is increased salinity in the local water resources (e.g., Lofgren, 2001) and salt application has resulted in instream concentrations as high as 18,000 mg Cl^-/L (Environment Canada, 2000). Many studies showed that salt in highway runoff is typically quickly diluted in receiving waters resulting in concentrations lower than 15 mg Cl^-/L (as a guideline, it is usually considered that deicer salts are diluted 500 times from road application to environmental water; Fay and Shi, 2012). However, in stream sodium and chloride concentrations can be markedly variable, including a ten-fold concentration difference in a single day (Ruth, 2003). Generally, in-stream chloride concentrations are highest during winter (i.e., when the salt is being applied to the roadway) and early spring, but elevated chloride concentrations are also commonly observed during the spring and summer as well, due to base flow (Marsalek, 2003; Ramiakrishna and Viraraghavan, 2005). Small water bodies, where there is less dilution, are considered to be more at risk for salt-based deleterious effects on surface water ecosystems (Ramiakrishna and Viraraghavan, 2005). Similarly, Novotny et al. (2008) found that salinity seasonal cycling was related to catchment size, impervious cover, and lake size:depth ratio. Elevated salt concentrations result in increased water density, which can affect lake density gradients, induce stratification, or disrupt spring overturn (i.e., complete mixing); these impacts affect the lake ecosystem and the lakes physical-chemical processes (e.g., oxygen exchange, nutrient cycling, and toxic metal release; Ramiakrishna and Viraraghavan, 2005; Novotny et al., 2008). Long-term temporal trends in lake salinity have also been observed (Jackson and Jobbagy, 2005); Minnesota urban lakes were found to have 1.8% annual salinity increase (Novotny et al., 2008).

Nutrient are not intentionally included salt deicers, however phosphorus and nitrogen are common co-constituents (Marsalek, 2003). Organically-derived deicers have the potential to directly contribute to nutrients; nitrogen (N) and phosphorous (P), sulfur (S), and sodium (Na) can stimulate the growth of blue-green algae, leading to eutrophication and oxygen depletion (Ramiakrishna and Viraraghavan, 2005). One study compared the effects of abrasives to those of rock salt wetted with Magic Minus Zero, and found that the wetted rock salt contributed significantly less phosphorus than did the abrasives (Abright, 2009). Organic corrosion inhibitors, although often of proprietary composition, are known to contain high levels of phosphorous (P), nitrogen (N), and organic compounds that can be detrimental to water quality because of high biochemical oxygen demand (BOD; organic compounds), contribution to eutrophication (P and N), and toxicity (ammonia – NH_3; CDOT, 2001). Deicer salts have also been found to decrease the pore water total organic carbon (Bäckström et al., 2004).

Inorganic deicers are not expected to substantially directly affect pH. However, deicers have been found to release soil acidity; the released acidity is generally only expected to affect stream pH values for small, low buffering capacity catchments (Lofgren, 2001; Bäckström et al., 2004). Toxic heavy metals are not intentionally included salt deicers, however they can occur as co-constituents in the salt (e.g., copper and zinc; Marsalek, 2003). Salt deicer application has been found to lead to elevated zinc, copper, cadmium, and lead concentrations, and their increased concentrations can be attributed to cation exchange, decreased pH, formation of metal-chloride species, and complexation by organic matter (Lofgren, 2001; Marsalek, 2003; Bäckström et al., 2004).

To mitigate salts negative effects, Marsalek (2003) recommended employing appropriate source controls, especially in sensitive areas. Additionally, stormwater structural best management practices (BMPs) should limit the infiltration of high salinity water if groundwater contamination is a concern. Stormwater BMPs that have deeper storage compartments, including oil/grit separators and stormwater management ponds, were observed to accumulate total dissolved solids and to undergo chemo-stratification such that deeper water contained elevated dissolved solids concentrations (Marsalek, 2003).

Corrosion in the transportation industry leads to degradation of automobiles and the roadway infrastructure; corrosion can reduce the effective lifespan of the infrastructure, negatively impact the aesthetic, and impact ecosystem health. It was estimated that deicer use led to $32/year/vehicle in corrosion damage, while infrastructure corrosion was estimated to be $615/ton of road salt. For infrastructure corrosion, the following steps were identified: A) ingress into concrete, B) disruption of passive film and onset of corrosion, C) accumulation of corrosion products, and D) concrete cracking or spalling. One laboratory study found the deicer corrosivity rank order to be (most corrosive to least corrosive): $CaCl_2$, $MgCl_2$, NaCl, and calcium magnesium acetate (CMA); it was cautioned that testing method and conditions substantially affect the results and that laboratory results were often not indicative of field effects (Shi, 2009). Organic constituents, particularly nitrogen-containing heterocyclic compounds, have been observed to effectively inhibit corrosion (Ardagh, 1993).

Deicing toxicity and ecotoxicity effects:

The release of deicing materials in the environment adversely impacts living organisms through direct, toxic effects, either related to deicing components (e.g., Na^+ and Cl^-) or to co-contaminants (e.g., metals, ammonia), and indirect effects related to the alteration of their environment (i.e., water or soil) or nutrient sources. Deicer-induced changes in surface water properties and may affect aquatic organisms via the following mechanisms: increase of water density and stratification of lakes and ponds leading to oxygen and nutrient depletion in the bottom layers; increase of nutrients and essential ions (e.g., sodium, sulfate, phosphorous, and nitrogen) leading to eutrophication and oxygen depletion; increase of BOD leading to oxygen depletion; leaching of toxic metals; and reduction of hardness leading to higher toxicity of metals. Deicers also affect soil properties, which may negatively impact the vegetation as follows; reduction of soil permeability and water availability; displacement and leaching of nutrients (e.g., calcium and magnesium); increase of soil pH limiting nutrient uptake; and alteration of soil microbiology.

Salt deicers can directly negatively impact the roadside vegetation. Ten to 55% of roadside trees have been reported to be affected by application of chloride-based salts (Fay and Shi, 2012). The negative impact of salt on trees decreases quickly with the distance from the road, with little effects observed beyond 10 m from the roadside. Shrubs and grasses are generally more tolerant than trees, with pines and sumacs being among the most sensitive species. Plants take up dissolved deicer ions through the roots from where they are translocated to the aerial parts. Positive correlations have been observed between Na^+ and Cl^- concentrations in plant tissues and roadway salt application (Bryson and Barker, 2002). Both Na^+ and Cl^- are toxic to vegetation when excessive accumulation occurs. NaCl concentrations from 0.5 to 2% (dry weight) may cause a range of physiological damages to plant tissues and organs, including reduced germination, flowering, and shoot and root growth, osmotic stress, leaf browning, leaf drop, vulnerability to stresses and diseases, and death (Environment Canada, 2000; Fay and Shi, 2012).

Most aquatic species are rather tolerant to high salt concentrations (up to 1,000 mg/L; likely due to the natural high variability of salts in freshwater), which are rarely reached due solely to the presence of deicer salts: for instance, rainbow trout can tolerate up to 20,000 mg Cl^-/L, although some other species, such as water flea, are affected by concentrations below 1,000 mg Cl^-/L. As a point of reference, the EPA maximum concentration for chlorides in surface water is 860 mg/L and 230 mg/L for acute and chronic effects to aquatic organisms, respectively (CDOT, 2001).The effects of deicers on aquatic organisms decreases with the distance from the road, with the greatest impacts occurring within 50 m of the roadside.

Aquatic species often used for toxicity tests in fresh water include water fleas (e.g., *Daphnia magna*, *Ceriodaphnia dubia*), fishes (e.g., *Pimephales promelas*, *Oncorhynchus mykiss*), and microalgae (e.g., *Selenastrum capricornutum*); toxicity results are presented in the appendix Table 1 (Environment Canada, 2000). Rainbow trouts were shown to be the most tolerant, while water fleas and fathead minnows (and their embryos) were the most sensitive. Seven-day LC50 ranges from 1,440 mg NaCl/L for fathead minnows to 11,100 mg NaCl/L for rainbow trout. These levels are well above the reported concentrations in surface water, even impacted by deicer salts, which are usually in the range of 20 to 100 mg NaCl/L. Aquatic toxicity tests on the acetate-based deicer, CMA, reveals lower toxicity to fishes, but higher toxicity to water fleas (Appendix Table 2). Other studies have concluded that $MgCl_2$ deicers were more toxic to fishes and invertebrates than either NaCl or $CaCl_2$ (Environment Canada, 2000).

Specific components of deicers or deicer additives may also exert specific toxicity to aquatic wildlife. For instance, a study by Lewis (2000) on the deicer, Caliber M1000, which contains high levels of phosphorous, nitrogen, and organic carbon, showed that its regular usage can increase ammonia levels in surface water leading toxic effects to trout and other aquatic organisms at concentrations as low as 0.02 mg/L.

Conclusion:

Based on available literature, it seems that direct toxic effect of deicers on aquatic organisms and humans seems unlikely, due to the low inherent toxicity and high dilution rate of these materials in the receiving waters. Only very localized (e.g., roadside soil) or temporary events (e.g., pulse of deicers in streams after winter storm) can results in direct toxic effects on plants and aquatic organisms.

On the other hand, evidence of salt buildup in soil, groundwater, and lakes, and the resulting increase of the background concentration of deicer ions in surface water over the last 50 years is a greater concern as it could lead to unsuspected, long-term effects on the environment, such as changes in species distribution, reduction of biodiversity, and spread of invasive species. Potential long-term effect on aquifer quality and water supplies is also a serious concern.

References:

Adams, E. E., Alger, R. G., Chekan, J. P., Williams, F. D., and Valverde, R., "Persistence of Reduced Snow to Pavement Shear Strength for Two Aggregate Materials Treated with CMA and NaCl," Chemical Deicers and the Environment, F. M. D'Itri, Ed., Lewis Publishers, Chelsea, MI, 1992, pp. 481–493.

Akin, Michelle and Xianming Shi, "Development of Standard Laboratory Testing Procedures to Evaluate the Performance of Deicers", *Journal of Testing and Evaluation*, 40(6), 1-11, 2012.

Albright, M. "Changes in water quality in an urban stream following the use of organically derived deicing products," *Lakes and reservoir Management*, 21 (1), 119-124, 2005.

Ashworth, T., Weyland, J. A., Lu, L. L., Epwing, A. P., and Wheeler, R. D., "Evaluation of South Dakota Deicer No. 2 and Calcium Magnesium Acetate by Shear Testing," Transportation Research Record, 1246, Transportation Research Board, National Research Council, Washington, D.C., 1989, pp. 1–8.

ASTM D1177–12, "Standard Test Method for Freezing Point of Aqueous Engine Coolants," ASTM International, West Conshohocken, PA, 2012.

Backstrom M., Karksson, S., Backman, L., Foleson, L., and Lind, B. "Mobilization of heavy metals by deicing salts in a roadside environment," *Water Research*, 38 (3), 720-732, 2004.

Bernardin, S., Laforte, J. L., and Louchez, P., "Runway Deicer Study—Determination of a Testing Procedure," Transport Canada Airports, Ottawa, ON, 1996.

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

Chappelow, C. C., McElroy, A. D., Blackburn, R. R., Darwin, D., de Noyelles, F. G., and Locke, C. E., "Handbook of Test Methods for Evaluating Chemical Deicers," Strategic Highway Research Program Report No. SHRP-H-332, National Research Council, National Academy of Sciences, Washington, D.C., 1992.

Colorado Department of Transportation – CDOT, "Evaluation of Selected Deicers Based on a Review of the Literature", Report No. CDOT-DTD-R-2001-15, October 30, 2001.

Environment Canada, "Canadian Environmental Protection Act, 1999 Priority Substance List Assessment Report – Road Salts", Draft for Public Comments, Environment Canada, Health Canada, August 2000.

Fay, L. and Shi, X., "Environmental Impacts of Chemicals for Snow and Ice Control: State of the Knowledge," *Water Air and Soil Pollution*, 223 (5), 2751-2770, 2012.

Jackson, R. and Jobbagy, E., "From icy roads to salty streams," *Proceedings of the National Academy of Sciences of the USA*, 102 (41), 14487-14488, 2005.

Ketchum, S. A., Minsk, L. D., Blackburn, R. R., and Fleege, E. J., "Manual of Practice for an Effective Anti-Icing Program: A Guide for Highway Maintenance Personnel,"Report No. FHWA-RD-95–202, Federal Highway Administration, Washington, D.C., 1996.

Kakuturu, S.P. and Clark, S.E. “Clogging mechanisms of stormwater filter media by NaCl as a deicing salt,” *Environmental Engineering Science*, 32 (2), 141-152, 2015.

Kirchner, H. W., “Comparative Study of Chemical Deicers: Undercutting and Disbondment,” Chemical Deicers and the Environment, F. M. D’Itri, Ed., Lewis Publishers, Chelsea, MI, 1992, pp. 495–517.

Lewis, Jr. W., "Preliminary Environmental Evaluation of Caliber M1000 for Use in Colorado, Final Report,". Prepared for Colorado Department of Transportation, 2000.

Lofgren, S. “The chemical effects of dicing salt on soil and stream water of five catchments in southeast Sweden,” *Water Air and Soil Pollution*, 130 (1-4), 863-868, 2001.

McFarland, B. and O’Reilly, K., "Environmental Impacts and Toxicological Characteristics of Calcium Magnesium Acetate (CMA)," In Chemical Deicers and the Environment, D’Itri (ed), Lewis Publishers, Inc., 1992.

Muthumani, A., Fay, L., Akin, M., Wang, S., Gong, J., Shi, X., “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, 2014.

National Research Council – NRC, "Highway Deicing: Comparing Salt and Calcium Magnesium Acetate," Transportation Research Board, Washington, D.C., 1991.

Novotny, E.V., Murphy, D., and Stefan H.G. “Increase of urban lake salinity by road deicing salt,” *Science of the Total Environment*, 406 (1-2), 131-144, 2008.

Ramakrishna, D. and Viraraghavan, T., "Environmental impact of chemical deicers - A review," *Water Air and Soil Pollution*, 166 (1-4), 49-63, 2005.

Ruth, O. “The effects of de-icing in Helsinki urban streams, southern Finland,” *Water Science and Technology*, 48 (9), 33-43, 2003.

Shi, X.M., Fay, L., Yang, Z.X., Nguyen, T.A., and Liu, Y.J. “Corrosion of deicers to metals in transportation infrastructure: introduction and recent developments,” *Corrosion Reviews*, 27 (1-2), 23-52, 2009.

Shi, X., Veneziano, D., Xie, N., and Gong, J., "Use of chloride-based ice control products for sustainable winter maintenance: A balanced perspective," *Cold Regions Science and Technology*, 86, 104-112, 2013.

Smith, D.W., Facey, R.M., Novotney, V., Kuemmel, D.A. “Management of winter diffuse pollution from urban areas; effects of drainage and deicing operations” in *Cold Regions Impact on Civil Works*, pp 243-257, 1998.

Western Transportation Institute, Montana State University, “Development of Standardized Test Procedures for Evaluating Deicing Chemicals”, Clear Roads partners with the Pacific Northwest Snowfighters (PNS), Final report for Project 0092-08-32/CR07-02, March 2010.

Western Transportation Institute, Montana State University, “Correlating Lab Testing and Field Performance for Deicing and Anti-icing Chemicals (Phase I)”, Clear Roads partners with the Pacific Northwest Snowfighters (PNS), Final report for Project 0092-10-17/CR09-01, August 2010.

Appendix:

Table 1: Toxicity of Fish and Invertebrates Exposed to Sodium Chloride for One to Seven Days (Environment Canada, 2000; CDOT, 2001)

Species	Common Name	NaCl (ppm)	Chloride ion (ppm)	Response	Exposure	Reference
Lepomis macrochirus	Bluegill (fish)	14,000	8550	LC50[1]	24 hr	Doudoroff and Katz 1953
Daphnia magna	Water flea	7754	4704	LC50	24 hr	Cowgill et al 1990
Daphnia pulex	Water flea	2724	1652	LC50	24 hr	Cowgill et al 1990
Ceriodaphnia dubia	Water flea	2724	1652	LC50	24 hr	Cowgill et al 1990
Ceriodaphnia dubia	Water flea	2308	1400	LC50	72 hr	Cowgill et al 1990
Daphnia magna	Water flea	3054	1853	LC50	72 hr	Anderson 1948
Chironomus attenatus	Chironomid (midge)	6637	4026	LC50	72 hr	Thorton and Sauer 1972
Pimephales promelas	Fathead minnow	7650	4640	LC50	72 hr	Adelman et al 1976
Lepomis macrochirus	Bluegill (fish)	9627	5840	LC50	72 hr	Birge et al 1985
Oncorhynchus mykiss	Rainbow trout	11,112	6743	LC50	72 hr	Spehar 1987
Pimephales promelas	Fathead minnow embryos, survival	1440	874	LC50	7-day	Beak 1999
Ceriodaphnia dubia	Water flea, mean brood size	1761	1068	EC50	7-day	Cowgill and Milazzo 1990
Oncorhynchus mykiss	Rainbow trout egg embryo, survival	2400	1456	LC50	7-day	Beak 1999
Daphnia magna	Water flea, mean brood size	4040	2451	LC50	7-day	Cowgill and Milazzo 1990
Pimephales promelas	Fathead minnow larvae, growth	4990	3029	EC50	7-day	Beak 1999

[1] = Concentration that is lethal to 50% of the test organisms. A higher LC50 value means lower toxicity of the chemical.

Table 2. Aquatic toxicity of CMA to fish and invertebrates (McFarland and O'Reilly, 1992; CDOT, 2001).

Test Species	**Test Method**	**LC50[1] (ppm)**	**Reference**
Rainbow trout (*Oncorhynchus mykiss*)	Acute Static 96-hour	17,500	Horner 1990
Rainbow trout	Acute Static 96-hour	18,700	Winters et al 1985
Rainbow trout	Chronic Larval static Renewal-45 days	NOEC[2] = 1000	Horner 1990, Winters et al 1985
Fathead minnow (*Pimephales promelas*)	Acute Static 96 hour	12,500	Horner 1990
Fathead minnow	Acute Static 96 hour	21,000	Winters et al 1985
Daphnia magna	48-hour Acute	>1000	NW Aquatic Lab 1990
Daphnia magna	96-hour Acute	2000	Horner 1990
Amphipod (*Hyalella azteca*)	Flow-through 14 days	2000	Horner 1990

[1] = A higher the LC50 value means lower toxicity to test animals
[2] = No Observed Effects Concentration (NOEC)

Sodium chloride – rock salt and salt brine

1. General description: Sodium chloride – NaCl (as crystals - rock salt - or aqueous solution - salt brine) is by far the most common deicing material use for winter maintenance of roads and highways. NaCl has the advantage of being inexpensive and readily available in large quantities: 36 million metric tons of NaCl are mined annually in the U.S., with about 50% being applied on paved surfaces for deicing (Jackson and Jobbagy, 2005). However, NaCl has limited efficacy at low temperature and causes corrosion, rusting steel in motor vehicles, metallic structures, and concrete structures. NaCl applied on pavement can also negatively impact roadside vegetation, soils properties, surface and groundwater quality, and air quality, which in turn can result in secondary effects on aquatic wildlife and human health.

2. Intended uses and applications: NaCl is the most cost-effective deicing product available on the market for highway winter management. NaCl can be applied on pavement as rock salt (deicing) or salt brine (anti-icing). Since salt water still freezes at -18 °C (0 °F), it is therefore not effective below this temperature. As it simply consists of NaCl, both rock salt and salt brine are offered on the market by a multitude of distributors. Salt brine can be used as pre-wetting agent for rock salt: in order to start its deicing action, rock salt must first form brine. Pre-mixing rock salt with water therefore helps the salt dissolve more quickly and begins working faster.

3. Physical and chemical properties: Rock salt is made of 90 to 100% NaCl, which is an odorless, white crystal, with a specific gravity of 2.165 10^3 kg/m^3. It is readily soluble in water (solubility 359 g/L). Salt brine is an aqueous solution that contains approximately 26% NaCl by weight. It is odorless, white, and cloudy, with a specific gravity of approx. 1.2 kg/m^3 and a neutral pH (6-8). Rock salt and salt brine are stable and non-hazardous materials. They are corrosive to metal upon prolonged contact.

4. Toxicity and ecotoxicity:
Inhalation: NaCl dust is irritant to the respiratory tract.
Skin Contact: NaCl contact removes natural skin grease, causing dryness, cracking and dermatitis. Repeated and/or prolonged skin contact causes irritation.
Eye Contact: NaCl dust causes eye irritation.
Ingestion: Ingestion of NaCl in large quantities cause vomiting and diarrhea.
Long-Term Exposure: Repeated ingestion of large amounts of NaCl causes disturbance of body electrolyte and fluid balance.
Animal Toxicity: NaCl in the form of rock salt or salt brine is characterized by a rather low toxicity: e.g., rock salt: rat 4-hour oral lethal dose 50% (LD50) = 3,000 mg/kg, rat 1-hour inhalation (dust) lethal concentration 50% (LC50) > 42,000 mg/m^3; salt brine: rat 4-hour oral LD50 > 90 mL/kg.
Ecotoxicity: NaCl is practically non-toxic to aquatic organisms on an acute basis (LC50/EC50 >100 mg/L in the most sensitive species tested): LC50, fathead minnow (*Pimephales promelas*) 10,610 mg NaCl/L, LC50 water flea (*Daphnia magna*) 4,571 mg NaCl/L, IC50 algae > 1,000 mg NaCl/L.

5. Storage and stability conditions: Although guidelines for storage of rock salt and salt brine vary locally, general guidelines can be found from U.S. EPA (http://water.epa.gov/polwaste/npdes/swbmp/Road-Salt-Application-and-Storage.cfm). Generally speaking, storage guidelines intend to prevent the release of salts in soil, groundwater, and nearby streams and ponds, as contamination of local waterways often originates from improper storage. Deicer salts are very soluble when they come into contact with stormwater and they can contaminate groundwater used as

water supplies and surface waters. Rock salt should be stored indoor or properly covered, preventing salt from aggregation, salt loss with stormwater runoff, and contamination to streams and aquifers. Salt should be stored outside 100-year floodplain and at a minimum distance from stream, ponds, and wetland for preventing surface water contamination. Salt brine containers are recommended to be stored in secondary containment tanks or vessels.

6. <u>Advertised benefits</u>: Rock salt and salt brine are often presented as inexpensive deicers that are easy to store, handle, and apply. They are also presented as natural products that have been successfully applied on U.S. roads for decades. As compared with rock salt, salt brine is often described as more effective, leading to reduced application rates (e.g., 15 – 30 % less salt) and reduced release of chlorides into the environment.

7. <u>Application rate</u>: The recommended application rates for rock salt depend on the type of the storm (Type 1 to 5). For a Type 3 storm (i.e., 1 – 6 inches of snow/frozen precipitation in 24 hours), one recommends 100 lb. rock salt (or 44 gal. brine)/lane-mile above 32 °F and 200 lb. rock salt/lane-mile at 20 - 32 °F. (For application rates prior or during other storm types, see for instance http://epg.modot.org/index.php?title=133.5_Operator%E2%80%99s_Guide_for_Anti-Icing.)

8. <u>Cost:</u> Road salt is relatively inexpensive with an average cost of $50 - $60 per ton, i.e., $2.50 - $7.50 per lane-mile (based on application rates of 100 to 300 lb./lane-mile). 23%-salt brine costs approx. $0.05 – 0.06 per gal., i.e., $2.40 - $7.20 per lane-mile (based on application rates of 44 to 132 gal./lane-mile) (www.summitengineer.net/attachments/351_Salt%20Brine%20Use.pdf).

9. <u>Performance</u>: Lb. of ice melted per lb. NaCl: 3.7 at 0 °F, 4.9 at 10 °F, 8.6 at 20 °F, and 46.3 at 30 °F. One lb./lane-mile of rock salt is equivalent to approx. 0.44 gal./lane-mile of 23% by weight salt brine (www.summitengineer.net/attachments/351_Salt%20Brine%20Use.pdf).

<u>Performance:</u> SDS sheets from various distributors of rock salt and salt brine.

AquaSalina

1. General description: AquaSalina is manufactured by Nature's Own Source, LLC. The manufacture claims that AquaSalina is natural saltwater solution produced from ancient seas and naturally contains a combination of chlorides (10.3% calcium chloride, 7.7% sodium chloride, 2.6% magnesium chloride, and 1.5% potassium chloride). It is, in fact, made from brine that comes up from conventional oil and gas wells (not horizontal shale wells), i.e. produced water from wells that have been in production for a year or more (http://www.crainscleveland.com/article/20131201/SUB1/312019990/calling-a-deicer-toxic-leads-to-heated-exchanges).

2. Intended uses and applications: According to the manufacture, AquaSalina can be effectively used for pre-wetting rock salt, anti-icing, or deicing. For pre-wetting, it can achieve a water freezing point of -15 °F after applying the pre-wet rock salt to the road. To achieve anti-icing, it has been applied to the roadway up to 72 hours in advance of a storm to assist in the prevention of ice bond to the pavement. It should bond to the road surface better than conventional salt brine. For deicing, it can be applied to bridges prior to freezing, icing, or other winter weather conditions, or in heavier amounts to deicing ramps and bridges that have frozen.

3. Physical and chemical properties: Please see the table below.

4. Toxicity and ecotoxicity: Other than mild eye irritation, no acute local toxicity or other acute adverse effects have been reported.

5. Storage and stability conditions: According to the manufacture, AquaSalina does not require mixing, no additional chemicals, no storage maintenance, or no recirculation; it can be directly delivered into tanks, ready to use, and there is no need for brine makers or chemical additives. Plastic storage vessels are recommended. When handling the product, water-proof gloves and safety glasses are required._

6. Advertised benefits: Provided by manufacturer

- ♦ Reduces capital costs - requires no mixing, digesting and no clean-up and disposing of leftover limestone grit
- ♦ *Filtered* to one (1) micron absolute, keeping insolubles out of users' tanks and nozzles, thus less downtime on equipment
- ♦ *Produced* from natural sources, not freshwater
- ♦ Enhances performance of rock salt and extends users' supply
- ♦ ***Effective*** at colder temperatures
- ♦ ***Melts*** more ice than salt brine
- ♦ Delivered to users' tank ready to use

7. Application-volume: For pre-wetting – typically 10 gallons per lane mile of salt; for anti-icing – 50 gallons per lane mile, both depending on the operator and pavement condition. For deicing ramps and bridges, higher application rates are recommended but not specified by the manufacture.

8. Cost: $0.70 per gallon, $7.0 per lane mile of salt for pre-wetting or $35.0 per lane mile for anti-icing.

9. Performance: The manufacture reported a higher ice melting effectiveness of AquaSalina than salt brine: 1.4 vs. 0.8 mL ice melted per mL deicer at 15 °F, or 2.0 vs. 1.2 mL ice melted per mL deicer at 5 °F, respectively **(SHRP 205.1 Test)**. Its corrosion rate was reported by the manufacture to be 28.5% of that of salt brine **(NACE/PNS Corrosion Test**).

BEET HEET

1. General description: BEET HEET® Concentrate is an organic based calcium chloride deicer, to be used as an anti-icing and deicing agent. According to the manufacturer, BEET HEET® Concentrate is an organic based, corrosion inhibited, liquid pre-wetting agent, anti-icer/deicer containing four ice melting chlorides and four highly refined carbohydrates. BEET HEET® Concentrate has passed the testing standards of the Pacific Northwest Snowfighters and is listed on the PNS Qualified Products List.

2. Intended uses and applications: BEET HEET® Concentrate is a ready-to-use salt pre-wetting agent developed to provide ice melt, anti-bonding, and residual capacity. BEET HEET® Concentrate can also be blended with 23.3% NaCl brine to create a salt pre-wetting agent or direct application deicer/anti-icer.

3. Physical and chemical properties: BEET HEET is an aqueous solution containing an agricultural based organic, calcium chloride, magnesium chloride, sodium chloride, and potassium chloride. Please see table below.

4. Toxicity and ecotoxicity: BEET HEET can cause severe eye irritation and significant skin irrigation. Single dose oral exposures have not been conducted, but toxicity is not expected. When handling the product, normal precautionary measures are necessary including goggles, flushing of skin contact areas with fresh water, and avoiding contact with skin and eyes. Ecotoxicity data for BEET HEET is not available.

5. Storage and stability conditions: BEET HEET Concentrate and BEET HEET blends can be stored just like 23.3% salt brine; generally, 3,000-6,000 gallon plastic storage tanks (e.g., polyethylene) in a secondary container are suggested. BEET HEET is slightly corrosive to metals, and contact with strong acids should be avoided. BEET HEET does not require special tanks or pumps. If the product has been sitting idle for more than three weeks, the manufacturer does recommend that the product be recirculated prior to using. Per the manufacturer, BEET HEET is stable, and neither sedimentation nor bacterial growth should be expected._

6. Advertised benefits: Provided by manufacturer
- More effective at 15^{o}F and 25^{o}F than the competition
- Reduced salt application rate – e.g., 39.4% savings compared to untreated rock salt
- Financial savings
- Fully processed and contains no beet pump, dirt, or other sediments; does not need to be filtered

7. Application-rate: 5 gallons/ton rock salt.

8. Cost: $1.14 per gallon.

9. Performance: The manufacturer provides many points of contrast at 15^{o}F and 25^{o}F; only the contrasts to untreated and brine treated rock salt are shown below:
- At 25^{o}F, 64.1% more ice melted than brine (23.3%) treated salt
- At 25^{o}F, 65.1% more ice melted untreated salt
- At 15^{o}F, 150% more ice melted than brine (23.3%) treated salt
- At 15^{o}F, 153.2% more ice melted than untreated salt

GreenBlast (formerly Green Boost)

1. General description: GreenBlast™ from Cargill Deicing Technology is a patent pending magnesium chloride based liquid additive. When added at 20% to salt brine, it can enhance performance of salt brine by reducing the freezing point, increasing ice melting performance at cold temperatures, allowing the brine to absorb more precipitation before refreeze at cold temperatures, and reducing brine corrosiveness. It should have less biochemical oxygen demand (BOD) impact on the environment. It meets the Pacific Northwest States specifications for corrosion, storage, and trace element analysis.

2. Intended uses and applications: GreenBlast is a liquid performance enhancer for salt based anti-icing liquids, and pre-wetting agents. It should not be used as a stand-alone anti-icing or deicing liquid treatment.

3. Physical and chemical properties: Please see table below.

4. Toxicity and ecotoxicity: It has potential eye, skin, respiratory, and gastrointestinal irritation. Toxicological and ecological information is only available for magnesium chloride: Oral LD50 Rat > 90 mL/kg, 96 hr. LC 50 *Gambusia affinis* 4210 mg/L, 96 hr. LC50 *Pimephales promelas* 1970-3880 mg/L, 72 hr. EC50 *Desmodesmus subspicatus* 2200 mg/L, 24 hr. EC50 *Daphnia magna* 140 mg/L, and 48 hr. EC50 *Daphnia magna* 140 mg/L.

5. Storage and stability conditions: GreenBlast is stable, moderately viscous, and may flow slowly at very cold temperature. It may cause slipperiness hazards when diluted or over-applied. It is stored in bulk or 230 gallon totes and shipped by truck in bulk quantities. Containers should be tightly closed and kept in a cool, well-ventilated place. When handling the product, normal precautionary measures are necessary including goggles, flushing of skin contact areas with fresh water, and avoiding contact with skin and eyes._

6. Advertised benefits: Provided by manufacturer

- Greater residual effect to help delay freeze
- Corrosion protection
- Lower the freezing temperature of brine that is applied to the road, resulting in hard pack that will not stick
- Reduced environmental impact
- Budget-friendly

7. Application-volume: up to 20% with salt brine

8. Cost: $1.75 per gallon.

Magic Minus Zero

1. General description: Magic Minus Zero® is produced by Innovative Surface Solutions and is a proprietary blend of magnesium chloride and agricultural by-products that has been EPA recognized as safer for the environment and authorized to carry the Design for the Environment (DfE) emblem. The product meets the Pacific Northwest Snowfighters requirements for performance, corrosion, and toxicity.

2. Intended uses and applications: Magic Minus Zero® can be used as an anti-icer for pre-wetting salt. It should not be used as a stand-alone anti-icing or deicing liquid treatment.

3. Physical and chemical properties: Magic Minus Zero is an aqueous solution containing 22.4% magnesium chloride and 20% molasses. Please see table below.

4. Toxicity and ecotoxicity: Skin and eye irritation may occur, but very low toxicity is generally expected. When handling the product, normal precautionary measures are necessary including goggles, flushing of skin contact areas with fresh water, and avoiding contact with skin and eyes. Ecotoxicity data for Magic Minus Zero is not available, but is likely similar to that of magnesium chloride (e.g., 24 hr. EC50 *Daphnia magna* 140 mg/L).

5. Storage and stability conditions: Magic Minus Zero® can be stored in a standard 3,000 – 6,000 gallon plastic storage tank. If the product is going to be stored long term, an agitator is suggested to address potential settling. The product should be recirculated every 30 days. If the product is stored for several months, the specific gravity should be check (1.302 kg/L expected) prior to use to ensure that substantial evaporation has not occurred._

6. Advertised benefits: Provided by manufacturer

- Works at subzero temperatures
- Reduces cost based on time, labor, material, and fuel savings
- Superior residual effects
- Helps reduce chloride and sodium discharges into the environment; improves water quality
- Exhibits lower biochemical and chemical (BOD and COD, respectively) than other additives
- Is less corrosive than salt brine

7. Application-volume: per manufacturer recommendations

- Anti-icing: 25 gallons per lane mile
- Stockpile treatment: 5-7 gallons/ton
- Onboard pre-wetting: 5-15 gallons/ton

8. Cost: $1.11/ gallon.

9. Performance: Manufacturer provided eutectic points

- Salt brine: -6^{o}F
- Magic Minus Zero®: -40^{o}F

Tested Materials	Rock Salt (NaCl)	Salt Brine	AquaSalina	BEET HEET (Concentrate)	GreenBlast	Magic Minus O
Manufacturer		Compass Minerals International, Compass Minerals, etc.	Nature's Own Source	K-Tech Specialty Coatings	Cargill Deicing Technology	Innovative Surface Solutions
Physical State	Solid	Liquid	Liquid	Liquid	Liquid	Liquid
Composition						
NaCl	90 - 100%	20 – 40%	7.7%	3.7%		
KCl			1.5%	2.7%		
$CaCl_2$			10.3%	11.9%		
$MgCl_2$			2.6%	3.4%	26 – 29%	22.4%
Organic				Carbohydrate 28.8%		Molasses 20%
Other					Performance enhancer 0.2%	
					Corrosion inhibitor 0.3%	
					BOD 15,400 mg/L	
Physical Properties						
Specific Gravity (g/mL)	2.7	1.201 (26%)	1.21	1.28 – 1.30	1.270 – 1.295 @ 60 °F	1.302
pH	6 – 8 (neutral)	6 - 9	5.2 – 5.5	6 - 9	8.2 - 8.6 (1:4 dilution)	3 - 5
Freezing Point	N/A	29.6 °F	-8 °F	ND	ND	
Odor	Odorless	Odorless	Odorless	Chocolate, syrup, coffee	Odorless	Pleasant

Appearance	White crystal	Clear	Clear	Dark Brown liquid	Green liquid Moderately viscous liquid	Brown liquid
Recommended Application Rate			10 gal/lane mile of salt for pre-wetting, 50 gal/lane mile for anti-icing		Performance enhancer to be blended at up to 20% with salt brine	25 gal/lane mile
Cost			$0.70 per gallon	$1.14 per gallon	$1.75 per gallon	$1.11 per gallon
Use and advertised Benefits			Anti-icing or pre-wetting solution to wet rock salt, applied up to 72 hours in advance of a storm, deicer applied in heavier amounts to deice ramps and bridges that are frozen over	Higher ice melting capacity than 32% NaCl at 0, 10, and 20 °F	Lower brine freezing point, higher brine ice melting capacity at cold temperatures, absorb more precipitation before refreeze, lower brine corrosiveness	Used as an anti-icer, deicer or for pre-wetting salt. High viscosity making it effective as stockpile pre-treatment

Deicer performance evaluation:

- The modified SHRP ice melting test to measure the amount of brine formed after mixing the deicers with ice at (4) four different times (10, 20, 40, and 60 min) at 25, 15, and 0 °F. Specifically, 1.0 g of solid deicer or 0.9 mL of liquid deicer will be applied (equivalent field rate of 144 or 245 gal/lane mile, respectively) to 25 mL of ice (thickness of 0.19 in.). For pre-wetting agents or liquid additives, the product will be mixed with either rock salt or salt brine per manufacturer recommendation prior to conducting the tests. Rock salt and salt brine will be tested as references. Manufacturer recommended deicer concentrations will be tested if needed based on the above testing results. The team will estimate the field application rate based on the manufacturer recommended rate and the results of deicing performance tests.
- The freezing point test (ASTM D1177-12) to obtain eutectic curves of the deicers at different solution concentrations. A minimum of ten concentrations will be tested by dissolving/diluting the given products to different extents.

Deicer materials water quality and corrosion assessment:

- pH - APHA 4500-H^+
- Biochemical oxygen demand (BOD) - APHA 5210-B, 5 day test
- Chemical oxygen demand (COD) – APHA 5220 D (Hach)
- Metals analysis, including As, Ba, Cd, Cr, Cu, Pb, P, Se, and Zn, via Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis per PNS; mercury (Hg) will also be analyzed via ICP-MS, which is a state of science method
- Ammonia – APHA 4500-NH_3 D, ammonia selective electrode
- Nitrate – APHA 4500-NO_3^- D, nitrate selective electrode method
- Nitrite – APHA 4500- NO_2^- B, colorimetric method (Hach)
- Organic nitrogen – Block digestion (Hach)
- Total nitrogen – APHA 4500-N C, persulfate oxidation (Hach)
- Phosphorus – APHA 4500-P C, acid hydrolysable (Hach)
- Corrosion analysis testing per PNS 72 hr. cyclic method. Each round of testing will include four reference stations as follows: distilled water, NaCl, $MgCl_2$, and $CaCl_2$.

Deicer toxicity and ecotoxicity assessment:

Methods initially proposed for Task 4 - Deicer toxicity testing include the following fish bioassays: fathead minnow (*Pimephales promelas*) and rainbow trout (*Oncorhynchus mykiss*) toxicity tests - EPA-600/4-91/002, ASTM E729 – 96, ASTM E1192 − 97.

A review of the literature revealed that rainbow trout is much less sensitive than fathead minnow upon exposure to deicing materials: e.g., 72-hour LC50 11,100 mg NaCl/L for rainbow trout and 7,600 mg NaCl/l for fathead minnow. Because of the inherent low toxicity of deicers, we believe that the rainbow trout toxicity test will therefore provide limited information and will, at best, only duplicate the fathead minnow test.

We therefore propose to substitute the initial Rainbow Trout Toxicity Test with the Fathead Minnow Embryo-Larval Survival and Teratogenicity Test described in Section 12 of the EPA-600/4-91/002 method.

Task 4 methods will therefore include the followings:

- Freshwater alga, *Pseudokirchneriella subcapitata* (formerly known as *Selenastrum capricornutum*), algal growth assay - EPA-600/4-91/002, ASTM E1218 - 04.
- Aquatic daphnid (invertebrate), *Ceriodaphnia dubia*, survival and reproductive assays - EPA-600/4-91/002, ASTM STP971.
- Fathead minnow (*Pimephales promelas*) toxicity test and embryo-larval survival and teratogenicity test - EPA-600/4-91/002, ASTM E729 – 96, ASTM E1192 − 97.
- Duckweed (*Lemna minor*) and vetch (*Vicia sativa*) germination and root elongation tests - EPA OPPTS 850.4200, ASTM E1415 – 91.

Project Report for Task 2.1 – Deicer Performance Testing

Executive Summary

Deicer product performance is an important consideration, both for understanding the environmental conditions (e.g., temperature) for which a product is expected to be effective and for the effectiveness and expected cost associated with using a product. Performance was evaluated using two tests: the ice melting test for the deicing performance, to determine the amount of ice melted at a set temperature for a specified amount of product; and the freezing point test for the anti-icing performance, to determine the eutectic curve of a product (i.e., freezing point as a function of deicer concentration).

The modified ice melting test results of the six deicers suggest that when temperature drops to 0°F, deicers should not be used for deicing purposes because they do not effectively deice and there is a risk of them re-freeze. For the two pre-wetting agents, Magic Minus Zero effectively improved the performance of rock salt at both 15 and 25°F; BEET HEET generally improved the performance of rock salt, but not to the same extent as Magic Minus Zero. For the liquid deicers, AquaSalina has a slightly higher ice melting capacity than salt brine at 15°F, particularly at longer reaction times, but not at 25°F. GreenBlast did not significantly affect the performance of salt brine at both temperatures.

The freezing point testing of all deicer solutions indicates that the two liquid deicers, AquaSalina and GreenBlast, have lower freezing points than salt brine of the same concentration, and thus, will have better anti-icing ability than salt brine. The freezing points of BEET HEET and Magic Minus Zero were similar to those of rock salt, suggesting the usage of these two pre-wetting agents will not change the anti-icing ability of rock salt.

When evaluating the performance of all deicers based on both deicing and anti-icing, AquaSalina always has the best performance and BEET HEET always has the worst performance.

When it comes to deicing, Magic Minus Zero also performs very well, while GreenBlast performs second to AquaSalina when it comes to anti-freezing.

Task 2.1.1 Ice Melting Test

Introduction

The objective of this sub-task was to test the performance of different types of deicers by evaluating their ability to melt ice at three temperatures (25, 15, and 0 ± 0.5 °F). Six products were tested, three liquids and three solids, in accordance with the request of the Pennsylvania Department of Transportation (PennDOT). Rock salt and salt brine were tested as the bench-mark materials for the solid and liquid deicers, respectively. This test is one of the two main components of the performance aspect for the project "Effective Use and Application of Winter Roadway Maintenance Material Enhancers".

Deicers

Rock salt is a solid deicer containing mostly sodium chloride and is one of the most commonly used deicers in the industry. Magic Minus Zero (from Innovative Surface Solutions) and BEET HEET (from K-Tech) are liquid products that are added to rock salt as pre-wetting agents according to the manufacturers' recommendations. The former is composed of 22.4% of magnesium chloride and 20% of molasses, while the latter is an agricultural based organic. According to the manufacturers, these pre-wetting agents will enhance the performance of rock salt. Per manufacturer's recommendation, Magic Minus Zero was mixed with rock salt at 10 gallons per ton of rock salt (rock salt amended with Magic Minus Zero will be simply referred to as Magic Minus Zero hereafter), while BEET HEET was mixed with rock salt at 5 gallons per ton of rock salt (rock salt amended with BEET HEET will be referred to as BEET HEET hereafter).

Salt brine, a liquid deicer, is an aqueous solution of 20 to 40% sodium chloride. For this experiment, 23.3% sodium chloride salt brine was used. GreenBlast from Cargill Deicing Technology is a patent pending liquid deicer containing 26 to 29% magnesium chloride. Before testing, GreenBlast was added to salt brine at 20% of the total volume of the solution (salt brine amended with GreenBlast will be referred to as GreenBlast hereafter). The last liquid deicer used was AquaSalina from Nature's Own Source, LLC, containing a total of 22.1% chloride salts, including sodium, potassium, calcium and magnesium chlorides. AquaSalina was used as received.

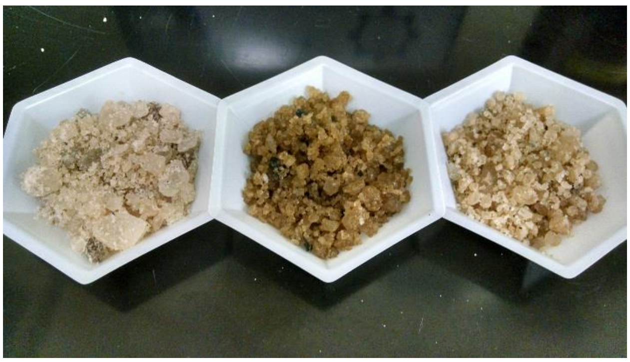

Figure 1: From left to right - Rock salt, Magic Minus Zero, and BEET HEET

Figure 2: From left to right - Salt brine, GreenBlast, and AquaSalina

Equipment and Materials

All equipment and materials used in this test matched those as specified by either the standard testing methods SHRP H-205.1 and H-205.2 or the modified ice melting test (Akin and Shi 2012). A Puffer Hubbard model IUF3023A upright freezer was used for all ice melting tests. The freezer was pre-set at -30°C by the manufacture but has a working temperature between -30 and -15°C. Prior to testing at each temperature, the freezer temperature was set to a few degrees lower than the required temperature. After each change of temperature, the freezer was allowed to equilibrate overnight. The freezer door was modified according to SHRP H-205.1 Annex 1, "Enclosure for Testing Deicers Inside an Upright Freezer" (Figure 3). A test enclosure was constructed according to the same source, with temperature controlled through the use of a 100W lightbulb attached to an Omega model CNI833 temperature controller and an Omega type T thermocouple with an accuracy of ± 0.5°C (Figure 4). The enclosure was kept inside the freezer for the duration of all tests. To allow for accurate temperature control at 25°F since the freezer has a maximum temperature of -15°C (5°F), a second 100W lightbulb was added to the enclosure and kept on continuously.

Figure 3: Modified freezer with a test enclosure inside.

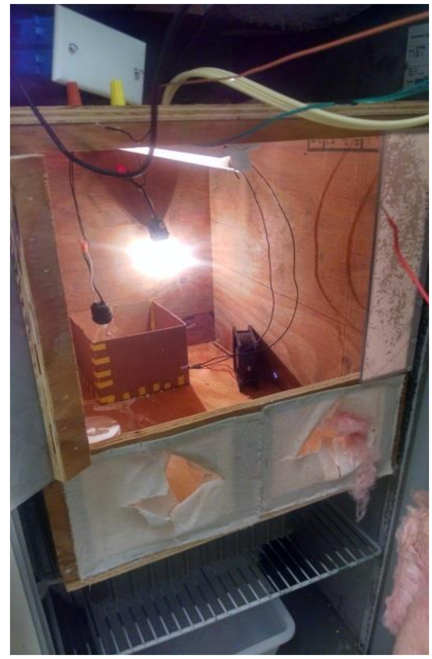

Figure 4: Test enclosure.

A large quantity of ice was added to the freezer beneath the enclosure to maintain stable temperatures, avoiding large and quick fluctuations with each opening of the hand port on the freezer door.

The Petri dishes used in this experiment were FisherBrand plastic 100 × 15 mm Petri dishes (Akin and Shi 2012). A 1-inch thick by 2.5-inch diameter of stock aluminum was used to smooth ice surfaces. For brine collection, 3 mL and 10 mL plastic disposable syringes were purchased. An analytical balance was used for measuring 1.000 ± 0.005 g samples of solid deicers. These samples were then placed in small labeled weighing dishes.

As specified in the standard methods, deicer solutions of 20%, 15%, and 10% (w:w) should be tested for their densities for converting volumes of brine collected into grams ice melted per gram deicer (details in "Data Analysis"). For the density testing, three 100 mL graduated cylinders were utilized. Samples of 20%, 15%, and 10% (w:w) concentrations of each product were prepared in 100 mL amber bottles with lids. Common personal protection equipment, including latex free gloves, goggles or other eye protection, and a lab coat were used.

Test Procedures

For this experiment, the modified Strategic Highway Research Program (SHRP) ice melting tests (SHRP H-205.1 and H-205.2) were followed. These modifications have been set forth by a PNS funded project entitled "Development of Standard Laboratory Testing Procedures to Evaluate the Performance of Deicers." The following temperatures were used for testing: 0°F (-17.78°C), 15°F (-9.44°C), and 25°F (-3.89°C).

The Petri dishes were filled with 25 mL of water prior to each experiment. Once the water froze, the surface of the ice was smoothed by the aluminum. After which the Petri dishes were returned to the enclosure set at the required testing temperature for at least an hour before testing. Samples of each deicer, 0.9 mL for liquid deicers in syringes and 1.0 gram for solid deicers in weighing dishes, were placed in the enclosure for at least one hour prior to each test.

Each product was run in triplicate at each temperature, with another Petri dish tested with salt brine as a control, necessitating four Petri dishes to be used at a time. Triplicate salt brine samples were also tested separately. Tests were begun by starting the timer and immediately broadcasting the sample evenly over the surface of the ice. This operation took no more than 30 seconds. There was a 2.5-minute interval between the start of each sample testing.

At 10, 20, 40, and 60 minutes, a syringe was used to intake the brine for measurement. In order to acquire all of the brine, it was helpful to slightly tilt the Petri dish and to lightly tap it on the bottom of the test enclosure. The ice remained attached to the Petri dishes mostly at 0 and 15°F. At 25 °F, the ice tended to float as a larger amount of ice had melted. Once all of the brine was within the syringe, the plunger was pulled until it rested at a predetermined measurement. After the volume of the brine was recorded, the brine was reapplied to the ice, making sure it evenly spread upon the surface. The measurement took no more than 1.5 minutes. The same procedure was repeated for the remainder of the Petri dishes at each time and for each of the remaining deicers.

At each temperature, it was also necessary to run density testing for later data analysis. Fifty gram solutions of 20%, 15%, and 10% concentration by weight were prepared for each product. Also, 50 gram solutions of salt brine, GreenBlast, and AquaSalina were prepared and referred to as 100%. The mass and volume of each solution at room temperature were first measured using a scale and a graduated cylinder. The solutions were then kept in the freezer preset at the current testing temperature for at least 1.5 hour before measuring their volumes. In order to calculate the density, the mass was divided by the volume so that density is measured in grams per milliliter. This process was repeated until all of the densities for each solution had been measured at the three testing temperatures.

Precautions

Care must be taken when extracting the brine from the Petri dishes, since heat can easily be transferred with handling the Petri dishes. When collecting the brine, we held the edge of the dishes instead of the bottom. Also, prolonged opening of the hand port can result in severe fluctuation in the temperature within the enclosure.

Data Analysis

In order to obtain the exact volume of brine collected, it was necessary to calibrate each type of syringe being used in the experiment. To do this, a known amount of liquid was withdrawn into the syringe. Then the plunger was slightly depressed to dispel any air from the needle, and the volume of the liquid was recorded (i.e., the actual volume). The syringe was turned so that the needle was pointing upward, and the plunger was pulled until it was in line with the last graduation. The volume of the liquid was recorded, and the difference between this apparent volume and the actual volume recorded above was then subtracted from each previously measured volume of brine to account for the conical shape of the plunger.

While volume of brine collected can be a useful measurement of the performance of deicers, a much more accurate comparison of ice melting capacities were made by calculating grams of ice melted per gram of deicer. To convert the volume of brine collected into grams of ice melted per gram of deicer for solid deicers, we took the average density of the three concentrations of the deicer solutions (10%, 15%, and 20%) and multiplied it by the volume of brine collected at the same temperature. For liquid deicers, it was necessary to find the density of each product first (the density of the liquid deicer applied, i.e., 100% concentration). This was done by multiplying 0.9 mL by the density to convert the amount of deicer applied into grams. Then we divided the volume of brine collected by the value above to convert into mL brine/g deicer. Finally, we took this value and subtracted it by the specific volume of the deicer solution, i.e., the inverse of the average densities at 10%, 15%, and 20% concentrations. An example of the calculations for salt brine is shown in Table 1.

Table 1. Example Calculation of Ice Melting Capacity in Gram Ice Melted per Gram deicer for Salt Brine.

Density: 1.1631 g/mL			0.9 ml salt brine = (0.9 ml) × (1.1631 g/ml) = 1.05 g	
Time (min)	mL Brine	mL Brine/g deicer	Average Density (g/mL)	Gram ice melted/gram deicer
10	1.8	1.7	1.0100	0.7
20	2.1	2.0		1.0
40	2.4	2.3		1.3
60	2.5	2.4		1.4

Results and Discussion

The values of the densities of the concentrations for each product at the three temperatures and at room temperature (70 °F) are listed in Table 2. The average densities of each deicer solution are shown in Table 3. Generally, density values of different concentrations at the same temperature have relative standard deviations of less than 5%. These numbers were used to convert brine volumes into grams of ice melted per gram deicer.

Table 2. Densities of Deicers at Different Temperatures (Unit: g/mL)

	10%				15%			
Deicer	**0°F**	**15°F**	**25°F**	**70°F**	**0°F**	**15°F**	**25°F**	**70°F**
Rock Salt	1.0124	1.0635	1.0560	1.0335	1.0323	1.0993	1.0776	1.0543
Magic Minus Zero	1.0134	1.0457	1.0527	1.0457	1.0536	1.0911	1.0849	1.0765
BEET HEET	1.0200	1.0533	1.0598	1.0415	1.0526	1.0864	1.0814	1.0639
Salt Brine	0.9343	0.9685	0.9988	0.9904	0.9491	0.9840	1.0025	1.0067
GreenBlast	0.9656	0.9752	1.0006	0.9946	0.9765	0.9856	0.9929	0.9960
AquaSalina	0.9383	0.9677	0.9987	0.9946	0.9459	0.9790	1.0206	1.0032

	20%				100%			
Deicer	**0°F**	**15°F**	**25°F**	**70°F**	**0°F**	**15°F**	**25°F**	**70°F**
Rock Salt	1.1375	1.1569	1.1511	1.1245	-	-	-	-
Magic Minus Zero	1.1384	1.1342	1.1448	1.1255	-	-	-	-
BEET HEET	1.1322	1.1450	1.1349	1.1193	-	-	-	-
Salt Brine	0.9765	1.0177	1.0288	1.0163	1.1814	1.1908	1.1814	1.1631
GreenBlast	0.9948	1.0118	1.0334	1.0151	1.1979	1.1890	1.1890	1.1715
AquaSalina	0.9759	1.0886	1.0389	1.0262	1.1871	1.1871	1.1778	1.1687

Table 3. Average Densities of Deicer Solutions with Standard Deviations (Unit: g/mL)

	Average Densities			Standard Deviations		
Deicer	**0°F**	**15°F**	**25°F**	**0°F**	**15°F**	**25°F**
Rock Salt	1.0607	1.1066	1.0949	0.0549	0.0385	0.0407
Magic Minus Zero	1.0685	1.0903	1.0941	0.0521	0.0361	0.0382
BEET HEET	1.0683	1.0949	1.0920	0.0471	0.0379	0.0316
Salt Brine	0.9533	0.9901	1.0100	0.0175	0.0205	0.0134
GreenBlast	0.9790	0.9909	1.0090	0.0120	0.0154	0.0176
AquaSalina	0.9534	1.0118	1.0194	0.0162	0.0545	0.0164

Table 4 includes the untreated data, showing the average volume of brine collected for each product at all three temperatures. Table 5 shows the corresponding standard deviations of the data points in Table 4. The average volumes of brine collected for rock salt and salt brine are mostly comparable to the reported values (Akin and Shin 2012). The small differences between our observed and the reported values are most due to the different sources and purity of the rock salt. Also, the small standard deviations in Table 5 suggest the quality of our data is acceptable.

Table 4. Average Volumes of Brine Collected for All Deicers (Unit: mL)

	0°F				15°F				25°F			
Time (min)	**10**	**20**	**40**	**60**	**10**	**20**	**40**	**60**	**10**	**20**	**40**	**60**
Rock Salt	0.0	0.0	0.1	0.2	0.6	1.0	1.8	3.7	1.3	3.0	5.3	6.3
Magic Minus Zero	0.0	0.0	0.0	0.1	1.0	1.9	3.3	4.4	1.9	3.9	5.9	7.2
BEET HEET	0.0	0.0	0.0	0.1	0.2	1.5	2.6	3.5	1.1	3.1	5.7	7.3
Salt Brine	0.8	0.7	0.7	0.5	1.2	1.3	1.4	1.3	1.8	2.1	2.4	2.5
GreenBlast	0.6	0.6	0.4	0.5	1.2	1.4	1.4	1.3	1.7	2.3	2.4	2.7
AquaSalina	0.8	0.7	0.6	0.6	1.1	1.3	1.4	1.5	1.8	2.1	2.3	2.6

Table 5. Standard Deviations of Average Volumes of Brine Collected in Table 4 (Unit: mL)

	0°F				15°F				25°F			
Time (min)	**10**	**20**	**40**	**60**	**10**	**20**	**40**	**60**	**10**	**20**	**40**	**60**
Rock Salt	0.0	0.0	0.1	0.0	0.1	0.0	0.1	0.3	0.4	0.1	0.3	0.2
Magic Minus Zero	0.0	0.0	0.0	0.1	0.1	0.5	0.4	0.1	0.2	0.2	0.4	0.4
BEET HEET	0.0	0.0	0.0	0.1	0.1	0.6	0.7	0.5	0.2	0.5	0.4	0.5
Salt Brine	0.1	0.1	0.2	0.2	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1
GreenBlast	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0
AquaSalina	0.0	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.2	0.1	0.1

Tables 6-8 and Figure 5 show the average grams of ice melted per gram of deicer for each product at all three temperatures.

At 0°F, little ice was melted for all deicers within 60 minutes. The two pre-wetting agents, i.e., Magic Minus Zero and BEET HEET, did not affect the ice melting capacity of rock salt. For the liquid deicers, the negative values in the ice melting capacities suggest that the deicers began to freeze as the test progressed. The amount of GreenBlast or AquaSalina began to freeze is comparable with that of salt brine. These results suggest that deicers will not effectively melt ice at or approaching 0°F. Fortunately, winter temperature in Pennsylvania rarely drops to this temperature. Besides, cold and dry snow at around 0°F can be easily removed by plowing.

At 15°F, Magic Minus Zero melted more ice than rock salt at all times (17 – 91% increase). BEET HEET melted more ice at 20 and 40 min (40 – 45% increase), but did not improve the performance of rock salt at 10 and 60 min. All these numbers for BEET HEET are much smaller than the manufacture reported value, that is, 153.2% more ice melted than untreated salt at 15°F. Among the liquid deicers, AquaSalina has a slightly higher ice melting capacity than salt brine, but not to the extent the manufacture reported: 2.0 vs. 1.4 mL ice melted per mL AquaSalina vs salt brine at 15 °F; GreenBlast melted slightly more ice than salt brine at 10 and 20 min, but did not affect the performance of salt brine at 40 and 60 min. There is no reported value for ice melting capacities of Magic Minus Zero and GreenBlast.

At 25°F, both Magic Minus Zero and BEET HEET increased the ice melting ability of rock salt by 13% and 16%, respectively, at 60 min. For comparison, the manufacture of BEET HEET reported 65.1% more ice melted than untreated rock salt. There is no reported ice melting values for all other products at 25°F. Magic Minus Zero outperformed BEET HEET at short durations (10 and 20 min), but both pre-wetting agents performed comparably at longer durations (40 and 60 min). For the liquid deicers, no significant difference was observed among the ice melting capacity of the three products except at 60 min, where both AquaSalina and GreenBlast increased the ice melting capacity of salt brine by 7%.

The discrepancy between the performance of the liquid and solid deicers can be mostly explained by the fact that more chlorides were applied from the solid deicers than from the liquid deicers during the tests. An example of this is salt brine vs. rock salt. For the 0.9 mL of salt brine (23.3% NaCl) applied during the tests, it contains 0.24 g of NaCl. At 25°F, it melted 2.3 g ice, equivalent to 9.6 g ice per g NaCl. For rock salt, it melted 6.9 g ice per g NaCl at the same temperature. Based on deicer dry weight, liquid deicers are more effective because it allows direct deicing while solid deicers need to dissolve first (which takes energy) before they can deice. Note that there are additional costs associated with salt brine preparation from rock salt; therefore, a more accurate comparison between solid and liquid deicers should take cost, handling, performance, and other relevant factors into consideration.

Table 6. Ice Melting Capacities of Deicers at 0°F

	Average Grams Ice Melted/Gram Deicer				Standard Deviation			
Time (min)	**10**	**20**	**40**	**60**	**10**	**20**	**40**	**60**
Rock Salt	0.0	0.0	0.1	0.2	0.0	0.0	0.1	0.1
Magic Minus Zero	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.1
BEET HEET	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.2
Salt Brine	-0.3	-0.4	-0.4	-0.6	0.0	0.1	0.2	0.2
GreenBlast	-0.4	-0.5	-0.6	-0.6	0.0	0.1	0.1	0.0
AquaSalina	-0.3	-0.4	-0.3	-0.5	0.0	0.0	0.1	0.1

Table 7. Ice Melting Capacities of Deicers at 15°F

	Average Grams Ice Melted/Gram Deicer				Standard Deviation			
Time (min)	**10**	**20**	**40**	**60**	**10**	**20**	**40**	**60**
Rock Salt	0.7	1.1	2.0	4.1	0.1	0.1	0.1	0.3
Magic Minus Zero	1.1	2.1	3.6	4.8	0.1	0.5	0.4	0.1
BEET HEET	0.2	1.6	2.8	3.8	0.1	0.7	0.8	0.5
Salt Brine	0.1	0.2	0.3	0.2	0.0	0.1	0.1	0.1
GreenBlast	0.1	0.3	0.3	0.3	0.0	0.0	0.0	0.0
AquaSalina	0.1	0.3	0.4	0.4	0.1	0.0	0.1	0.0

Table 8. Ice Melting Capacities of Deicers at 25°F

	Average Grams Ice Melted/Gram Deicer				Standard Deviation			
Time (min)	**10**	**20**	**40**	**60**	**10**	**20**	**40**	**60**
Rock Salt	1.4	3.3	5.8	6.9	0.5	0.1	0.4	0.2
Magic Minus Zero	2.1	4.2	6.5	7.8	0.3	0.2	0.4	0.4
BEET HEET	1.2	3.4	6.2	8.0	0.2	0.5	0.5	0.5
Salt Brine	0.8	1.0	1.3	1.4	0.0	0.1	0.1	0.1
GreenBlast	0.7	1.2	1.3	1.5	0.1	0.1	0.1	0.0
AquaSalina	0.7	1.0	1.2	1.5	0.1	0.2	0.1	0.1

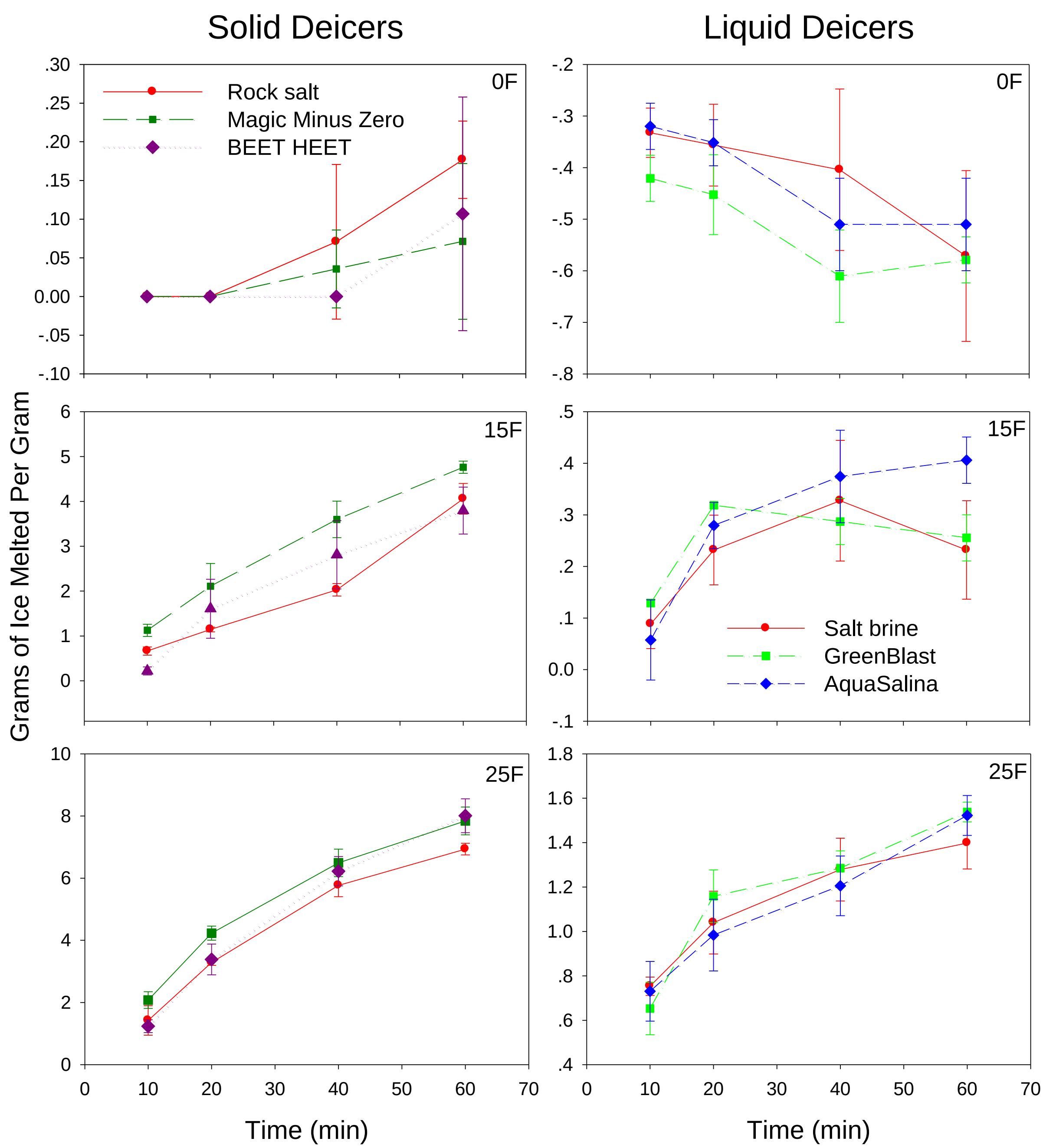

Figure 5. Time course of ice melting capacities (grams of ice melted per gram deicer) of all deicers at three different temperatures. Error bars indicate standard deviations of three replicates; note that y-axis ranges were selected for each graph to best display the data.

Task 2.1.2 Freezing Point Test

Introduction

The objective of this sub-task was to obtain the eutectic curves for different types of deicers by examining the freezing points of the deicer solutions at different concentrations. The experiments were conducted according to the American Society for Testing Materials (ASTM) “Standard Test Method for Freezing Point of Aqueous Engine Coolants” (ASTM D1177 – 12). This test is the second component of the performance aspect for the project “Effective Use and Application of Winter Roadway Maintenance Material Enhancers”.

Eutectic curves provide valuable information on the anti-icing performance of the deicer products. As examples shown in Figure 6 (Ketchum et al. 1996), the freezing point of deicer solutions decreases with increase in deicer solution until it reaches a point (i.e., eutectic point, the minimum freezing temperature) where further increase in deicer concentration yields higher freezing points. Above the eutectic curves, the deicers exist as solution, while below the curves, the deicers exist as solid. During field applications, deicer solutions will be continuously diluted with water from either the melting of ice/snow or falling rain/freezing rain. With decreasing deicer concentration upon dilution, the freezing point of the solution increases such that there is a risk of solution refreezing when its freezing point reaches the pavement temperature (FHA

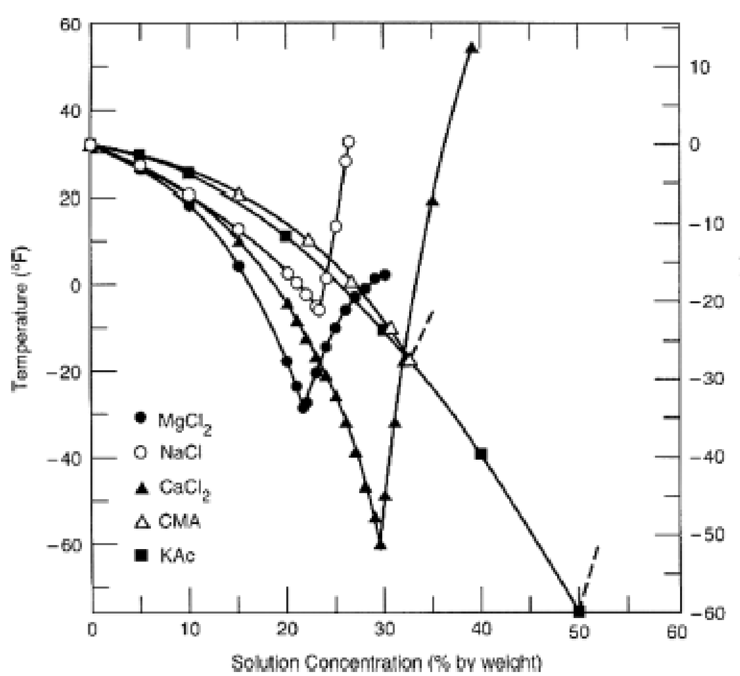

Figure 6. Eutectic temperature and eutectic concentration of five chemicals (Ketchum et al. 1996).

1996). The lower the freezing point, the less likely the solution refreezes, thus resulting in better anti-icing ability. For example, the refreeze concentrations of NaCl and $CaCl_2$ at -10 °C (14 °F) are about 13.5% and 12.5%, respectively. This means that at 14°F, NaCl solution freezes at a higher concentration than $CaCl_2$ solution, therefore, $CaCl_2$ is a better anti-icing product.

Deicers

The same six deicers as described in the above section were used in this experiment, i.e., untreated rock salt, Magic Minus Zero and BEET HEET treated rock salt (referred to as Magic Minus Zero and BEET HEET hereafter), 23.3% salt brine, GreenBlast treated salt brine (referred to as GreenBlast hereafter), and AquaSalina. This time, each solid deicer was dissolved in water to form an aqueous solution. Each test used a different concentration by weight of chloride for each deicer so that they could readily be compared. We found that any concentration approximately greater than 30% did not completely dissolve in the water, since the solution reaches saturation at about this concentration.

For the liquid deicers, the undiluted concentrations of chlorides varied for each deicer. Salt brine is 23.3% sodium chloride, GreenBlast is considered the same since it is combined with salt brine in a 1:4 ratio by volume, and AquaSalina contains a total of 22.1% of chloride salts in its undiluted state.

Equipment and Materials

The standard procedure established by ASTM was followed. Minor changes were made along to accommodate little issues. A windshield wiper motor was attached to a stand and was wired to plug into a standard wall socket. Attached to one end with a clamp was a bent stainless steel wire, so that the wire was perpendicular to the driving apparatus of the motor (Figure 7). A loop was bent on the end so that it could be hooked to a similar wire that was approximately two feet long. At the end of this wire was a coil with eight loops in it. This stirring mechanism is to ensure faster heat transfer within the sample.

A two liter Dewar was set on a flat surface at the base of the stand. Sitting inside of it was a 200 mL Dewar, preferably completely unsilvered to allow for faster heat exchange. At the top of the smaller Dewar was a cork with two small holes drilled into it (Figure 7). The temperature sensor of a thermometer passed through the center hole, and the stirrer passed through the other hole. Insulation material was then put at the top of the larger Dewar to hold the smaller Dewar in an upright position and to keep liquid nitrogen (used as the coolant) from evaporating during the tests. Personal protective equipment was used in this experiment, including latex free gloves, safety glasses, a lab coat, and thermally insulated gloves when handling the liquid nitrogen.

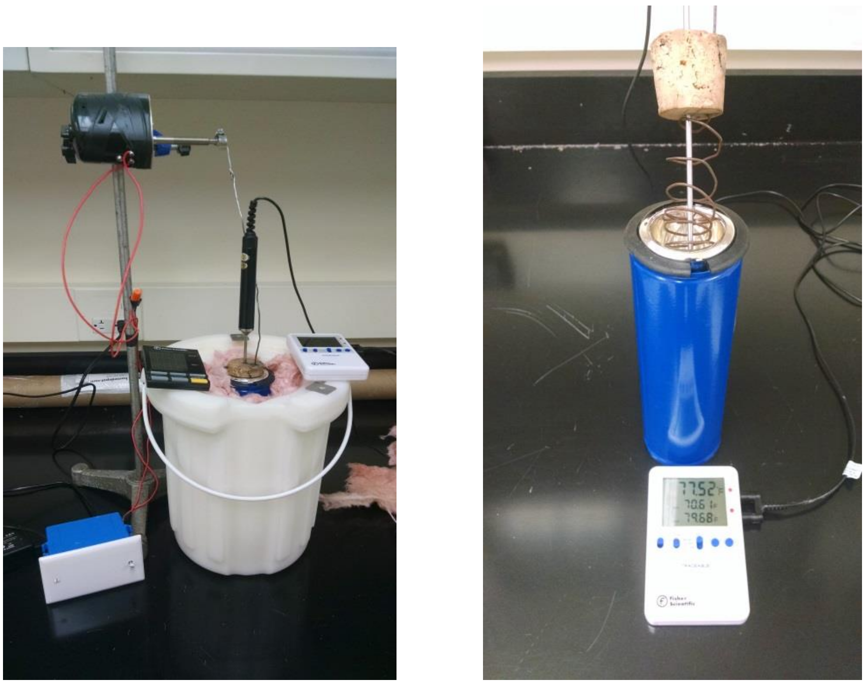

Figure 7. Testing apparatus for freezing points. Left – entire setup; right – close-up of the stirring mechanism and the 200-mL Dewar.

Test Procedures

Samples of each product were prepared so that the total mass of each sample was 75 g. These samples were stored in 100 mL amber bottles in a freezer or refrigerator a few degrees above the expected freezing point in order to ensure a shorter duration for each test. The 200-mL Dewar was also kept in the freezer or refrigerator between experiments to expedite the process.

To begin, liquid nitrogen was added to the 2-L Dewar, filling in about two thirds full. Then the sample was poured into the smaller Dewar. The cork, with the stirring coil and thermometer already in place, was situated tightly in the mouth of the 200-mL Dewar. The smaller Dewar was then carefully placed into the liquid nitrogen bath, and insulation was packed into the gap between the Dewars. After that, the timer was started, and the initial temperature was recorded. At the beginning, temperatures were recorded every five minutes. When the temperature began to level off, temperatures were recorded every two minutes.

Nine to ten tests per product were run to obtain the eutectic curves. Fewer samples were run for rock salt and salt brine because their eutectic curves have been reported (Ketchum et al. 1996). To have better comparisons between the products, similar salt concentrations were tested for each product when possible.

Precautions

Caution must always be taken when handling liquid nitrogen because of its extremely low temperature. Proper training is also necessary.

It was quickly discovered that the windshield wiper motor was inefficient if not counterproductive. Not only did it heat up almost immediately, but it also caused fluctuations in the temperature of the solution. It was decided that from that point on, the coil would be stirred manually, twelve complete up and down cycles after each temperature was recorded.

We noticed the necessity for a completely unsilvered 200 mL Dewar for this experiment. If a silvered or partially silvered one is used, testing can take very long, up to five hours for one sample. The starting temperature of each solution is also important, it saves time if the starting temperature is only a few degrees above the estimated freezing point for a solution. Also, if a sample is left unstirred during the entire length of the experiment, it might freeze without the researcher realizing it. It is important not to end the test too early, in case of an upturn in the temperature.

Results and Discussion

The eutectic curves are shown in Figure 8 and the observed freezing points are summarized in Table 9. Based on Figure 8, all deicer solutions have comparable freezing points when the salt concentration is less than about 5%. BEET HEET has almost the same eutectic curve as rock salt, indicating it does not affect the anti-icing ability of rock salt. Magic Minus Zero has a freezing point 1.3 – 3.0 °F lower than the rock salt solution at concentrations between 11.5% and 30%. For the liquid deicers, both GreenBlast and AquaSalina have lower freezing points than the salt brine of the concentration between 11.5% and 23.3%. Within this range, the freezing point of GreenBlast solutions is about 2.0 – 3.0 °F lower than that of salt brine. The difference is most significant at about 20% where the freezing point of GreenBlast is 11.8 °F less, suggesting it having a much better anti-icing ability than salt brine. At 11.5%, the freezing point of AquaSalina is about 2.5°F lower than that of salt brine. At higher concentrations, the difference between the two solutions is even more significant. These results suggest that the liquid deicers tend to freeze at lower temperatures than salt brine, enabling better anti-icing ability.

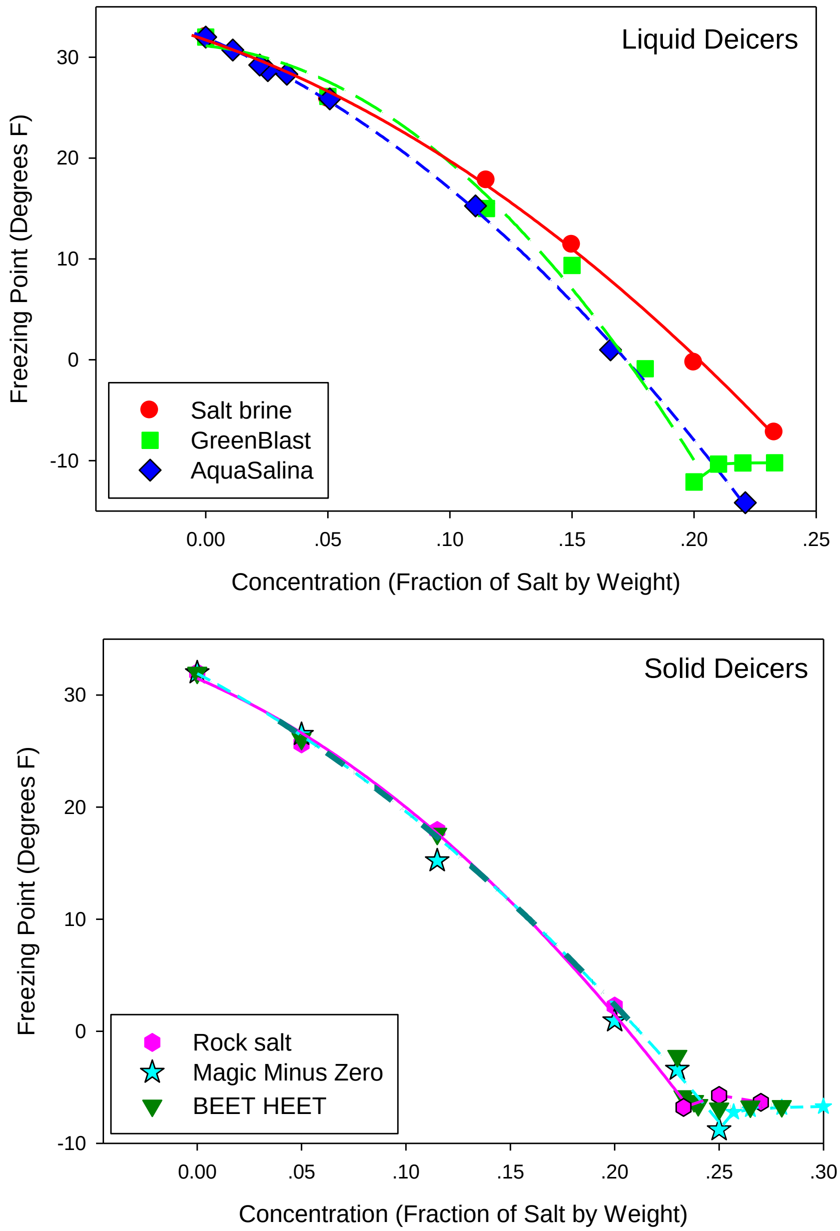

Figure 8. Eutectic curves of the deicer solutions.

Table 9. Freezing points of the deicer solutions of different concentrations. The eutectic point for each deicer is highlighted in red.

Salt Brine		**GreenBlast**		**AquaSalina**	
% Salt by Weight	Freezing Point °F	% Salt by Weight	Freezing Point °F	% Salt by Weight	Freezing Point °F
23.3%	***-7.22***	23.3%	-10.22	***22.1%***	***-14.18***
20.0%	-0.29	22.0%	-10.24	16.6%	0.98
15.0%	11.39	21.0%	-10.35	11.1%	15.25
11.5%	17.78	***20.0%***	***-12.12***	5.1%	25.86
5.0%	25.88	18.0%	-0.89	3.3%	28.31
0.0%	32.0	15.0%	9.35	2.5%	28.67
		11.5%	15.0	2.2%	29.22
		5.0%	26.11	1.1%	30.71
		0.0%	32.0	0.0%	32.0

Rock Salt		**Magic Minus Zero**		**BEET HEET**	
% Salt by Weight	Freezing Point °F	% Salt by Weight	Freezing Point °F	% Salt by Weight	Freezing Point °F
27.0%	-6.34	30.0%	-6.71	28.0%	-6.68
25.0%	-5.72	28.0%	-6.8	26.5%	-6.71
23.3%	***-6.79***	26.5%	-7.0	***25.0%***	***-6.9***
20.0%	2.25	25.7%	-7.22	24.0%	-6.59
11.5%	17.92	***25.0%***	***-8.78***	23.8%	-6.23
5.0%	25.65	23.0%	-3.38	23.3%	-5.8
0.0%	32.0	20.0%	0.93	23.0%	-2.2
		11.5%	15.22	11.5%	20.66
		5.0%	26.5	5.0%	26.1
		0.0%	32.0	0.0%	32.0

The eutectic points for each product are as follows, in percent salt: 23.3% rock salt at -6.79°F, 25% Magic Minus Zero at -8.78°F, 25% BEET HEET at -6.90°F, 23.3% salt brine at -7.22°F, 20% GreenBlast at -12.12°F, and 22.1% AquaSalina at -14.18°F (Table 9). Note that the freezing point of AquaSalina solutions keeps decreasing with increasing concentration and has not reached its eutectic point for all the concentrations tested, but because the original concentration of AquaSalina is 22.1%, we treated this as its eutectic point. Rock salt and salt brine were used as controls in this experiment, since their freezing points for each concentration are known. The reported eutectic point for 23.3% salt brine is -6°F (Figure 6). The slight difference in our observed and the reported eutectic points of salt brine is most likely due to the slight difference in the source and purity of rock salt and how the solutions are prepared. The salt brine used in this work was provide by the PennDOT and prepared by dissolving 2.28 lbs. of rock salt per gallon of water, while the 23.3% rock salt solution was prepared by us by dissolving 17.475 g of rock salt in 57.525 g of water.

To better predict the freezing points of the deicer solutions at different concentrations, we fit the points between 0% and the eutectic point for each curve into the quadratic equation and obtained the following fitting equations:

Rock salt: $Freezing\ Point = 31.4897 - 0.7998 \times C - 0.0351 \times C^2$ $R^2 = 0.998$

Magic Minus Zero: $Freezing\ Point = 32.3606 - 1.2744 \times C - 0.0140 \times C^2$ $R^2 = 0.998$

BEET HEET: $Freezing\ Point = 31.4402 - 0.5763 \times C - 0.0408 \times C^2$ $R^2 = 0.994$

Salt brine: $Freezing\ Point = 31.7050 - 0.8349 \times C - 0.0364 \times C^2$ $R^2 = 0.999$

GreenBlast: $Freezing\ Point = 31.1067 - 0.2576 \times C - 0.0898 \times C^2$ $R^2 = 0.987$

AquaSalina: $Freezing\ Point = 31.9059 - 0.9957 \times C - 0.0499 \times C^2$ $R^2 = 0.999$

where *C* stands for the deicer concentration in weight %. With these equations, we are able to quickly estimate freezing points at any given concentration for all the deicer products.

Accumulative Evaluation of Performance Data

A scoring system with variable weighting factors is recommended to evaluate the performance of each product. Rock salt and salt brine were used as the reference for solid and liquid deicers, respectively, so their scores were set at 1.0.

At 15 or 25°F, if the ice melting capacity of the reference and a deicer *i* at the same sampling time is C_0 and C_i, respectively, the fraction of change in ice melting capacity F_i is calculated as:

$$F_i = \frac{C_0 - C_i}{C_0}$$

For each temperature, we obtained four fractions for the four sampling times. The fractions were then averaged, and the score of the deicer at that temperature was one minus the average. The overall score for a deicer was the average of the two scores at 15 or 25°F. Due to the poor ice melting capacities of all deicers at 0°F, they were excluded from the performance evaluation.

For freezing point tests, the freezing points at four concentrations (23%, 18%, 10%, and 5%) were used during the evaluation. When experimental results were available, they were used directly in the score calculation; if not, the equations developed in the previous section were used to estimate the missing freezing points. Similar to the equation above, fractional changes in freezing points for a deicer of a given concentration were calculated as:

$$F_i = \frac{P_0 - P_i}{P_0}$$

where P_0 and P_i are the freezing point of the reference and the deicer solution of the same concentration. For the four selected concentrations, we also obtained four fractions, which were then averaged, and the final score is one plus the average.

Depending on the relative importance of ice melting and anti-freezing, three different sets of weighting factors were assigned to the above two scores and the final scores are shown in Table 10:

4. Deicing and anti-freezing are equally important (referred as “Equal” in Table 10), the final performance score of the deicer will be the average of the above two scores;
5. Deicing is valued more important than anti-freezing (referred to as “De-icing in Table 10), we assigned a weighting factor of 1.5 and 0.67 to ice-melting and freezing point, respectively, and the final score of the deicer is the weighted average of the above two scores;
6. Anti-freezing is valued more importantly than deicing (referred to as “Anti-icing in Table 1), we assigned a weighting factor of 0.67 and 1.5 to ice-melting and freezing point, respectively, and the final score is again the weighted average of the above two scores.

To be consistent with ranking in the other two thematic areas, the smaller the final score is, the better the performance is.

In Scenario 1 when deicing and anti-freezing are equally weighted, the ranking of the deicers is AquaSalina ≈ GreenBlast > Magic Minus Zero > rock salt ≈ salt brine > BEET HEET.

Table 10. Performance scores and ranking of the deicers in three different scenarios.

	Performance Score			Rank		
	Equal	De-icing	Anti-freezing	Equal	De-icing	Anti-freezing
Rock Salt	1.00	2.17	2.17	4	4	4
Magic Minus Zero	0.79	1.53	1.91	3	2	3
BEET HEET	1.07	2.25	2.41	6	6	6
Salt Brine	1.00	2.17	2.17	4	4	4
GreenBlast	0.66	1.60	1.28	1	3	2
AquaSalina	0.63	1.49	1.23	1	1	1

In Scenario 3 when anti-icing is more valued, the ranking of the deicers is AquaSalina > GreenBlast > Magic Minus Zero > rock salt ≈ salt brine > BEET HEET.

Conclusions

The modified ice melting test results of all the six deicers suggest that when temperature drops to 0°F, deicers should not be used for deicing purposes because they do not effectively deice and there is a risk of them re-freeze. For the two pre-wetting agents, Magic Minus Zero effectively improved the performance of rock salt at both 15 and 25°F; BEET HEET improved the performance of rock salt at all sampling times at 25°F but only at 20 and 40 min at 15°F. For the liquid deicers, AquaSalina has a slightly higher ice melting capacity than salt brine at 15°F, particularly at longer reaction times, but not at 25°F. GreenBlast did not significantly affect the performance of salt brine at both temperatures.

The freezing point testing of all deicer solutions indicates that the two liquid deicers, AquaSalina and GreenBlast, have lower freezing points than salt brine of the same concentration, and thus, will have better anti-icing ability than salt brine. The eutectic curves of the two solid deicers, BEET HEET and Magic Minus Zero, however, almost overlap with that of rock salt, suggesting the usage of these two pre-wetting agents will not change the anti-icing ability of rock salt.

In all three scenarios, AquaSalina always has the best performance and BEET HEET always has the worst performance. When it comes to deicing, GreenBlast also performs very well, while GreenBlast performs next to AquaSalina when it comes to anti-freezing. Note that we assumed rock salt and salt brine have the same performance which is not necessarily the case in the field. Future fielding testing is necessary to compare them under more realistic conditions.

Despite the above testing results, we should be careful when trying to extend the lab test findings to the field performance of these deicers. Their field performance will be affected by many factors, such as sunlight exposure, snow condition, pavement type and condition, wind, traffic, relative humidity, and size and purity of solid deicer particles. To achieve a more realistic comparison of the performance of the deicers, future field tests are warranted.

References

Akin, Michelle and Xianming Shi, "Development of Standard Laboratory Testing Procedures to Evaluate the Performance of Deicers", *Journal of Testing and Evaluation*, 40(6), 1-11, 2012.

ASTM D1177–12, "Standard Test Method for Freezing Point of Aqueous Engine Coolants," ASTM International, West Conshohocken, PA, 2012.

Chappelow, C. C., McElroy, A. D., Blackburn, R. R., Darwin, D., de Noyelles, F. G., and Locke, C. E., "Handbook of Test Methods for Evaluating Chemical Deicers," Strategic Highway Research Program Report No. SHRP-H-332, National Research Council, National Academy of Sciences, Washington, D.C., 1992.

Federal Highway Administration**,** Manual of Practice for an Effective Anti-icing Program: A Guide For Highway Winter Maintenance Personnel, Electronic Version of Publication No. FHWA-RD-95-202, June 1996

Ketchum, S. A., Minsk, L. D., Blackburn, R. R., and Fleege, E. J., "Manual of Practice for an Effective Anti-Icing Program: A Guide for Highway Maintenance Personnel," Report No. FHWA-RD-95–202, Federal Highway Administration, Washington, D.C., 1996.

Western Transportation Institute, Montana State University, “Development of Standardized Test Procedures for Evaluating Deicing Chemicals”, Clear Roads partners with the Pacific Northwest Snowfighters (PNS), Final report for Project 0092-08-32/CR07-02, March 2010.

Western Transportation Institute, Montana State University, “Correlating Lab Testing and Field Performance for Deicing and Anti-icing Chemicals (Phase I)”, Clear Roads partners with the Pacific Northwest Snowfighters (PNS), Final report for Project 0092-10-17/CR09-01, August 2010.

Task 3.1 – Deicer Chemical Analysis and Corrosion Testing

Executive summary

Deicer product chemical analysis and corrosion testing were conducted to identify potential direct environmental and infrastructure effects associated with deicer product use. For a typical watershed, the direct environmental effects are expected to be minimal and to *not* exceed relevant environmental water quality criteria. However, this may not apply to very small watersheds, in which less dilution occurs, or watershed that are known to have existing water quality issues. Results of the thematic cumulative analyses suggested that the following novel deicer formulations are least likely to result in direct negative environmental or infrastructure effects:

- pH – Magic Minus Zero and GreenBlast
- Nutrients – GreenBlast
- Oxygen demand – Magic Minus Zero and AquaSalina
- Metals – AquaSalina (though it contained elevated Pb), followed by Magic Minus Zero
- Corrosion – Green Blast, followed by AquaSalina

Taken together, there was no universal top performer, however Magic Minus Zero consistently was a strong performer, and was ranked overall as the top performer.

Project Report for Task 3.1 – Deicer Chemical Analysis and Corrosion Testing

Deicer product chemical analysis and corrosion testing are important as they identify potential direct environmental and infrastructure effects associated with deicer product use. In this project, ten chemical analyses were conducted as follows: pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), phosphorus, ammonia, nitrate, nitrite, organic nitrogen, total nitrogen, and metals. Additionally, corrosion testing was conducted. These analyses have been thematically grouped as follows: pH, oxygen demand (BOD and COD), nutrients (phosphorus, ammonia, nitrate, nitrite, organic nitrogen, and total nitrogen), metals, and corrosion. Analytical methods have been summarized, and details are included in the appendix. The report includes results of the analyses, accompanied by a discussion of the significance of the results with respect to environmental context; the data have been assessed to identify potential likely direct environmental impacts, compared to environmental regulations, and also compared to determine product ranking.

Task 3.1.1 Project background and approach

Task 3.1.1.1 Acronyms

APHA	American Public Health Association
AWWA	American Water Works Association
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
EPA	Environmental Protection Agency, U.S.
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
DEP	Department of Environmental Protection, Pennsylvania

PNS Pacific Northwest Snowfighters

WEF Water Environmental Federation

Task 3.1.1.2 Deicer products

The deicer products that were detailed in "Project Report for Task 2.1 – Deicer Performance Testing" were also employed for product chemical analysis and corrosion testing. BEET HEET and Magic Minus Zero are used to refer to rock salt amended with the respective product; similarly, GreenBlast is used to refer to salt brine amended with GreenBlast. For chemical analysis and corrosion testing, the solid formulations were dissolved in Nanopure™ water (18 MΩ-cm) prior to use; unless otherwise listed, the solid formulations were dissolved using the PennDOT protocol to produce a 23.3% NaCl solution.

For analyses that did not require dilution, salt brine, rock salt, Magic Minus Zero, and BEET HEAT contained 23.3% NaCl from rock salt (plus additional components from amendments, as appropriate)and GreenBlast contained 80% salt brine (i.e., 18.6% NaCl from salt brine plus GreenBlast constituents);AquaSalina was analyzed as distributed. This is known as "not diluted" or "23.3% NaCl and equivalent," though actual NaCl concentration may vary depending on product composition. To enable comparisons among all products, results are expressed as aqueous concentrations for the 23.3% NaCl or equivalent. Dilutions were only employed when analytically necessitated; no further sample processing was employed.

Task 3.1.1.3 Method selection

For the chemical constituents of interest and corrosion testing, several analytical methods were available. In general, an analytical method is selected to balance the cost, infrastructure, and personnel needs with the project goals including detections limits and sample-specific conditions. For the current project, selection of analytical methods was based on Pacific Northwest Snowfighters recommendations (PNS, 2010) and ability and ease of completing testing in the Temple University laboratory. For deicer product chemical analysis, PNS commonly recommended using an analytical approach from "Standard Methods for the examination of Water and Wastewater" that is jointly published by the American Public Health Association, the American Water Works Association, and the Water Environmental Federation (APHA-AWWA-WEF, hereafter referred to as APHA).

APHA methods were considered, and viable methods, based on required equipment and expertise, were identified. Per PNS recommendations, APHA methods were used for the analysis of ammonia, nitrate, and biochemical oxygen demand (BOD). Hach is a company that produces self-contained and easy to use kits for water analysis; they are readily accessible and commonly used. For several chemical analyses, Hach produces test kits that employed the same general analytical approach that is suggested by APHA. For example, APHA method 5220 B is an a potassium dichromated and sulfuric acid oxidation-based test for the determination of chemical oxygen demand (COD); Hach sells a potassium dichromated and sulfuric acid oxidation-based test kit will all required reagents. A Hach kit-based approach, where the Hach kit was identified to have a similar analytical approach to that described in APHA standard methods, was used in the following analyses (analytical approach, as suggested by APHA and employed in the Hach kit, is shown in parentheses): phosphorus (acid hydrolysable), total nitrogen (persulfate oxidation), nitrite (colorimetric; EPA compliant method), and chemical oxygen demand (COD; EPA compliant method). For these analyses, Hach kits were purchased and the Hach-provided directions were followed.

PNS recommends using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for most metals analysis; interference corrections were calculated according to the equations prescribed in EPA method 6020. PNS recommends conducting mercury (Hg) analysis using Cold Vapor Atomic Absorption Spectrophotometry; in this study, Hg analysis was conducted using the ICP-MS, which is a state-of-the-science approach.

Corrosion analysis, at the suggestion of PennDOT, was conducted according to the PNS method (PNS, 2010).

Task 3.1.1.4 Analytical challenges

The goal of all analytical chemistry methods is to produce high quality data – i.e., the concentration of a target constituent, the analyte. To produce high quality data, potential for contamination must be minimized. In the current study, all testing was conducted in a clean laboratory environment, and operators wore appropriate personal protective equipment, including lab coat, goggles, and gloves. A clean space was maintained, and all sample bottles and vials were thoroughly cleaned prior to each use. Nanopure™ water (18 ΩM-cm) was used to create all solutions. To minimize potential temperature effects, samples and standards were analyzed at room temperature. To understand variability, samples were analyzed in triplicate.

However, analytical challenges can arise based on the sample composition. In analytical chemistry, interferences are non-target constituents that impact the target constituent's measured values; interference can impact numerical values for the target either to artificially elevate them or depress the analytically-derived values (e.g., the presence of chloride, Cl^-, may impact the accurate measurement of nitrate, NO_3^-). A salt brine deicer, containing 23.3% NaCl, is considered a "high matrix" sample due the presence of very high concentrations of dissolved solids (i.e., sodium and chloride). For the current study, analytical challenges were encountered in a number of analyses due to potential interferences from chloride, calcium, magnesium, oxygen demand, and organic carbon. In the current project, some efforts to address chemical interferences were taken, however they were not always successful. The appendix includes a detailed description of the project's efforts to understand interferences. The appendix also includes a description of more involved approaches to address matrix interference, however these methods were deemed to be beyond the scope of this project.

For some analyses, the presented data includes lower confidence values. Low confidence values may arise from low abundance (e.g., samples concentrations below the analytical detection limit) or due to analytical chemistry challenges such as matrix interference. If a value is below the detection limit, it should be considered as evidence of low constituent concentration, but the nominal value should be taken as a low confidence estimate. Low confidence values are presented in the results tables, however their low confidence status is also indicated. Each of the analytical method is summarized below, and the appendix includes further details about the employed calibration curve, detection limits, and replicate variability.

Task 3.1.1.5 Data presentation, statistical analysis, and ranking

The chemical analysis and corrosion testing was conducted to understand the potential impact of the novel deicers to the environment and infrastructure. For each parameter (chemical analysis or corrosion data), the data was evaluated to assess the following three goals: 1) compare to the salt reference; 2) compared to environmental regulations; and 3) compare among all evaluated products to determine ranking.

Each product was tested in triplicate for each analysis, where the results are presented as arithmetic mean (i.e., average) ± standard deviation (σ). Relative standard deviation (RSD) is a measure of the variability among sample replicate analyses (i.e., how similar are the values), where a lower RSD% value indicates greater similarity (lower variability). RSD was calculated each product, based on the three replicate analyses, as follows:

$$RSD\% = \frac{stdev}{arithemtic\ mean} \bullet 100\%$$

RSD values are further discussed in the appendix, however in this report, sample variability is qualitatively discussed (e.g., "low variability" or "high reproducibility" associated with calculated low RSD%; low variability is desired).

To determine if the novel deicer parameter values were different than the sodium chloride reference, a comparison of the novel deicer average to the salt reference average was calculated. Evaluation of the salt reference is discussed in the appendix. This is shown in the results table in the column labeled "Value/Ref" which was produced by calculating a ratio of the averages (i.e., for a given chemical analysis, product average divided by average the salt reference). A statistical analysis, the analysis of variance (ANOVA) statistical test, was conducted to determine if a novel deicer average was statistically different than the salt reference average. ANOVA evaluations were conducted using the software package R; statistical significance was set at $\alpha=0.05$. If a novel deicing product was found to be statistically different than the salt reference, this is shown as a "*" in the result table column labeled "Statistically different."

Parameter values were compared to environmental regulations under assumed dilution and water quality conditions. This analysis was done to identify potential regulatory concerns and environmental impacts. To evaluate the effect of nutrients and metals, the measured values were divided by 500 (i.e., a 500-fold dilution or 1 part product to 499 parts clean water; Fay and Shi, 2012) and compared to published Pennsylvania Department of Environmental Protection criterion. In general, a 500-fold dilution is likely a conservative approach, and that in most scenarios, the dilution will be greater than 500. However, is small watersheds, there is a potential that dilution would be less than 500, and in such cases, the risk of negative effects is likely greater. Metals criteria are often not constant point values, but rather are influenced by other water quality parameters, which can include hardness and organic matter concentration. For the purposes of illustration, the nominal metal's criteria have been calculated for an assumed receiving water body hardness of 100 mg/L as $CaCO_3$, which is considered a moderately hard water. A discussion comparing relevant water quality criteria to likely in-stream concentrations is included in each section.

The third goal in the data analysis is to rank the tested products. The general approach to product ranking is shown in Figure 1. The analyses are thematically grouped as follows: pH, nutrients, oxygen demand, metals, and corrosion. The data from each analysis is transformed and then the transformed data are subjected to z-score analysis. The transformation is used to make the data more comparable, while the z-score analysis assesses relative performance of a deicer product for a given analysis. The z-scores are then combined to produce a cumulative theme score (weighted summation). An overall chemical analysis and corrosion testing score is calculated based on a weighted summation from all five themes. For the current analysis, all parameters were weighted equally within a theme, and all themes were weighted equally for the overall summation.

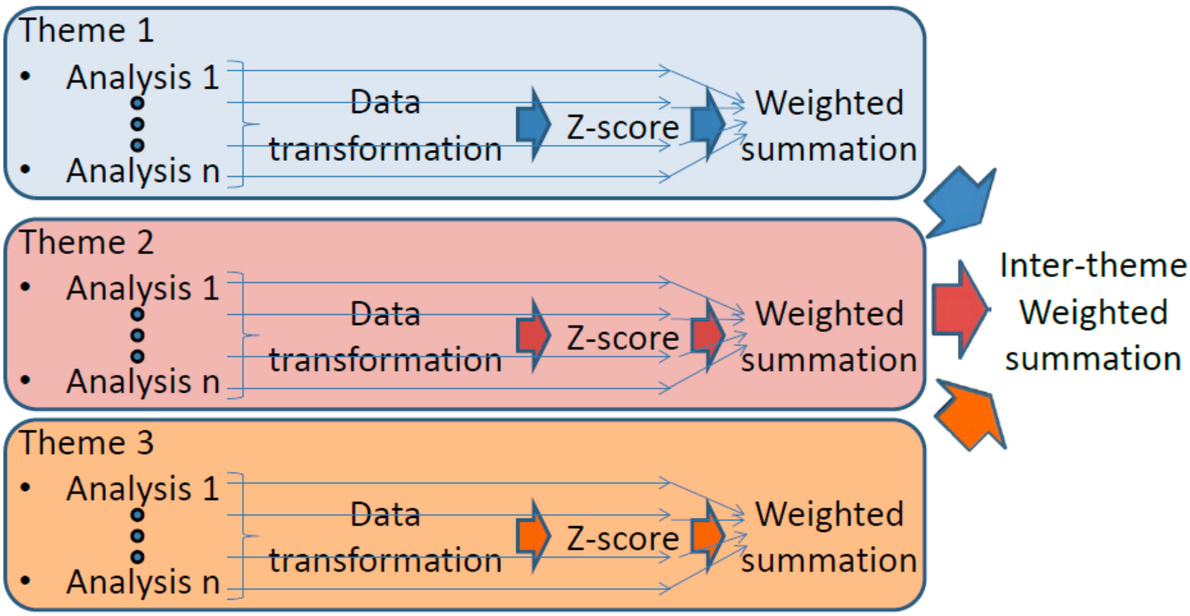

Figure 1. Schematic of data processing approach for product ranking. Each analysis parameter will be appropriately transformed and z-scores will be calculated; the calculated z-scores will be included in a weighted summation within the theme to produce a theme ranking. The theme scores will be included in an overall weighted summation to produce an overall inter-theme ranking.

The employed approach, known as z-score analysis, compares the measurement for a product (shown as product i) to all of the measurements made for all the evaluated products (for n=18 measurements across all evaluated products). Rankings for each analysis (chemical and corrosion) were conducted individually, and then the results were combined. For each analysis, a z-score was calculated as follows:

$$z-score_i = \frac{average_{product_i} - \left(\sum measurement \Big/ n \right)_{all\,measurements\,for\,all\,products}}{standard\ deviation_{all\,measurements\,for\,all\,products}}$$

Further details are included in the appendix. For this approach, all z-scores follow a "lower is better" paradigm, thus a product with a lower z-score (more negative score) is considered more favorable than a product with a higher z-score.

Task 3.1.2 Analytical methods, results, discussion, and ranking

Task 3.1.2.1 pH

Summary of finding

Products analysis of pH revealed that most of the products had pH values that were near neutral and that were consistent with environmental regulations. AquaSalina had a noticeably lower pH value than did other products. The effect of pH on the environment is complex and hard to predict. Magic Minus Zero, BEET HEET, and GreenBlast z-score analysis suggest low potential for pH-based negative environmental effects, while the potential for pH-based negative environmental effects is expected to be higher for AquaSalina.

Context

Often, pH is referred to as the “master variable,” as it impacts the behavior and interactions of many other system components. It’s bearing on an environmental system can be straightforward (e.g., pH values that are circumneutral are generally preferred for biological growth), or can be very complex and intricate (e.g., particle-particle interactions or metal speciation). A deicer product’s effect on receiving water body’s pH will be complex, depending not only on dilution, but also on the receiving water body’s water quality (e.g., buffering capacity); small water bodies with minimal buffering capacity are at the greatest risk for substantial pH changes. It is important to understand that there is a substantial interplay between pH and many chemical reactions, which will be dependent on the water quality of the receiving water body.

Environmental pH has a large effect on both biotic and abiotic conditions. Circumneutral pH values are generally desired to support biological growth, though microbiological communities can exist at a vast range of pH values. Particles found in the environment are often negatively charged, however that can shift and even change to a positive charge depending on the pH; the particle charge can affect particle-particle interactions including particle aggregation and porous media hydrologic properties. Additionally, pH will affect the way that contaminants exist in the environment, including: inorganic speciation, precipitation and dissolution equilibrium, and ionogenic organic compound charge. Finally, pH can affect contaminant sorption to solids (suspended solids or porous media), thus contaminant fate and transport in engineered treatment works (e.g., BMPs), surface water, and subsurface porous media.

Methods

Standard method 4500H^+ was employed for analyzing pH, using an accumet® Basic AB15 pH meter with automatic temperature compensation (exemplified in Figure 1). The pH meter was calibrated with three buffered solutions: pH 4, 7, and 10. Samples were measured at room temperature, and no sample dilution was employed (i.e., 23.3% NaCl or equivalent). Sample replicate analysis produced highly reproducible results (i.e., low variability).

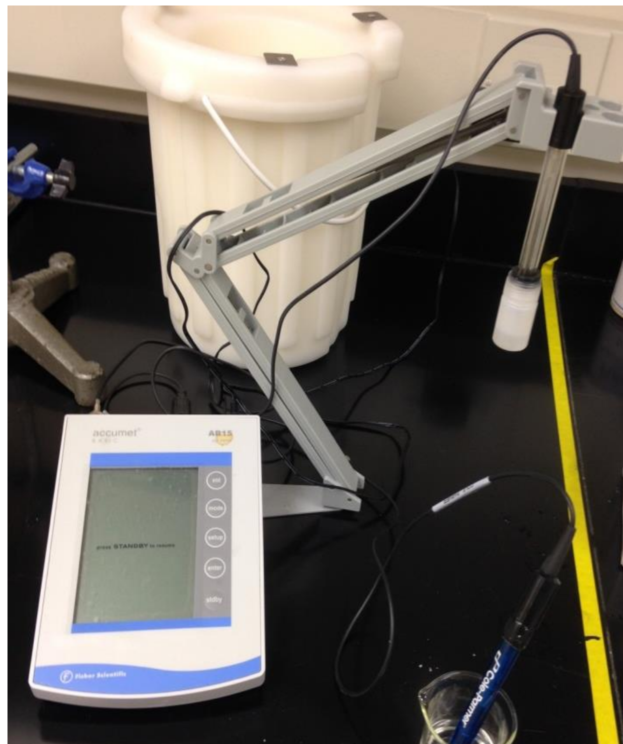

Figure 2. Example of ion selective electrode; applicable for pH (H^+), ammonia (NH_3), and nitrate (NO_3^-).

Results and discussion

The results of sample triplicate analysis are shown in Table 1. As previously mentioned, the products were not diluted for analysis. Several of the products fell outside the expected pH range per the manufacturer specifications, which may be due to the use of unbuffered Nanopure™ water as a diluent (e.g., rock salt), pH differences between the pure product compared to the salt as amended by the product (e.g., Magic Minus Zero and GreenBlast), or changes during transport and storage (e.g., AquaSalina). The Pennsylvania Department of Environmental Protection has set a pH criterion of 6.0-9.0 (PA DEP), which is similar to the U.S. EPA criterion of 6.5-9.0 (U.S. EPA). A deicer product's effect on receiving water body's pH will depend not only on dilution, but also on the receiving water body's buffering capacity, where small water bodies with minimal buffering capacity are at the greatest risk for substantial pH changes.

Table 1 Sample temperature compensated pH triplicate analysis results

		Observed pH		
Sample	**Expect pH**	**Mean**	**±**	**σ**
Rock salt	6 to 8	8.53	±	0.06
Magic Minus Zero	3 to 5	7.27	±	0.02
BEET HEET	6 to 9	8.45	±	0.02
Salt brine	6 to 9	7.51	±	0.02
GreenBlast	8.2 to 8.6	7.31	±	0.01
AquaSalina	5.2 to 5.5	3.78	±	0.02

Ranking analysis, following the described data transformation and z-score approach, was applied to the pH data; the calculations are included as an example in the appendix. The z-scores are summarized below in Table 2, where a lower score (more negative) suggests lower potential for environmental harm. Products that have a pH near 7 (e.g., Magic Minus Zero) have lower scores and therefore are considered less likely to have a negative pH effect on the environment, but AquaSalina has a high positive score suggesting that it has the greatest potential for a negative environmental effect due to pH.

Table 2. Results of pH theme product ranking analysis. A lower (more negative) scores suggests a lower potential for environmental harm.

Product	z-score
Rock salt	0.29
Magic Minus Zero	-0.89
BEET HEET	0.22
Salt brine	-0.66
GreenBlast	-0.86
AquaSalina	1.89

Task 3.1.2.2 Nutrients

Summary of finding

This study includes evaluations of various forms of nitrogen and phosphorus. For reasonable dilution factors and water quality in the receiving water body, it is expected that deicer application alone would *not* result in exceeding nutrient water quality criteria. In spite of this, nutrients are an important consideration, particularly for sensitive watersheds that are currently experience nutrient challenges (e.g., the Chesapeake Bay watershed). GreenBlast was typically statistically equivalent to the salt brine reference for most of the nutrient analyses. By contrast, AquaSalina frequently had elevated nutrient concentrations compared to the reference and other products. Salt brine or GreenBlast are expected to have the lowest potential for negative environmental effects due to nutrients, and they may be good options in nutrient sensitive watersheds.

Context

Nutrients are required to support life. However, in anthropocentrically-impacted areas, an excess of these nutrients is more common than depletion. The presence of elevated nutrient levels can lead to growth of aquatic plants, including phytoplankton and algae; this is referred to as eutrophication and is considered a problem. Excessive algal growth can turn the water green and result in substantially depressed dissolved oxygen concentrations; this is discussed further in the next section.

Methods, Results, and Discussion

The following nutrient endpoints were analyzed: ammonia, nitrate, nitrite, organic nitrogen, total nitrogen, and phosphorus. Nutrient results are summarized in Table 3, and further details on each of the analyzed components are provided below.

Table 3. Nutrient summary for triplicate analysis of deicer products. Potential interferences may have impacted some assessed values; the values are reported as lower confidence values, as indicated by { x ± z }.

	Nutrient analyses *											
	P (mg/L)			NH_3 - N (mg/L)			NO_2^- - N (mg/L)			Total N (mg/L)		
Sample	**Mean**	**±**	**σ**	**Mean**	**±**	**σ**	**Mean**	**±**	**σ**	**Mean**	**±**	**σ**
Rock salt	0.89	±	0.01	1.05	±	0.13	0.006	±	0.005	3.26	±	0.4
Magic Minus Zero	1.31	±	0.04	0.29	±	0.01	0.015	±	0.006	{3.67	±	0.3}
BEET HEET	1.08	±	0.03	0.84	±	0.09	0.007	±	0.001	{7.10	±	0.6}
Salt brine	0.17	±	0.10	0.58	±	0.14	0.005	±	0.003	1.67	±	0.1
GreenBlast	0.09	±	0.03	0.05	±	0.01	0.031	±	0.009	{2.54	±	0.3}
AquaSalina	1.10	±	0.05	{53.04	±	5.46}	0.041	±	0.005	6.72	±	0.6

* Analysis was conducted for organic nitrogen, however owing to necessary dilution, all values were below the detection limit; Analysis was conducted for nitrate, however owing to chloride interferences, the results were deemed not valid.

Phosphorus

Phosphorus was measured as acid hydrolysable phosphorus using a Hach kit (method 8180) that was analyzed spectrophotometrically (λ=880 nm). Samples were diluted 2-fold (i.e., 1 part sample and 1 part Nanopure™ water) to fit into the calibration curve range, and results are reported in mg/L P. The manufacturer stated detection limit is 0.023 mg/L P.

Phosphorus results, presented as phosphorus (i.e., not as phosphate), are shown in Table 4. As described in the appendix, for each chemical analysis, statistical analysis was conducted to evaluate if rock salt and salt brine values were equivalent. Phosphorus was found to be significantly greater in the rock salt than in salt brine, therefore comparisons are made to the separate reference products (i.e., rock salt and salt brine for solid and liquid formulations, respectively). The ratio to the reference (product average divided by average the salt reference average) is shown in the column labeled "Value/Ref".

Generally, solid formulations had higher phosphorus concentrations than did liquid formulations. Among the solid deicers, both of the prewetting agents result in statistically significant increases in phosphorus compared to the rock salt. AquaSalina was found to have significantly elevated phosphorus concentrations compared to salt brine; GreenBlast was statistically equivalent to salt brine. There is no Pennsylvania Department of Environmental Protection or U.S. EPA criterion for total phosphorus.

Table 4. Phosphorus results for triplicate analysis of deicer products. All salt references and samples were found to have phosphorus concentrations in excess of the published detection limit of 0.023 mg/L.

Sample	Measured P (mg/L) Mean	±	σ	Statistically Different**	Value/Ref.**
Rock salt	0.888	±	0.008	-	-
Magic Minus Zero	1.312	±	0.044	*	1.5
BEET HEET	1.077	±	0.026	*	1.2
Salt brine	0.169	±	0.100	-	-
GreenBlast	0.090	±	0.025		0.5
AquaSalina	1.096	±	0.053	*	6.5

**Rock salt and salt brine were statistically different (α=0.05); ANOVA contrasts made to appropriate reference. "Value/Ref" is the product average divided by average the salt reference average.

Ammonia

Ammonia was measured according to APHA standard method 4500-NH_3 D using an ammonia ion selective electrode (ISE). Sample dilution was not required (i.e., 23.3% or equivalent) and low variability among replicates was observed. Ammonia results are detailed in Table 5. Ammonia was found to be significantly greater in the rock salt than in salt brine (~factor of two), therefore comparisons are made to the separate reference products (i.e., rock salt and salt brine for solid and liquid formulations, respectively). Magic Minus Zero and BEET HEET both had nominal ammonia values that were statistically significantly less than their appropriate reference (i.e., rock salt). GreenBlast was equivalent to the salt brine reference, however AquaSalina ammonia values were significantly elevated. The AquaSalina ammonia value is considered a low confidence value, as it is greater than the measured total nitrogen value; this could be due to some un-identified interference that is present in the proprietary product. The Pennsylvania Department of Environmental Protection ammonia criterion is pH and temperature dependent (PA DEP). For an assumed pH of 7 and temperature of 0^o C (e.g., as might occur during winter when deicing products would be used), the freshwater criterion is 0.017 mg/L as unionized ammonia. With an assumed 500-fold dilution, all instream ammonia values would be at least an order of magnitude less than the criterion, save AquaSalina (low confident ammonia value). If measured total nitrogen value for AquaSalina is used, and all of the total nitrogen is assumed to be ammonia, then instream ammonia concentration is below the criterion.

Table 5. Ammonia results for triplicate analysis of deicer products. All salt reference and sample values were greater than the lowest calibration curve point (0.1 mg/L NH_3-N). AquaSalina had a measured ammonia value that exceeded its total nitrogen value, potentially due to an unknown interference; it is therefore, considered lower confidence estimates, as indicated by { x ± z }.

	Measured NH_3-N (mg/L)				
Sample	**Mean**	**±**	**σ**	**Statistically different****	**Value/Ref.****
Rock salt	1.052	±	0.126	-	-
Magic Minus Zero	0.287	±	0.007	*	0.3
BEET HEET	0.837	±	0.085	*	0.8
Salt brine	0.577	±	0.136	-	-
GreenBlast	0.055	±	0.008		0.1
AquaSalina	{53.039	±	5.462}	*	92.0

**Rock salt and salt brine were statistically different (α=0.05); ANOVA contrasts made to appropriate reference. "Value/Ref" is the product average divided by average the salt reference average.

Nitrate

Nitrate was measured according to APHA standard method 4500-NO_3^- D using a nitrate ion selective electrode (ISE; similar to that shown in Fig. 1). Samples required no additional dilution (i.e., were analyzed as 23.3% or equivalent), however significant analytical challenges were encountered due to chloride interferences (discussed in appendix). Various approaches were employed to overcome this, however were not successful and the resultant data was not considered valid due to matrix interference. Alternative analytical methods should be employed in the future, but were considered beyond the scope of the current project.

Nitrite

Nitrite was measured using a Hach colorimetric assay (Hach method 8507 analyzed at λ=507 nm). Samples were analyzed undiluted (i.e., 23.3% and equivalent). Samples were found to have low but detectable nitrite concentrations; however the replicate reproducibility was poor, especially among very low nitrite samples (namely, rock salt and salt brine references which were near the published detection limit).

Nitrite results are detailed in Table 6. Nitrite was present in low concentrations, such that replicate variability was greater for nitrite than for most other chemical analyses. Nitrite concentrations in rock salt and salt brine were statistically equivalent, however nitrite concentrations were significantly elevated in Magic Minus Zero, Green Blast, and AquaSalina; BEET HEET was equivalent to salt. Pennsylvania Department of Environmental Protection provides a 10 mg/L as nitrogen for combined nitrate and nitrite (PA DEP); as total nitrogen was less than that for all deicers in their undiluted form, this is not a concern.

Table 6. Nitrite results for triplicate analysis of deicer products. All salt references and samples were found to have nitrite in excess of the published detection limit of 0.002 mg/L.

	Measured NO_2^- - N (mg/L)				
Sample	**Mean**	**±**	**σ**	**Statistically Different***	**Value/Ref.***
Rock salt	0.006	±	0.005	-	-
Magic Minus Zero	0.015	±	0.006	*	2.5
BEET HEET	0.007	±	0.001		0.4
Salt brine	0.005	±	0.003	-	-
GreenBlast	0.031	±	0.009	*	4.9
AquaSalina	0.041	±	0.005	*	6.4

*Rock salt and salt brine were statistically equivalent (α=0.05); ANOVA contrasts made to appropriate reference. "Value/Ref" is the product average divided by average the salt reference average.

Organic nitrogen

Organic nitrogen was measured using the Hach simplified TKN (s-TKN) assay, which measures total Kjeldahl nitrogen as the sum of free ammonia and organic nitrogen. Test components for the Hach kit are shown in Figure 3. The employed method is less labor intensive, less expensive, and less dangerous than the traditional APHA method that employs high temperature sulfuric acid digestion. Substantial dilution, to overcome interferences, was employed and resulted in non-detectable concentrations in all samples; more information is included in the appendix. Future work should investigate other analytical methods, however that was deemed to be beyond the scope of this project.

Figure 3. Example of Hach kit components and digester.

Total nitrogen

Total nitrogen was measured via persulfate oxidation using a Hach Total Nitrogen kit (Hach method 10071; measured at λ=410 nm); the published detection limit is 0.5 mg/L total nitrogen. All products had replicate good replicate reproducibility. Potential inferences were present in BEET HEET, Magic Minus Zero, and GreenBlast, which resulted in lower confidence total nitrogen values for these products.

Total nitrogen results are shown in Table 7. Salt brine had significantly lower total nitrogen than did rock salt, which could be a result of incomplete dissolution of the solid to produce the brine, non-representative sampling of either product, or losses during brine storage either due to biological consumption or to sorption losses to the container. Owing to the differences, Magic Minus Zero and BEET HEET were compared to rock salt and GreenBlast and AquaSalina were compared to salt brine. BEET HEET was found to have significantly elevated total nitrogen concentrations that were approximately double that of rock salt. AquaSalina also had significantly elevated total nitrogen concentrations that were approximately double that of salt brine. Magic Minus Zero and GreenBlast were statistically similar to their respective references. There is no Pennsylvania Department of Environmental Protection or U.S. EPA criterion for total nitrogen.

Table 7. Total nitrogen results for triplicate analysis of deicer products. All salt references and samples were found to have nitrite in excess of the published detection limit of 0.5 mg/L, however potential interferences may be present in Magic Minus Zero, BEET HEET, GreenBlast, therefore they are lower confidence estimates, as indicated by { x ± z }.

	Measured Total N (mg/L)				
Sample	**Mean**	**±**	**σ**	**Statistically different****	**Value/Ref.****
Rock salt	3.26	±	0.42	-	-
Magic Minus Zero	{3.67	±	0.27}		1.1
BEET HEET	{7.10	±	0.60}	*	2.2
Salt brine	1.67	±	0.12	-	-
GreenBlast	{2.54	±	0.27}	*	1.5
AquaSalina	6.72	±	0.60	*	4.0

**Rock salt and salt brine were statistically different (α=0.05); ANOVA contrasts made to appropriate reference. "Value/Ref" is the product average divided by average the salt reference average.

Measured total nitrogen was compared to summed nitrogen components (i.e., NH_3 +NO_2^-), and generally the recovery was modest at best. Rock salt and salt brine had the best recoveries (NH_3 +NO_2^-/total N~35%). Not having valid values for nitrate and organic nitrogen may have contributed to the under-recovery for Magic Minus Zero, BEET HEET, and GreenBlast. AquaSalina was substantially over-recovered and had a measured ammonia concentration that was in excess of the measured total nitrogen concentration.

Cumulative nutrient analysis

Z-score analysis results for the individual nutrient data are shown in Table 8; the cumulative nutrient value is an average of each of the included nutrient z-score analyses (i.e., equal weighting). Salt brine was consistently among the lowest nutrient z-scores, which is not surprising given that the nutrients likely only come from impurities. Similarly, rock salt also generally produced low nutrient z-scores. Among the novel deicers, AquaSalina consistently had the highest nutrient z-scores, suggesting that AquaSalina poses the greatest threat for nutrient impacts. GreenBlast was had the lowest cumulatively nutrient z-score, in no small part to its low phosphorus concentration.

Table 8. Results of the nutrient theme product ranking analysis. A lower (more negative) score suggests a lower potential for environmental harm.

	z-score				
Product	**P**	**NH_3**	**NO_2^-**	**Total N**	**Cumulative**
Rock salt	0.24	-0.41	-0.76	-0.42	-0.34
Magic Minus Zero	1.11	-0.45	-0.21	-0.23	0.06
BEET HEET	0.63	-0.42	-0.69	1.38	0.22
Salt brine	-1.24	-0.43	-0.85	-1.17	-0.92
GreenBlast	-1.40	-0.46	0.93	-0.76	-0.42
AquaSalina	0.67	2.16	1.57	1.20	1.40

Task 3.1.2.3 Oxygen demand

Summary of finding

Oxygen is imperative to support normal ecosystem functioning, however oxygen depletion is a challenge that is sometimes encountered in highly impacted systems. BOD and COD analyses were conducted to assess likely oxygen demand implications. Salt references produced the lowest oxygen demand, which is consistent with expectations. Among the novel deicers, Magic Minus Zero had the exerted the lowest oxygen demand, while GreenBlast produced the greatest oxygen demand. There are not regulations directly governing oxygen demand, however in areas that where dissolved oxygen concentrations are a point of concern, conventional salt is least likely to result in oxygen depletion; Magic Minus Zero had the lowest oxygen demand among the novel formations, but is likely to contribute noticeably more to oxygen depletion than conventional salt.

Context

Elevated nutrient inputs are often associated with increased plant and algal growth and thus increased oxygen demand; this can result in depleted dissolved oxygen (DO) concentrations. Low DO concentrations have been associated with wide-spread fish kills. In fact, eutrophication-induced hypoxic water bodies (very low dissolved oxygen) have been referred to as "dead zones" when they can no longer support aquatic life. Two noteworthy examples of this are the Chesapeake Bay and the Mississippi Delta into the Gulf of Mexico.

Methods

Biochemical oxygen demand (BOD) was measured in a five day test according to APHA standard method 5210-B. In brief, a sample was combined with oxygenated dilution water (containing nutrients and salt), and then a seed microbiological community was introduced. The initial dissolved oxygen (DO) concentration was determined, and then the samples are incubated for five days; DO was measured at the conclusion of five days. All samples were tested at 3.5% NaCl and equivalent; details on quality control and assurance measures, as well as calculations, are included in the appendix. Salt references, conducted at 3.5% NaCl, and did not exert the requisite DO demand of 2.0 mg/L, however this was considered a valid result for the salt references as BOD of the salt was expected to be minimal. All other quality control and assurance measures, including the blank check and seed check, were satisfied (see appendix). Replicate variability was low in all novel formulations, but was considerable in the salt references, likely due to low exerted BOD.

Chemical oxygen demand (COD) was measured via dichromate oxidation and colorimetric assay (Hach TNT 821 kit using Hach method 8000). In brief, constituents are oxidized by dichromate under heated acidic conditions (sulfuric acid), and then measured spectrophotometrically (λ=420 nm). The published detection limit is 3 mg/L; high sample COD values resulted in a necessary 100-fold dilution with Nanopure™ water (i.e., 0.233% NaCl and equivalent) to fit within the calibration curve range. Replicate variability was generally low, save BEET HEET which had moderate variability.

Results and discussion

In this study, oxygen demand was measured using two tests: COD and BOD. COD is a measure of everything that can be oxidized in the presence of a strong oxidizing agent ($Cr_2O_7^{2-}$), which can include previously mentioned nutrients, organic matter, and dissolved and solid inorganic species. BOD is a measure of a biologically-mediated oxidation process, as measured in a five day test. Therefore, BOD reflects bioavailable material that can be oxidized within the test duration (5 days). COD and BOD results are shown in Table 9; COD is expected, and was found, to be greater than BOD.

Table 9. COD and BOD results for triplicate analysis of deicer products. Values in parentheses (x ± z) indicate that the measured value is APHA prescribed DO depletion (similar to a detection limit), and therefore is a low confidence estimate.

	Measured COD (mg/L)				Measured BOD (mg/L)			
Sample	**Mean**	**±**	**σ**	**Different***	**Mean**	**±**	**σ**	**Different***
Rock salt	2366	±	225	-	(4	±	2)	-
Magic Minus Zero	2506	±	115		555	±	19	*
BEET HEET	2916	±	721	*	879	±	32	*
Salt brine	2020	±	222	-	(3	±	1)	-
GreenBlast	5259	±	385	*	1198	±	68	*
AquaSalina	3236	±	230	*	663	±	38	*

*Rock salt and salt brine were statistically equivalent (α=0.05); ANOVA contrasts made to appropriate reference.

Salt brine and rock salt COD results were statistically similar (α=0.05), and the results were combined for further analysis (2190 ± 280 mg/L COD, mean ± standard deviation). Among novel deicers, GreenBlast, AquaSalina, and BEET HEET had significantly higher COD values than salt. Magic Minus Zero has statistically similar COD as salt.

Salt brine and rock salt each exerted a BOD that was below the requisite 2.0 mg/L DO depletion; therefore, salt brine and rock have non-detectable BOD, which was in line with expectations. Each of the deicer products exerted a measurable BOD, and no product's 95% confidence interval included 0, as shown in Table 9. GreenBlast had the largest BOD values, followed by BEET HEET, then AquaSalina, and Magic Minus Zero had the lowest BOD among novel deicers.

As expected, the COD values for each product were greater than the BOD values. This indicates that the products contain some material that chemically oxidizable, but is not readily bioavailable to be biologically oxidized in a timely manner. The lack of consistency among BOD/COD ratios can be attributed to differences in readily biodegradable material (BOD/COD range was 0.2 – 0.3 for non-reference products). Taken together, GreenBlast will likely to exert that greatest oxygen demand in both the short and longer term. Neither the Pennsylvania Department of Environmental Protection nor U.S. EPA have BOD or COD criteria (PA DEP, US EPA). However, a range of dissolved oxygen criteria do exist that depend on flowing status (flowing or lake), monitoring duration, season, and if the ecosystem is a naturally used for salmonid early life stage; in all cases, the minimum dissolved oxygen concentration is greater than 5.0 mg/L, and for sensitive cases is up to 9.0 mg/L. Under a 500-fold dilution scenario, the greatest oxygen depletion would be ~2.4 mg/L (GreenBlast) which would possibly be harmful to sensitive receiving waters.

Oxygen demand z-score analysis results are shown in Table 10; BOD and COD were equally weighted for the cumulative analysis. The lowest oxygen z-scores were observed for the salt references, which is consistent with expectations for salt. Among novel formulations, Magic Minus Zero and AquaSalina exerted lower oxygen demand. GreenBlast exhibited the highest score for both BOD and COD, suggesting that it has the greatest potential for environmental harms associated with oxygen demand.

Table 10. Results of the nutrient theme product ranking analysis. A lower (more negative) score suggests a lower potential for environmental harm.

	z-score		
Product	**BOD**	**COD**	**Cumulative**
Rock salt	-1.08	-0.60	-0.84
Magic Minus Zero	0.13	-0.48	-0.17
BEET HEET	0.85	-0.12	0.37
Salt brine	-1.09	-0.91	-1.00
GreenBlast	1.55	1.94	1.75
AquaSalina	-0.37	0.16	-0.10

Task 3.1.2.4 Metals

Summary of finding

Metals analysis was conducted, and the presented results reflect background interference subtraction, which was considered to the best estimate of deicer product concentrations. Deicer application is *not* expected to directly result in water quality criteria violations for the assessed metals. It should be noted that water quality criteria are often water quality dependent, however the expected direct deicer contribution would result in concentrations would typically be less than 1/10 of the criteria. Solid formulations typically had higher As, Ag, and Cd concentrations than did the liquid formulations. By contrast, Ni, Zn, and Cu were generally higher in liquid formulation than in solid. GreenBlast commonly had the highest metal concentrations, though Pb was highest in AquaSalina. Sample corrected Hg concentrations were below the detection limit. Overall, salt brine is expected to have the lowest potential for negative metals harmful effects, followed by AquaSalina, though high Pb concentrations were measured in AquaSalina.

Context

Several metals are required in trace amounts to support biological growth (e.g., Zn), while others are not needed (e.g., Cd, Hg, and Pb). At elevated concentrations, many metals can become toxic to aquatic biota. These analyses are conducted to measure the potential direct concentration effect of deicer product metals. However, it should be noted that roadway runoff metals have been demonstrated to be a problem, and reflection contributions from roadway-associated sources including tires, brakes and roadside soil (particularly for Pb as a legacy from leaded gasoline use). While the stormwater runoff metals may originate for sources other than the deicer products, the presence of elevated salt concentrations may change the metals' fate, transport, and toxicity.

Methods

Metals analysis was conducted on acidified samples using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS), with interference correction calculations based on EPA method 6020. The instrument was tuned each day to minimize oxides and double charged ions. For general analysis, samples were acidified to 1% HNO_3 and were analyzed in a single analytical run (56 mass peaks were analyzed, including six internal standards); He gas was included in the collision cell to minimize polyatomic interferences for most elements, but H_2 gas was included in the reaction cell for determination of arsenic. A separate analytical run was conducted for the determination of mercury (three mass peaks, including one internal standard); 1% HCl acidification was employed to minimize Hg sorption to instrument components. Samples were analyzed without any aqueous dilution using Agilent's "ultra-high matrix introduction" capabilities (pneumatic dilution). At high salts concentration, polyatomic interferences are more likely and were further investigated via analysis of ACS grade NaCl; corrections have been applied to the presented data. Detection limits were determined for each element, and are shown in the appendix, along with other quality control and assurance measures including matrix interference analysis and rinse blanks.

Results and discussion

The results of the metals analysis are shown in Table 11, including the elemental concentrations for the following metals (and the mass-to-charge value at which the analysis was conducted): Cr (52), Ni (60), Zn (64), Cu (65), As (75), Ag (107), Cd (111), Hg (202), and Pb (summation of 206 and 208 isotopes). Generally, the environmental isotopic ratios are expected to be constant, so total concentration can be inferred based on a single isotope; in the case of Pb, the ratios are non-constant, so the total values is determined based on the summation of the two most common isotopes. The presented values are corrected for matrix interferences, which was determined through the analysis of a 23.3% ACS grade NaCl solution.

Table 11. Metals results for triplicate analysis of deicer products. Detection limit and inter-sample rinse are based on as-measured values. Sample values are corrected for matrix interferences (ACS salt analysis) as described in the appendix; if the correction resulted in a negative value, then a 0 was used in average and standard deviation calculations. Corrected values that fall less than the detection limit are considered low confidence values and are shown as (x ± z)

Concentration (ug/L (ppb) in 23.3% NaCl and equivalent; samples concentrations are corrected for interferences as measured in 23.3% ACS salt samples)

	Cr (52)			Ni (60)			Zn (64)			Cu (65)			As (75)		
Sample	**Mean**	±	**σ**	**Mean**	±	**σ**	**Mean**	±	**σ**	**Mean**	±	**σ**	**Mean**	±	**σ**
Detection limit	0.48			0.07			0.46			0.21			0.02		
Inter sample rinse	1.91	±	1.44	0.79	±	0.61	0.37	±	0.38	1.02	±	1.32	0.18	±	0.12
Rock salt	10.92	±	0.88	2.45	±	0.83	2.80	±	1.64	(0.00	±	0.00)	154.33	±	11.14
Magic Minus Zero	17.46	±	2.99	4.71	±	2.62	9.00	±	5.80	4.00	±	1.98	99.88	±	9.25
BEET HEET	17.90	±	3.13	9.37	±	2.94	4.53	±	3.09	0.84	±	1.45	119.48	±	21.82
Salt brine	0.48	±	0.25	7.74	±	1.08	193.22	±	9.14	31.73	±	0.82	4.86	±	4.29
GreenBlast	101.91	±	140.04	95.65	±	82.86	446.31	±	243.83	100.54	±	74.79	135.27	±	6.34
AquaSalina	10.19	±	4.71	29.60	±	6.09	200.70	±	50.24	11.29	±	8.63	7.01	±	0.99

	Ag (107)			Cd (111)			Hg (202)			Pb (206 + 208)		
Sample	**Mean**	±	**σ**	**Mean**	±	**σ**	**Mean**	±	**σ**	**Mean**	±	**σ**
Detection limit	0.07			0.00			3.05			0.13		
Inter sample rinse	0.04	±	0.04	0.04	±	0.09	0.63	±	0.60	0.30	±	0.18
Rock salt	6.22	±	0.30	19.93	±	0.63	(0.00	±	0.01)	17.48	±	0.87
Magic Minus Zero	3.10	±	0.29	9.00	±	0.94	(0.00	±	0.00)	31.24	±	1.65
BEET HEET	4.08	±	0.37	11.57	±	0.93	(0.00	±	0.00)	33.41	±	1.95
Salt brine	(0.05	±	0.07)	0.39	±	0.04	(1.91	±	3.15)	4.26	±	0.10
GreenBlast	(0.00	±	0.00)	(0.00	±	0.00)	(0.00	±	0.00)	6.65	±	0.19
AquaSalina	0.09	±	0.06	(0.00	±	0.00)	(0.00	±	0.00)	78.64	±	3.50

Among the nine measured metals, Zn was commonly the most abundant metal, and Cu, Cr, and As were also commonly more abundant. Ag and Hg were commonly the least abundant elements. Sample Hg concentrations were generally lower, while the calculated detection limit was considerably higher than other elements, likely due to sorption and release from system components; as a result, the Hg analysis is lower confidence. Magic Minus Zero and BEET HEET are rock salt amendments, and as such, are expected to contain equivalent or greater concentration of each metal than the rock salt reference. This was generally observed, though rock salt contained higher concentrations of As, Ag, and Cd than the amended products. This could be a result of non-representative sampling. Green Blast generally had metal concentrations greater than the salt brine, which was generally expected as it is 80% salt brine. GreenBlast commonly had the highest concentration, thought sample variability was higher for GreenBlast than for other products. AquaSalina exhibited the highest Pb concentration.

Metals criteria are often not constant point values, but rather are set for dissolved metal concentrations (i.e., not particle or organic matter associated) and the criteria are influenced by other water quality parameters, which can include hardness and organic matter concentration. The influence of water quality on metal toxicity is discussed in Di Toro et al (2001). Pennsylvania Department of Environmental Protection criteria equations can be found in Chapter 93 (Table 5; PA DEP); for the purposes of illustration, the nominal criteria have been calculated for an assumed receiving water body hardness of 100 mg/L as $CaCO_3$, which is considered a moderately hard water. Furthermore, maximum concentration criteria and continuous concentration criteria have been developed to be protective for fish and aquatic life of short-term and long-term exposure scenarios, respectively. The following metals have hardness-dependent criteria (and calculated nominal maximum and continuous criteria assuming 100 mg/L as $CaCO_3$): Cr(III) (570 and 74 µg/L), Ni (470 and 52 µg/L), Cu (13 and 9 µg/L), Zn (120 and 120 µg/L), Ag (3.2 µg/L maximum criterion, no continuous criterion), Cd (2 and 0.25 µg/L), and Pb (65 and 2.5 µg/L). The As criteria are set nominal values (i.e., are not water quality-specific) at 340 and 150 µg/L maximum and continuous criteria. Hg criteria are also set nominal values (i.e., are not water quality-specific) at 1.4 and 0.77 µg/L maximum and continuous criteria. Selective metals have more restrictive drinking water standards as follows: As (10 µg/L) and Hg (0.05 µg/L). It should be noted that the U.S. EPA surface water criteria for Cu is based on the biotic ligand model with accounts for other water quality parameters, include dissolved organic carbon concentration (U.S. EPA). Assuming a 500-fold dilution (Fay and Shi, 2012) in the receiving water and an assumed receiving water body hardness of 100 mg/L as $CaCO_3$, none of the deicers would exceed continuous, maximum, or drinking water criteria, and generally expected concentrations are over an over of magnitude below all criteria (i.e., expected concentration are less than 1/10 of the criterion).

The z-score analyses for each metal, and the equal-weighting cumulative metals z-score analysis, are shown in Table 12. Mercury was excluded from the z-score analysis, as the corrected Hg concentrations generally resulted in non-detectable concentrations. In general, GreenBlast was found to contain the highest concentration of several metals, and thus had a high cumulative metals z-score suggesting greater potential for direct negative environmental impact (lower z-score is better). However, rock salt was found to have elevated As, Ag, and Cd concentrations. This should be regarded with care, as elevated concentration should have also been observed in the pre-wetting products. Salt brine had the overall lowest cumulative metal z-score (no additions to contribute to concentrations). AquaSalina generally had low individual metal z-scores, however elevated Pb concentrations increased the cumulative score. Magic Minus zero was also a stronger performer among novel deicers, with lower concentrations of Cr, Ni, Zn, and Cu, but higher concentrations of As, Ag, Cd, and Pb.

Table 12. Results of the metals theme product ranking analysis. A lower (more negative) score suggests a lower potential for environmental harm.

	z-score								
Product	**Cr**	**Ni**	**Zn**	**Cu**	**As**	**Ag**	**Cd**	**Pb**	**Cumulative**
Rock salt	-0.26	-0.42	-0.43	-0.44	3.69	3.75	3.85	0.31	1.26
Magic Minus Zero	-0.15	-0.37	-0.39	-0.35	2.23	1.65	1.50	1.09	0.65
BEET HEET	-0.14	-0.26	-0.42	-0.42	2.75	2.31	2.05	1.21	0.88
Salt brine	-0.44	-0.30	0.75	0.31	-0.31	-0.41	-0.36	-0.43	-0.15
GreenBlast	1.27	1.76	2.33	1.94	3.18	-0.44	-0.44	-0.30	1.16
AquaSalina	-0.27	0.21	0.80	-0.17	-0.25	-0.38	-0.44	3.76	0.41

Task 3.1.2.5 Corrosion testing

Summary of findings

Triplicate corrosion analysis resulted in high variability between corrosion testing rounds, which may be due to differences in ambient temperature and humidity. However, in general, all reference salts and novel deicer products were less corrosive than the ACS salt reference. Generally, the novel deicer products were less corrosive than the rock salt and salt brine. Among novel deicing formulation, GreenBlast and AquaSalina were the top performers and resulted in the least corrosion, while BEET HEET resulted in the greatest corrosion.

Context

Corrosion can negatively impact infrastructure including deicer equipment, roadway and bridge components, and civilian automobiles, which is costly to all parties. Additionally, corrosion can contribute metals to roadway runoff. As discussed in the last section, metals have been identified as a roadway runoff issue in some places.

Methods

Corrosion testing was conducted per Pacific Northwest Snowfighters 72 hr. cyclic method (PNS, 2010). The method specifies the cleaned steel washers, and corrosion is assessed based on mass lost over a 72-one hour cycles, where each cycling includes a submerged (wet) and in air (drying) component. The testing apparatus is shown in Figure 4. NaCl, $MgCl_2$, and $CaCl_2$ were included as references. Corrosion was calculated according the PNS guidelines as mils penetration per year (MPY), adjusted corrosion (corrected for same-test Nanopure™ water corrosion MPY), and NaCl normalized (referred to as "% NaCl"). Further details on the testing and calculations can be found in the appendix.

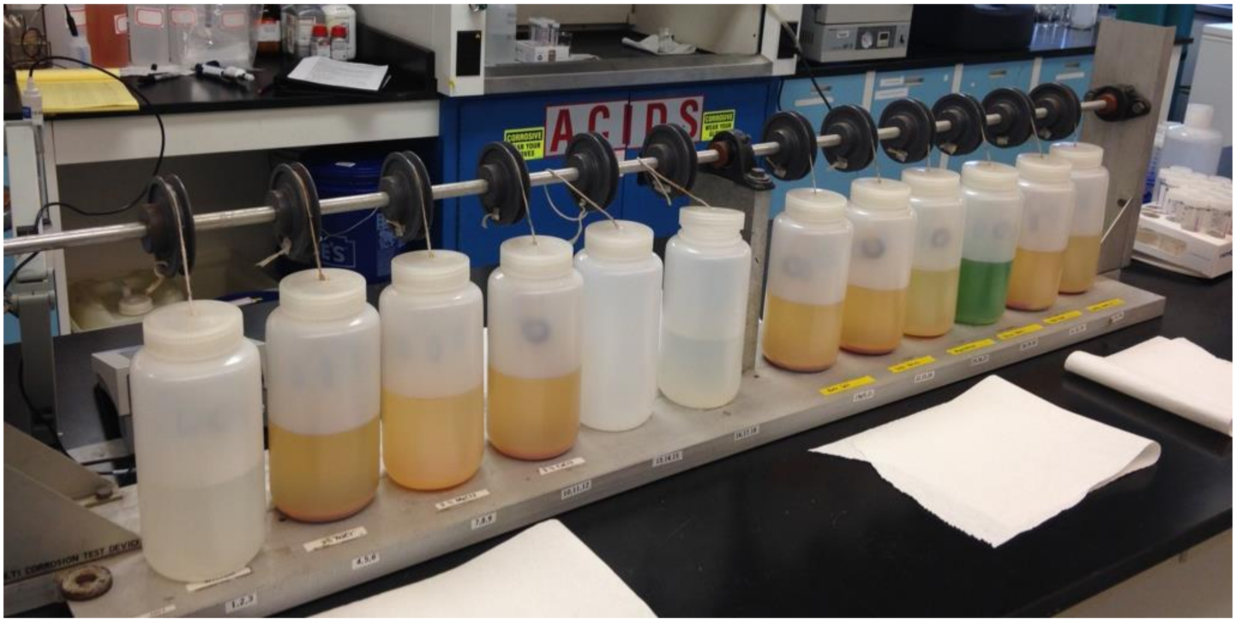

Figure 4. Corrosion testing apparatus in use to test reference and deicer solutions.

Results and discussion

The overall results of the corrosion analysis are shown in Table 13, which includes the results collected over three testing rounds. In order to try to understand the effect of solution chemistry and environmental conditions, a variety of reference solutions were analyzed. With each testing round, the following solutions were included: Nanopure™ water, 3% NaCl, 0.78% $MgCl_2$, and 0.93% $CaCl_2$. Additionally, 3% $MgCl_2$ and 3% $CaCl_2$ were tested, as were equivalent Cl^- solutions (i.e., 3% NaCl, 2.44% $MgCl_2$, and 2.85% $CaCl_2$). Each testing round exhibited a corrected MPY less than the max allowable value (< 30, as specified by PNS, 2010). There was variability among testing results, particularly between different testing rounds which could be influenced by environmental conditions including temperature and humidity. Variability for washers in the same solution (i.e., same testing round) was also observed, but generally to a lesser degree; the observed intra-round variability could be influenced by cleaning and handling practices. High variability was observed in the corrosion values (MPY), the corrected corrosion values (corrected MPY), and the comparison to the NaCl reference (% of NaCl), which are shown in Table 11. The testing vessels (1 L bottles) were thoroughly cleaned (detergent, acid washed, and thoroughly rinsed) and then reused for subsequent tests; it was not anticipated that this would impact the results, however round 1 is dissimilar from rounds 2 and 3, with lower corrosion values.

New bottles are suggested for each round of future testing, to ensure that bottle carryover is not a contributing factor. The effect of testing round is shown in Figures 5 and 6.

Generally, all reference solutions and deicer products were found to be less corrosive than the 3% NaCl standard, which is expected based on published literature (Shi et al., 2009). The noteworthy exception is that equivalent Cl from $MgCl_2$ (i.e., 2.44% $MgCl_2$), was found to be slightly more corrosive than 3% NaCl, as is seen in the positive value for "% of NaCl." By contrast, equivalent Cl from $CaCl_2$ was far less corrosive than the 3% NaCl reference, which suggests that Cl^- concentration is not the only factor affecting corrosion rates. Statistical analyses were not pursued, due to elevated variance values; general trends are discussed. The deicer salts (i.e., rock salt and salt brine) were also found to be less corrosive that the 3% NaCl reference, which is potentially due to impurities present in the salt sources. Rock salt and BEET HEET had similar average corrosion rate values, while Magic Minus Zero had a lower average corrosion rate. Among liquid deicers, GreenBlast was consistently less corrosive than was AquaSalina, however the relative corrosivity of salt brine was more variable making comparisons challenging.

Table 13. Corrosion testing results for mils of penetration per year (MPY), Nanopure™ water corrected MPY, and ratio to salt (% of NaCl). Deicer products were tested at 3% NaCl and equivalent. Most conditions were tested with three washers with three testing rounds (i.e., 9 washers total). Select reference conditions were only tested once. One of the rock salt washers fell off the hanger during the test, therefore the values are presented for 8 washers. Reference salts are calculated in g/L; all products were tested at 3% and equivalent concentrations.

		MPY			Corrected MPY			% of NaCl		
Sample	**Number of samples**	**Mean**	**±**	**σ**	**Mean**	**±**	**σ**	**Mean**	**±**	**σ**
Nanopure™ H2O	9	95	±	69						
3% NaCl ref	9	130	±	63	36	±	13			
0.78% $MgCl_2$ ref	9	64	±	63	-30	±	77	-117	±	225
0.93% $CaCl_2$ ref	9	50	±	101	-45	±	84	-144	±	219
3% $MgCl_2$ ref	3	60	±	22	-87	±	22	-321	±	80
3% $CaCl_2$ ref	3	58	±	27	-89	±	27	-326	±	98
$MgCl_2$ chloride eq.	3	142	±	5	9	±	5	24	±	14
$CaCl_2$ chloride eq.	3	33	±	11	-101	±	11	-283	±	32
Rock salt	8	60	±	29	-28	±	63	-111	±	205
Magic Minus Zero	9	46	±	17	-49	±	65	-175	±	210
BEET HEET	9	64	±	40	-31	±	65	-125	±	220
Salt brine	9	46	±	9	-48	±	68	-173	±	209
GreenBlast	9	29	±	23	-66	±	65	-227	±	232
AquaSalina	9	41	±	23	-54	±	60	-189	±	206

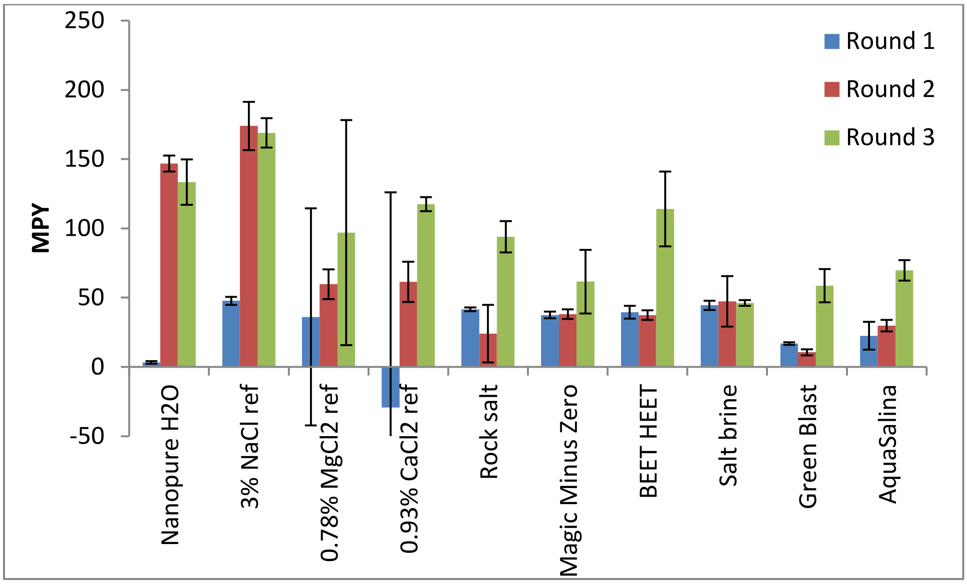

Figure 5. Corrosion testing results by solution to demonstrate round effects.

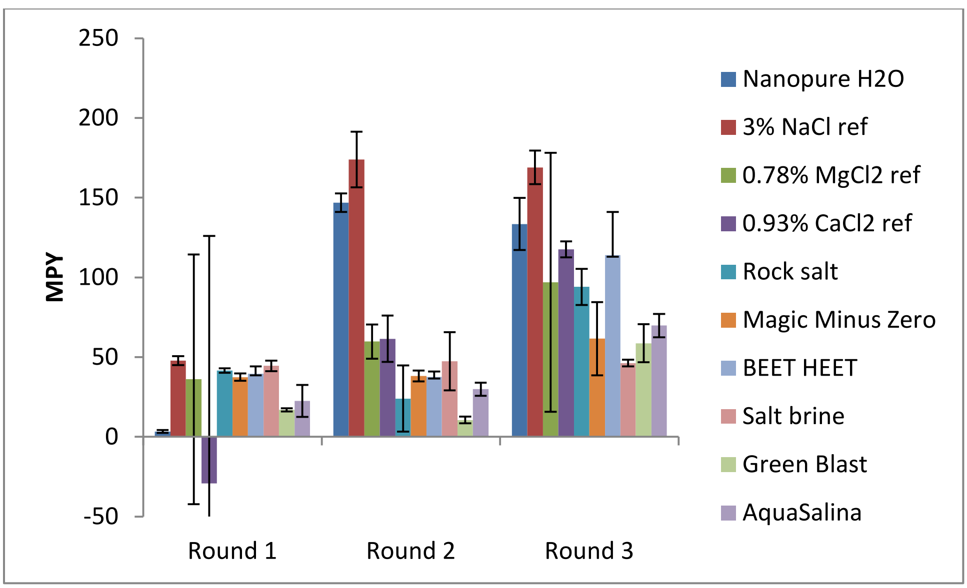

Figure 6. Corrosion testing results by testing round to show solution (product) effects.

Results of corrosion z-score analysis are shown in Table 14. Rock salt and BEET HEET consistently had higher z-scores, indicating that they have the greatest potential to cause corrosive harm. GreenBlast, followed by AquaSalina, had the lowest z-scores suggesting that the corrosive harms associated with these products would be lowest.

Table 14. Results of the corrosion theme product ranking analysis. A lower (more negative) score suggests a lower potential for environmental harm.

Product	Corrosion	Corrected corrosion	NaCl ratio	**Cumulative**
Rock salt	0.47	0.29	0.28	0.35
Magic Minus Zero	-0.06	-0.04	-0.04	-0.04
BEET HEET	0.62	0.25	0.21	0.36
Salt brine	-0.04	-0.03	-0.03	-0.03
GreenBlast	-0.70	-0.31	-0.29	-0.43
AquaSalina	-0.24	-0.12	-0.10	-0.16

Task 3.1.2.6 Overall ranking

An overall chemical analysis and corrosion testing ranking was undertaken, using the theme area z-scores; this is shown in Table 15. The overall ranking was calculated by applying equal weighting to each of the five thematic areas. Overall, salt brine is likely to have the lowest potential for negative environmental impact. This is expected for the chemical analysis, most of the products are salt amendment and therefore are expected to contain the same of more of the chemical constituents. However, some of the novel deicer formulations were less corrosive than the salt brine and the rock salt. Among the novel deicers, Magic Minus Zero was hard the lowest overall score (lower is better), as is was not a poor performer in any of the thematic areas, and was the strongest performer for pH.

Table 15. Results of the corrosion theme product ranking analysis. A lower (more negative) score suggests a lower potential for environmental harm.

	z-score					
Product	pH	Nutrients	Oxygen demand	Metals	Corrosion	Overall
Rock salt	0.29	-0.34	-0.84	1.26	0.35	0.14
Magic Minus Zero	-0.89	0.06	-0.17	0.65	-0.04	-0.08
BEET HEET	0.22	0.22	0.37	0.88	0.36	0.41
Salt brine	-0.66	-0.92	-1.00	-0.15	-0.03	-0.55
GreenBlast	-0.86	-0.42	1.75	1.16	-0.43	0.24
AquaSalina	1.89	1.40	-0.10	0.41	-0.16	0.69

Task 3.1.3 Summary

Chemical analysis and corrosion testing was conducted to evaluate some potential environmental implications of deicer products. Overall, it seems unlikely that use of any of the tested deicer products will result in direct negative environmental impacts to typical receiving water bodies, assuming adequate dilution. Direct negative environmental impacts may occur for small water bodies, where there is likely to be less dilution, or sensitive receiving waters. In particular, AquaSalina may reduce the pH. For receiving waters that are sensitive to nutrients or low dissolved oxygen concentrations, BEET HEET and AquaSalina generally had the highest nutrient concentrations, however GreenBlast exerted the greatest oxygen demand; taken together, it is likely that Magic Minus Zero will have the least negative effect on receiving waters that are sensitive to nutrients or low dissolved oxygen concentrations. None of the products exceeded metals criteria, for the given dilution and receiving water hardness assumptions. Corrosion results among tested products was highly variable; all products were less corrosive than that 3% NaCl reference and were similar to the rock salt or salt brine corrosivity. It should be noted that field corrosion results are often different than those observed in the laboratory. Furthermore, indirect negative effects that have previously associated with deicer use include metals release from soils due to cation exchange, lake stratification that can disrupt seasonal turnover, and decrease soil permeability.

References

APHA (2012). Standard Methods for the Examination of Water and Wastewater (22nd edition). American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF). Baltimore, MD.

Fay, L. and Shi, X., "Environmental Impacts of Chemicals for Snow and Ice Control: State of the Knowledge," *Water Air and Soil Pollution*, 223 (5), 2751-2770, 2012.

PA DEP. “Chapter 93. Water Quality Standards.” Copyright 2010. Accessed August 12, 2015. http://www.pacode.com/secure/data/025/chapter93/025_0093.pdf

PNS. “Pacific Northwest Snowfighters, Snow and Ice Control Chemical Products Specifications and Test Protocols.” 2010.

Shi, X., Veneziano, D., Xie, N., and Gong, J., "Use of chloride-based ice control products for sustainable winter maintenance: A balanced perspective," *Cold Regions Science and Technology*, 86, 104-112, 2013.

U.S. EPA. “National Recommended Water Quality Criteria.” Accessed August 12, 2015. http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

Task 3.1.4 - Appendix for Task 3.1 – Deicer Chemical Analysis and Corrosion Testing

This appendix contains greater details on the analytical methods and analyses that were conducted under task 3.1. Deicer products and method selection were previously described.

Task 3.1.4.1 Data presentation, statistical analysis, and ranking

Analysis of variance (ANOVA) statistical analyses were conducted using R to determine if differences in treatment means were present; statistical significance was set at $\alpha=0.05$. For each parameter, ANOVA was first applied to the salt brine and rock salt data to test for statistical equivalence. If salt brine and rock salt were found to be statistically dissimilar, then they were treated as separate references; this was determined to be the case for phosphorus, total nitrogen, and ammonia. In these cases, the pre-wetting agents were compared to rock salt, while the liquid formulations were compared to salt brine. For BOD and COD, salt brine and rock salt were found to be statistically equivalent, and then measurement from both rock salt and salt brine were considered the reference and were jointly used as the reference for all novel deicer formulations.

Best estimate values are reported and used in statistical analysis, even if they fall below the detection limit; however, values that are below the detection limit should be regarded simply as low and not as accurate values (i.e., low confidence estimate of a low concentration). Each of the analytical method sections also includes information about the employed calibration curve, detection limits, and replicate variability.

The third goal in the data analysis is to rank the tested products, which was conducted for each of the five thematic groups (pH, nutrients, oxygen demand, metals, and corrosion) and also cumulatively for all five groups combined. The data is processed using the approach shown in Figure 1. Data for each chemical analysis parameter is subjected to a transformation, and then z-score analysis, as is shown in Table 16. The data is transformed to minimize differences in parameter concentration or reference point. For example, pH was transformed such that the difference from neutral pH (i.e., 7) to reflect an appropriate reference point. Table 16 shows the thematic groupings and the parameter transformations.

Table 16. Data processing approach for cumulative analysis.

Theme	Parameter	Transformation	Analysis	Intra-theme weighting	Inter-theme weighting
pH	pH	absolute value(measured-7)	z-score	1	0.2
Nutrients	Phosphorus	(observed - min)/(max-min)	z-score	0.25	0.2
	Total nitrogen	(observed - min)/(max-min)	z-score	0.25	
	Ammonia	(observed - min)/(max-min)	z-score	0.25	
	Nitrate	Excluded due to low data quality	z-score	0	
	Nitrite	(observed - min)/(max-min)	z-score	0.25	
	Organic nitrogen	Excluded due to non detectable values	z-score	0	
Oxygen demand	BOD	(observed - min)/(max-min)	z-score	0.5	0.2
	COD	(observed - min)/(max-min)	z-score	0.5	
Metals (corrected concentrations)	Cr (52)	(observed - min)/(max-min)	z-score	0.125	0.2
	Ni (60)	(observed - min)/(max-min)	z-score	0.125	
	Zn (64)	(observed - min)/(max-min)	z-score	0.125	
	Cu (65)	(observed - min)/(max-min)	z-score	0.125	
	As (75)	(observed - min)/(max-min)	z-score	0.125	
	Ag (107)	(observed - min)/(max-min)	z-score	0.125	
	Cd (111)	(observed - min)/(max-min)	z-score	0.125	
	Hg (202)	Excluded due to non-detectable values	z-score	0	
	Pb (206+208)	(observed - min)/(max-min)	z-score	0.125	
Corrosion	Measured MPY	(observed - min)/(max-min)	z-score	0.33	0.2
	Corrected MPY	(observed - min)/(max-min)	z-score	0.33	
	Ratio to NaCl	(observed - min)/(max-min)	z-score	0.33	

The employed approach, known as z-score analysis, compares the measurement for a product (shown as product i) to all of the measurements for that parameter (for n=18 measurements across all evaluated products). Rankings for each analysis (chemical and corrosion) were conducted individually, and then the results were combined. For each analysis, a z-score was calculated as follows:

$$z - score_i = \frac{average_{product\,i} - \left(\sum measurement / n \right)_{all\,measurements\,for\,all\,products}}{standard\ deviation_{all\,measurements\,for\,all\,products}}$$

In all cases, the evaluation approach is set up such that “less is better” meaning that a lower score is expected to have a lower potential for negative environmental impact. As an example, pH is used as a demonstration of the full process, which is shown in Table 17. With the knowledge that a lower score (more negative) suggests lower potential for environmental harm, it can be seen that the products that have a pH near 7 have lower scores and therefore are considered less likely to have a negative pH effect on the environment. AquaSalina has a high positive score suggesting that it has the greatest potential for a negative environmental effect due to its low pH that is farther from neutral.

Table 17. Example of data transformation and z-score analysis using product pH data.

Solution	Data	Transformed data; absolute values(measured - 7)	Transformed average	z-score: (transformed average - all measurement average)/all measurement standard deviation
AquaSalina	3.8	3.2	3.22	1.89
AquaSalina	3.77	3.23		
AquaSalina	3.76	3.24		
Salt brine	7.49	0.49	0.51	-0.66
Salt brine	7.52	0.52		
Salt brine	7.53	0.53		
Rock salt	8.46	1.46	1.53	0.29
Rock salt	8.56	1.56		
Rock salt	8.56	1.56		
GreenBlast	7.3	0.3	0.31	-0.86
GreenBlast	7.31	0.31		
GreenBlast	7.31	0.31		
BEET HEET	8.43	1.43	1.45	0.22
BEET HEET	8.45	1.45		
BEET HEET	8.47	1.47		
Magic Minus Zero	7.25	0.25	0.27	-0.89
Magic Minus Zero	7.28	0.28		
Magic Minus Zero	7.29	0.29		

All measurement (n=18)	Average	1.215555556
	Stdev	1.062179902

Task 3.1.4.2 Analytical challenges

Analytical challenges existed in the current project due to the presence of substantial dissolved solids including sodium and chloride, and at times calcium, magnesium, potassium, and organic matter. There are a number of approaches that can be used to try to understand and overcome these analytical challenges, which include: 1) matrix interference check, 2) matched matrix standards, 3) spike recovery, 4) standard addition, and 5) matrix interference removal.

Matrix interference check requires a high purity version of the matrix be produced or acquired. In this case, it would be using a high purity NaCl that was known to not contain nutrients, oxygen demanding constituents, or metals. It would be included and processed the same as a sample to determine if it produced an artificially high value. This approach was employed for ICP-MS metals analysis.

Matched matrix standards, in which the standards are composed in a matrix similar to the samples, can be used to decrease the matrix artifacts if the matrix is causing signal enhancement or suppression (i.e., a change in the analyte detection). However a matched matrix (i.e., 23.3% NaCl concentration) could also result in an invalid result if the matrix reagents contain impurities of the analyte in question. Owing to this, NaCl matched matrix was only employed when suggested by the manufacturer of the nitrate ISE.

Spike recovery is an approach that is employed assesses if a sample matrix is interfering with accurate analyte analysis. In this approach, an analyte spike is added to a samples and also to a non-matrix blank. Spike recovery is assessed based on the recovered concentration (or mass) in the matrix sample compared to that in the non-matrix sample. Spike recovery was completed for typical ICP-MS analysis. For the other analyses, this approach was considered beyond the scope of the current project.

Standard addition is method to determine both the analyte concentration in the sample and also the matrix effects on analysis. For this approach, a sample is divided into aliquots where one aliquot is left unspiked, and other aliquots are spiked with varying concentrations of the analyte of interest. The measured analyte concentration is compared to the spike concentration; a regression is performed to determine the concentration in the unspiked sample. This approach is time and resource intensive and was considered beyond the scope of the current project.

Matrix interference removal can be accomplished, though this approaches will depend on the analyte of interest and the interfering matrix. Matrix removal was considered beyond the scope of the current project.

The below section details when matrix interference was a challenge and steps that were taken to try to overcome these challenges.

Task 3.1.4.3 pH

Methods

Standard method $4500H^+$ was employed for analyzing pH, using an accumet® Basic AB15 pH meter with automatic temperature compensation. The pH meter was calibrated with three buffered solutions: pH 4, 7, and 10. Samples were measured at room temperature, and no sample dilution was employed (i.e., 23.3% NaCl or equivalent). Sample replicate analysis produce highly reproducible results, and standard deviations were less than 0.1 pH units.

Task 3.1.4.3 Nutrients

Phosphorus

Phosphorus was measured acid hydrolysable phosphorus, using a Hach kit (method 8180) that was analyzed spectrophotometrically (λ=880 nm). A six point calibration curve was employed, ranging from 0 – 3 mg/L as PO_4^{3-} ($R^2 = 0.9711$). Samples were to be diluted 2-fold (i.e., 1 part sample and 1 part Nanopure™ water) to fit into the calibration curve range, and results are reported in mg/L P. Strong replicate reproducibility was observed for samples with phosphorus > 0.5 mg/L P (i.e., RSD < 5%), however substantial replicate variability was observed for samples that had low phosphorus concentrations. Though not thought to have impacted the results in this study, suspended particles or high turbidity samples can result in inconsistent results to variable sorption (or desorption) of phosphorus to particles.

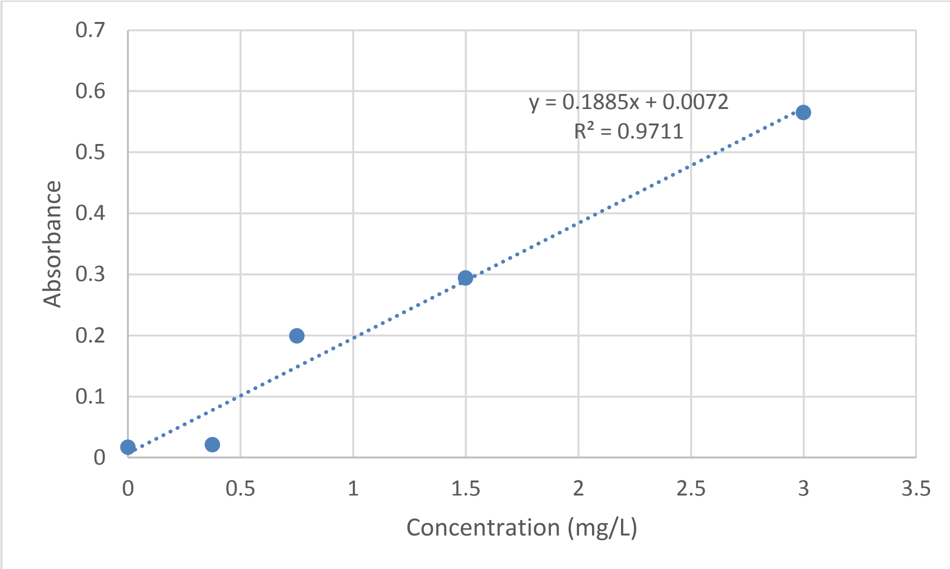

Figure 7. Phosphorus calibration curve.

Total nitrogen

Total nitrogen was measured using a Hach persulfate oxidation and spectrophotometric analysis (Hach method 10071; measured at λ=410 nm). A five point calibration curve, ranging from 0 mg/L to 25 mg/L total nitrogen was produced (R^2 = 0.988); the published detection limit is 0.5 mg/L total nitrogen. All products had replicate RSD values <15%. Magnesium, calcium and organic carbon interferences were noted (500 mg/L Mg, 300 mg/L Ca, and 150 mg/L organic carbon), and among the expected deicer product concentrations, the organic carbon interference was the most restrictive. To overcome potential effects of interferences, BEET HEET, Magic Minus Zero, and GreenBlast were each diluted 20-fold (i.e., 1.165% equivalent) and analyzed, however this resulted in concentrations that were below the detection limit. Rock salt, salt brine, and AquaSalina were assessed to have no published interference concerns. All presented results are from analyses at 23.3% and equivalent concentrations, however matrix interference effects may be present for BEET HEET, Magic Minus Zero, and GreenBlast.

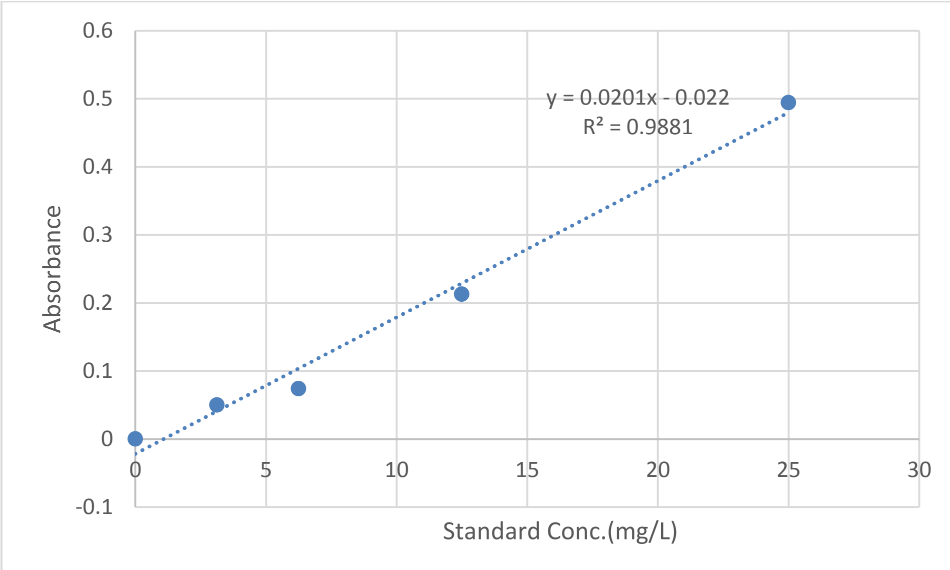

Figure 8. Total nitrogen calibration curve.

Ammonia

Ammonia was measured according to APHA standard method 4500-NH_3 D using an ammonia ion selective electrode (ISE). In brief, a sample was amended with a commercially-available ionic strength and pH adjustment solution, and then analyzed with the ISE. A five point calibration curve, ranging from 0.1 – 1000 mg/L NO_3^--N, was analyzed, and the semilog fit was strong (R^2 = 0.9959; shown in Figure 9). Sample dilution was not required (i.e., 23.3% or equivalent) and replicate analysis RSD % values were less than 15%, save salt brine which has an RSD of near 25%. Chloride interference was not indicated to be an issue.

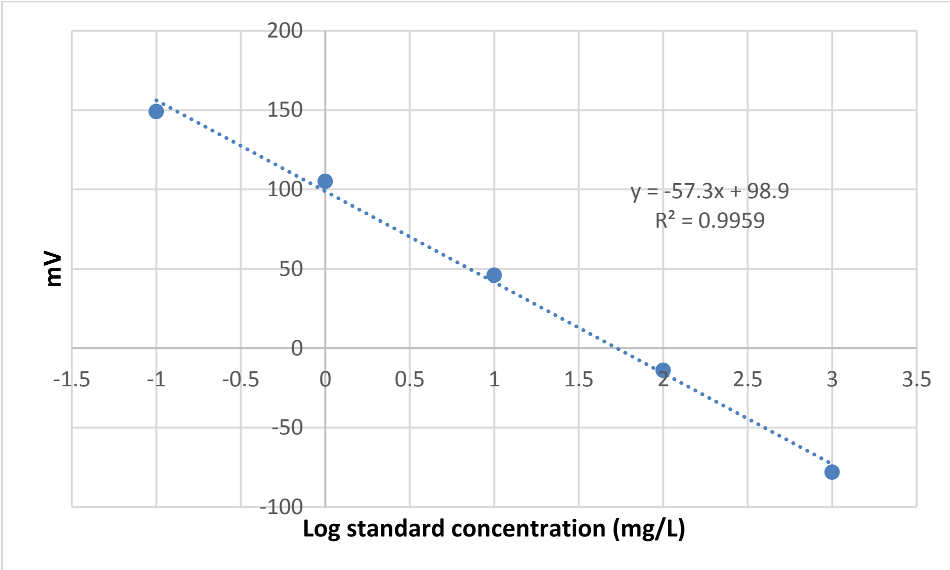

Figure 9. Ammonia calibration curve.

Nitrate

Nitrate was measured according to APHA standard method 4500-NO_3^- D using a nitrate ion selective electrode (ISE). In brief, a sample is supplemented with equal parts buffer solution (2 M $(NH_4)_2SO_4$) and measured with the ISE. A six point calibration curve was produced (ranging from 1 to 500 mg/L as NO_3^-), however improved semi-log linearity was found if the low concentration standards were omitted. The employed calibration curve included four standards ranging from 10 to 500 mg/L (R^2 = 0.966). Samples required no additional dilution (i.e., were analyzed as 23.3% or equivalent). Based on initial analysis, chloride interference is possible at the NO_3^-:Cl^- ratios present in the samples. In order to minimize these effects, 23.3% NaCl match matrix standards were prepared and used in the subsequent and reported analysis, which resulted in a steep calibration curve slope such that small differences in probe analyses (in mV) resulted in large differences in estimated concentrations. This resulted in high replicate variability for some deicers. Additionally, repeated analysis of the same standards resulted in substantially different outputs values (in mV), which suggests that there may be a matrix stabilization period. However, attempted to stabilize the probe response by pre-soaking it in 23.3% NaCl solution did not produce reasonable results. Furthermore, the matrix is likely well matched to the rock salt and salt brine samples, however the matrix effect from the other deicers, especially AquaSalina, is unknown and may contribute to some of the strange values that were observed. The matched-matrix approach was repeated and did not consistently result in sensical values. As a results, the produced data were not considered valid and are not presented.

Nitrite

Nitrite was measured using a Hach colorimetric assay (Hach method 8507 analyzed at λ=507 nm). A five point calibration curve, ranging from 0 to 0.3 mg/L NO_2^- as N was employed (R^2 = 0.9997), and the published detection limit is 0.002 mg/L. The replicate reproducibility was poor, especially among low nitrite samples (namely, rock salt and salt brine references). Samples were analyzed undiluted (i.e., 23.3% and equivalent), and there were no noted chloride interferences.

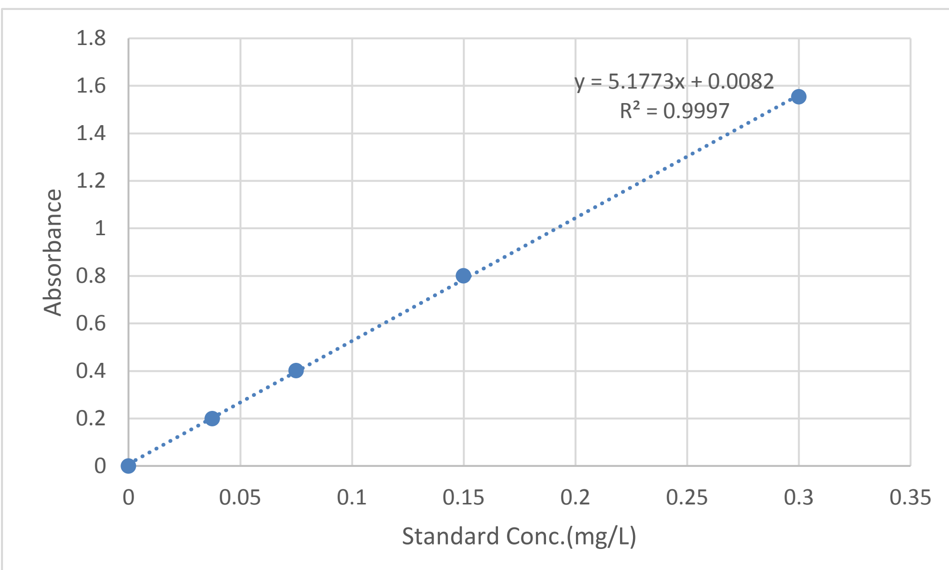

Figure 10. Nitrite calibration curve.

Organic nitrogen

Organic nitrogen was measured using the Hach simplified TKN (s-TKN) assay, which measures total Kjeldahl nitrogen as the sum of free ammonia and organic nitrogen. The employed method is less labor intensive, less expensive, and less dangerous than the traditional high temperature sulfuric acid digestion method. In brief, inorganic and organic nitrogen constituents are oxidized via peroxodisulfate to nitrate which is then measured spectrophotometrically. The published detection limit is 1 mg/L TKN. Chloride and COD interferences are indicated in the methods, and between the two, chloride interference was likely to be greater. To avoid a potential chloride interference, indicated to occur at 500 mg/L Cl^- or greater, samples were diluted 300-fold which should have ~470 mg/L Cl^-. The required dilution resulted in non-detectable sample concentrations.

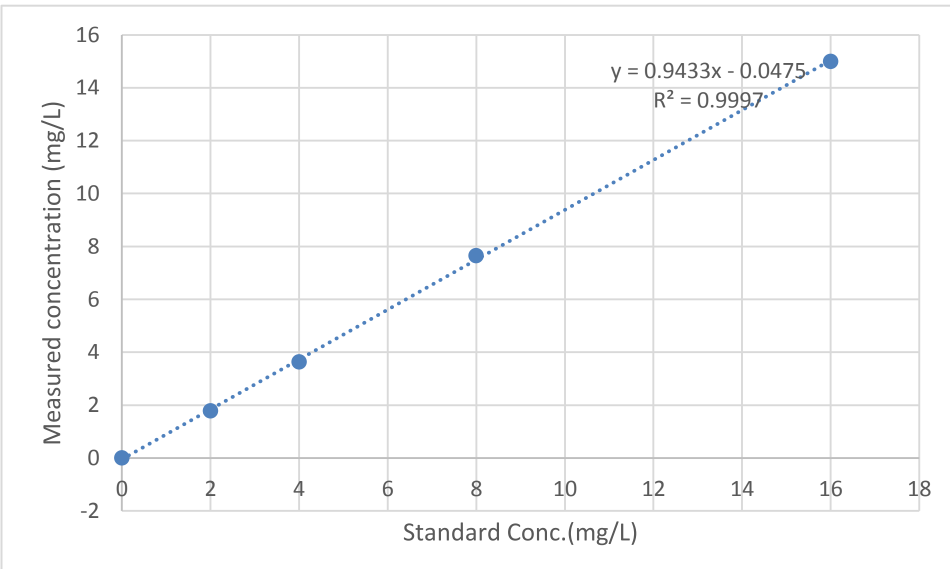

Figure 11. TKN calibration curve.

Task 3.1.4.4 Oxygen demand

Biochemical oxygen demand (BOD)

Biochemical oxygen demand was measured in a five day test according to APHA standard method 5210-B. In brief, a sample is combined with oxygenated dilution water (containing nutrients and salt), and then a seed microbiological community was introduced. A soil microbial community that had been exposed to a salt broth was used in this test. The initial dissolved oxygen (DO) concentration was determined, and then the samples are incubated for five days; DO was measured at the conclusion of five days. A nitrification inhibitor was not deemed necessary for the 5 day test and was not included. Per APHA, sample pH neutralization was completed for the AquaSalina sample. Appropriate quality control and assurance measures were followed, per prescribed methods, including: dilution water blank (negative control), seed check, and glucose-glutamic acid check (positive control). Deicer samples were diluted, to provide a solution that was hospitable to growth of the microbial community, so that the maximum salt concentration was 3.5% NaCl or equivalent. Preliminary BOD testing was conducted to determine the appropriate dilution factor for the novel deicers, and dilution to salt values less than 3.5% salt were required to meet BOD quality control and assurance requirements. BOD was calculated as follows:

$$BOD_5 = \frac{(D_1 - D_2) - (S)V_s}{P}$$

Where:

D_1= initial DO of diluted sample

D_2= final DO after 5-day incubation

S = oxygen uptake of seed

V_s= volume of seed

P = decimal volumetric fraction of sample used; 1/P = dilution factor

Dilution water blank, seed check, and glucose-glutamic acid measures met prescribed standards. Additionally, for a sample to be considered valid, the sample must have a residual DO concentration of at least 1.0 mg/L at the final DO measurement (D_2 > 1.0 mg/L), and must exert a DO demand of at least 2.0 mg/L (D_1 - D_2 > 2.0 mg/L). Salt brine and rock salt analyses were conducted at 3.5% NaCl and did not exert a DO demand of 2.0 mg/L, however this was considered a valid result as BOD of the salt was expected to be minimal. Replicate variability in novel deicer products was low (i.e., RSD% < 6).

Chemical oxygen demand (COD)

Chemical oxygen demand was measured via a dichromate oxidation and colorimetric assay (Hach TNT 821 kit using Hach method 8000). In brief, constituents are oxidized by dichromate under heated acidic conditions (sulfuric acid). Oxygen demand is determined via spectrophotometric analysis (λ=420 nm) to determine the amount of Cr^{6+} in solution, where Cr^{6+} is reduced to Cr^{3+} in the presence of an oxygen demand. A five point calibration curve, using potassium acid phthalate as a standard, included a range from 0 mg/L to 150 mg/L COD; the calibration curve produced a strong linear fit (R^2 = 0.9996); the published detection limit is 3 mg/L. For COD analysis, all samples were diluted 100-fold with Nanopure™ water (i.e., 0.233% NaCl and equivalent) to fit within the calibration curve range. Replicate analysis was generally fairly good, with RSD % values generally less than 10%, though BEET HEET was more variable (RSD ~25%). Chloride concentrations greater than 2,000 mg/L are noted to interfere with COD analysis; as analyzed (i.e., 100-fold dilution), the expected concentration was ~1,400 mg/L Cl^-, therefore chloride interferences was deemed to not be an issue.

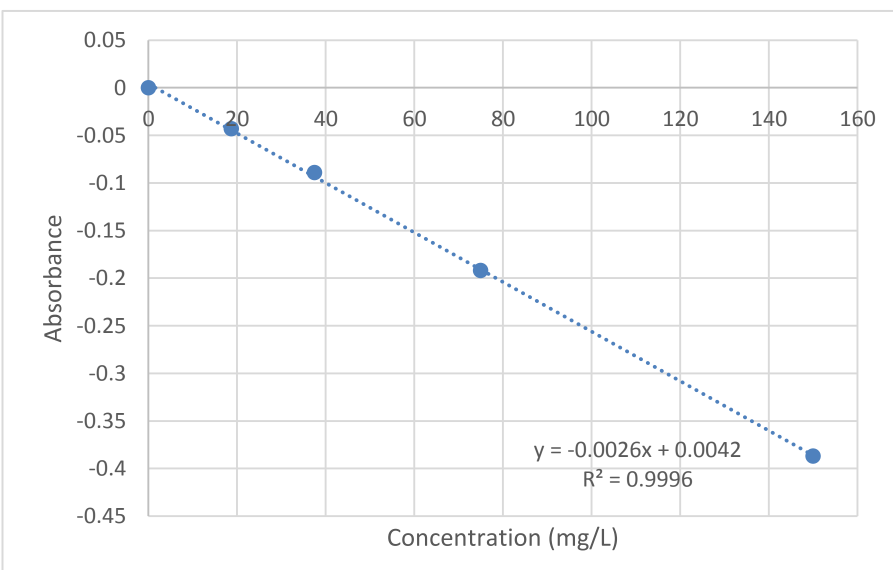

Figure 12. COD calibration curve.

Task 3.1.4.5 Metals

Metals analysis was conducted on acidified samples (1% HNO_3) using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS). Before each use, the instrument was tuned to minimize oxides and double charged ions; He gas was typically included in the collision cell to minimize polyatomic interferences. Conventional ICP-MS analysis does not allow for analysis of high matrix samples (i.e., high salt samples), which thus necessitates substantial sample dilution. This is often accomplished via manual sample manipulations which have the potential to introduce errors. However, ICP-MS technologies have advanced to allow for the analysis of higher matrix samples, including Agilent's "ultra-high matrix introduction" capabilities (UHMI), which is similar to pneumatic dilution. Samples were analyzed undiluted (i.e., 23.3% and equivalent), however to address the high matrix (i.e., high salinity), maximum UHMI capabilities were employed. While this approach does accommodate high matrix solutions and does not require manual sample manipulation, but it does decrease the counts (i.e., signal) that reach the detector, and thus increases the detection limits.

For routine metals analysis, 1% HNO_3 was employed and a 13 point calibration curve was used with concentrations ranging from 1 ng/L to 100 µg/L. The analysis run included a calibration curve including a calibration

Table 18. ICP-MS potential polyatomic interferences (from Agilent user handbook).

Table 1. Principal Polyatomic Interferences from an Aqueous Matrix Containing N, S, Cl, C, Na, and Ca

Isotope	Principal interfering species
^{51}V	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$
^{52}Cr	$^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{16}OH$, $^{37}Cl^{14}NH$
^{53}Cr	$^{36}Ar^{16}OH$, $^{40}Ar^{13}C$, $^{37}Cl^{16}O$, $^{35}Cl^{18}O$, $^{40}Ar^{12}CH$
^{54}Fe	$^{40}Ar^{14}N$, $^{40}Ca^{14}N$
^{55}Mn	$^{37}Cl^{18}O$, $^{23}Na^{32}S$
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$
^{57}Fe	$^{40}Ar^{16}OH$, $^{40}Ca^{16}OH$
^{58}Ni	$^{40}Ar^{18}O$, $^{40}Ca^{18}O$, $^{23}Na^{35}Cl$
^{59}Co	$^{40}Ar^{18}OH$, $^{43}Ca^{16}O$
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$
^{61}Ni	$^{44}Ca^{16}OH$, $^{38}Ar^{23}Na$, $^{23}Na^{37}ClH$
^{63}Cu	$^{40}Ar^{23}Na$, $^{12}C^{16}O^{35}Cl$, $^{12}C^{14}N^{37}Cl$
^{64}Zn	$^{32}S^{16}O_2$, $^{32}S_2$, $^{36}Ar^{12}C^{16}O$, $^{38}Ar^{12}C^{14}N$, $^{48}Ca^{16}O$
^{65}Cu	$^{32}S^{16}O_2H$, $^{32}S_2H$, $^{14}N^{16}O^{35}Cl$, $^{48}Ca^{16}OH$
^{66}Zn	$^{34}S^{16}O_2$, $^{32}S^{34}S$, $^{33}S_2$, $^{48}Ca^{18}O$
^{67}Zn	$^{32}S^{34}SH$, $^{33}S_2H$, $^{48}Ca^{18}OH$, $^{14}N^{16}O^{37}Cl$, $^{16}O_2{}^{35}Cl$
^{68}Zn	$^{32}S^{18}O_2$, $^{34}S_2$
^{69}Ga	$^{32}S^{18}O_2H$, $^{34}S_2H$, $^{16}O_2{}^{37}Cl$
^{70}Zn	$^{34}S^{18}O_2$, $^{35}Cl_2$
^{71}Ga	$^{34}S^{18}O_2H$
^{72}Ge	$^{40}Ar^{32}S$, $^{35}Cl^{37}Cl$, $^{40}Ar^{16}O_2$
^{73}Ge	$^{40}Ar^{33}S$, $^{35}Cl^{37}ClH$, $^{40}Ar^{16}O_2H$
^{74}Ge	$^{40}Ar^{34}S$, $^{37}Cl_2$
^{75}As	$^{40}Ar^{34}SH$, $^{40}Ar^{35}Cl$,$^{40}Ca^{35}Cl$
^{77}Se	$^{40}Ar^{37}Cl$, $^{40}Ca^{37}Cl$
^{78}Se	$^{40}Ar^{38}Ar$
^{80}Se	$^{40}Ar_2$, $^{40}Ca_2$, $^{40}Ar^{40}Ca$

blank, seven preparation blanks, and rinse blanks that were intermixed through the analytical run. The seven preparation blanks were used to establish the detection limit as follows: average + 3*standard deviation. Additionally, a matrix interference sample was analyzed in triplicate (23.3% ACS NaCl). The 23.3% NaCl matrix sample was additionally spiked with the standard stock solution to test recovery of a 5 µg/L and 25 µg/L working solution (each in triplicate); this was validated against Nanopure™ water spiked with 25 µg/L working solution. Fifty-six mass peaks, including six peaks for internal standards, were analyzed as follows: 6, 7, 9, 27, 31, 32, 35, 39, 45, 51, 52, 53, 54, 55, 56, 57, 59, 60, 63, 64, 65, 66, 68, 89, 71, 75, 77, 78, 82, 85, 88, 89, 103, 107, 111, 133, 137, 139, 140, 141, 146, 147, 153, 157, 159, 163, 169, 172, 175, 195, 205, 206, 208, 209, 232, and 238. Spectral interferences were corrected according to EPA method 6020. He and H_2 gasses were used in the collision/reaction cell to minimize polyatomic interferences. Interferences were assessed based on potential expected interferences, shown in Table 18, combined with observed data, where lower detected concentrations was taken as indicative of fewer polyatomic interferences; based on these analyses Cr(52), Cu(65), and Zn(64) are presented. Elemental analysis conditions and detection limits are reported in Table 19.

Table 19. ICP-MS analysis conditions and calibration.

Element	Mass	Mode	Matrix	R	DL (µg/L)
Cr	52	He	1% HNO3	0.9992	0.48
Ni	60	He	1% HNO3	0.9992	0.07
Zn	64	He	1% HNO3	0.9996	0.46
Cu	65	He	1% HNO3	0.9996	0.21
As	75	H2	1% HNO3	0.9990	0.02
Ag	107	He	1% HNO3	0.9998	0.07
Cd	111	He	1% HNO3	0.9980	0.00
Hg	202	He	1% HCl	0.9999	3.05
Pb	206 + 208	He	1% HNO3	0.9999	0.13

Quality control and quality assurance values, as measured for the standard metal suite analysis, are shown in Table 20.

Table 20. ICP-MS analysis conditions and calibration.

	Triplicate average concentration (ug/L)							
	52 Cr [He]	60 Ni [He]	63 Cu [He]	64 Zn [He]	75 As [H2]	107 Ag [He]	111 Cd [He]	Tot Pb [He]
Detection limit	0.477	0.073	0.000	0.459	0.024	0.069	0.000	0.127
Inter sample rinse	1.909	0.791	1.277	0.368	0.178	0.044	0.044	0.296
ACS salt	1.959	1.285	4.450	6.316	0.343	0.054	0.000	0.482
ACS salt+5 ppb	6.549	4.962	8.667	10.032	3.683	4.495	4.647	7.983
ACS salt+25 ppb	24.253	24.281	26.765	30.620	16.122	22.967	22.205	40.617

Substantial interference was observed for several elements (ACS salt analysis (23.3%) shown in Table 20). To overcome that, values were corrected for the matrix interference by subtracting the average ACS salt concentration; this assumes that the entire value is attributable to a molecular interference and that the ACS salt does not contain any of the analytes of interest. If the corrected concentration ($C_{corrected}$) was calculated to be negative, then it was assigned a value of 0.

$$C_{corrected} = C_{measuredsample} - C_{ACS\ salt}$$

The calculated values were then compared to their expected values (5 ug/L spiked, 25 ug/L spiked, or spike recovery compared to 25 ug/L as measured in a no salt matrix; values close to unity indicate expected recovery); this is shown in Figure 13. Generally, recovery was fairly good (between 0.8-1.2), but As was under-recovered and Pb was over-recovered.

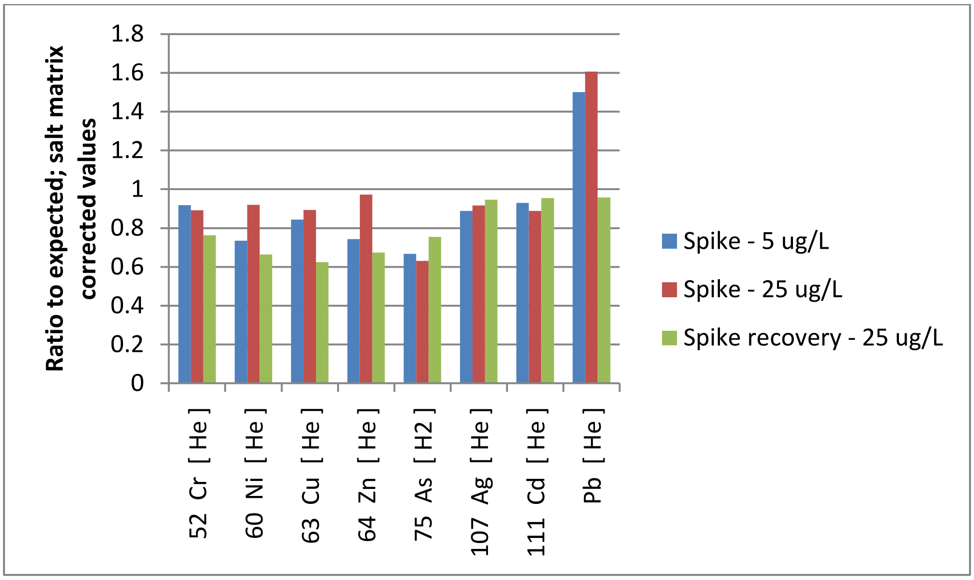

Figure 13. Recovery of elemental spikes to expected values based on corrected concentrations; expected values are based on nominal spike concentration (5 or 25 µg/L) or spike recovery as compared to no salt matrix spike.

Mercury (Hg) was similarly analyzed, however 1% HCl was employed to improve Hg washout; a seven point calibration curve was used ranging from 100 ng/L to 100 µg/L. Two Hg mass peaks (201 and 202) were monitored and 209 was used as the internal standard. Hg(202) is presented. The analysis run included a calibration curve including a calibration blank, seven preparation blanks, and rinse blanks that were intermixed through the analytical run. The seven preparation blanks were used to establish the detection limit as follows: average + 3*standard deviation. Additionally, a matrix interference sample was analyzed in triplicate (23.3% ACS NaCl). The 23.3% NaCl matrix sample was additionally spiked with the standard stock solution to test recovery of a 5 µg/L (triplicate). Results are shown in Figure 14. The Hg detection limit was high (~3 ug/L) and the spike was under-recovered, especially for the corrected value. Corrected sample values were commonly negative and thus assigned a value of 0.

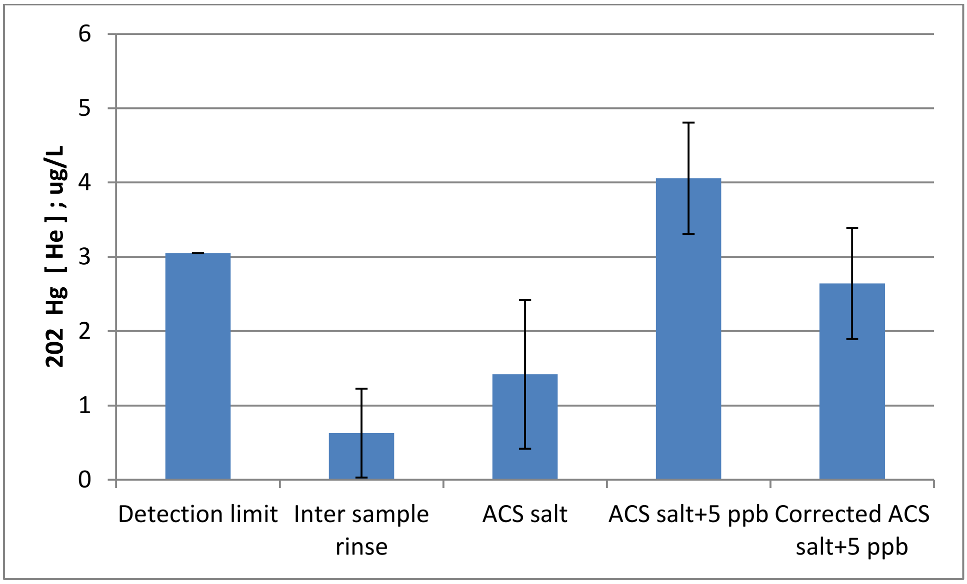

Figure 14. Results of quality control and quality assurance analyses for Hg. Data are presented as measures, expect for "Corrected ACS salt+5 ppb" (corrected as previously discussed).

Task 3.1.4.6 Corrosion testing

Corrosion testing was conducted per Pacific Northwest Snowfighters 72 hr. cyclic method. The method specifies the steel washers (dimension, materials, and hardness) and the pre-cleaning technique. The cleaned washers are then measured to determine individual dimensions and mass. There are three washers per reaction vessel which contains ~450 mL of solution (i.e., reference solution or deicer product); the deicer products were tested at 3% NaCl or equivalent. The washers are completely submerged for 10 minutes, and then held in the headspace above the solution for 50 minutes; this process is repeated for 72 hours, and care was taken to ensure that the washers are completely submerged in the appropriate phase (i.e., completely submerged or completely above the fluid), and that the washers remain separate (i.e., not touching). At the conclusion of 72 hours of cycling (10 minutes submerged, 50 minutes above during each cycle), the washers are removed, carefully cleaned as specified, and re-weighed. Corrosion (as mils penetration per year; MPY), adjusted corrosion (corrected for same-test Nanopure™ water corrosion MPY), and NaCl normalized (referred to as "% NaCl") were calculated per PNS guidelines (2010) as shown below.

$$MPY = \frac{\left(m_{initial} - m_{final}\right) \cdot 1000 \, {}^{mg}\!/_{g} \cdot 534}{Area \cdot 72hrs \cdot 7.85 \, {}^{g}\!/_{mL}}$$

$$MPY_{corrected} = MPY_{treatment} - MPY_{nanopure}$$

$$\% \, NaCl = \frac{MPY_{corrected,\, treatment}}{MPY_{corrected,\, NaCl}} \cdot 100\%$$

Executive Summary

The release of deicing materials in the environment has been shown to potentially impacts living organisms. Laboratory toxicity tests were conducted to assess the effects of the five deicing materials on model living organisms from different trophic levels, including a green alga (*Pseudokirchneriella subcapitata*), an aquatic invertebrate (*Ceriodaphnia dubia*), a fish (fathead minnow, *Pimephales promelas* – larval and embryonic stage), an aquatic plant (duckweed, *Lemna minor*), and a terrestrial plant (soybean, *Glycine max*).

The toxicants tested include the following deicing agents used in their liquid form: salt brine (23.3% NaCl); AquaSalina (22.1% mixed salt solution); BEET HEET (pre-wetting agent, used as additive to 23.3% NaCl brine); Magic Minus Zero (pre-wetting agent, used as additive to 23.3% NaCl brine); GreenBlast (26 - 29% $MgCl_2$ solution, used in mixture with 4 volumes of 23.3% NaCl brine). For each test, five concentrations of deicer solutions and a control (diluent without deicer) were used.

Results from the toxicity testing consist in various toxicity endpoints, including the lethal and inhibitory concentration 50% (EC50 or IC50) and the non- and lowest-observed-effect concentration (NOEC & LOEC). The toxicity endpoints for the five deicer materials obtained using the different tests were then compiled to establish a ranking of the deicers based on their relative toxicity and to assess the associated environmental risk.

The toxicity endpoints were normalized by reference to the salt brine. For each material, a *toxicity score* was calculated using a weighted average of the normalized toxicity endpoints – referred to as *overall score*. In the absence of further rationale, the same weighting factor was used for all endpoints. Specific scores were also calculated for the plant and algal tests – referred to as *plant/algal score* – and animal tests –referred to as *animal score*. These scores were then calculated for all endpoints (NOEC, LOEC, and IC/LC50) and for the IC/LC50 only. The deicers were then ranked based on their relative toxicity score. The most toxic deicer materials were found

to be AquaSalina, based on the overall and plant/algal score, and GreenBlast, based on the animal score. These results may be explained by the relative toxicity of the cationic component of the composing salts, which follows the sequence: potassium (K) > magnesium (Mg) > sodium (Na)/calcium (Ca). Unlike the other deicer materials, AquaSalina contains KCl (1.5%) and $MgCl_2$ (2.6%) and GreenBlast contains $MgCl_2$ (5.2-5.8%), in addition to NaCl.

An environmental risk assessment was then conducted based on the lowest NOEC and LC/IC50 for aquatic organisms and three environmental exposure scenarios: 'low' exposure (25 mg salt/L), 'high' exposure (165 salt/L), and exposure to a 500-time dilution of the deicers (470 mg salt/L). In short, we used the *risk quotient* method, which compares toxicity thresholds (i.e., endpoints) with predicted environmental concentrations. Based on the results, none of the deicers tested seems to pose a significant threat to the environment at the concentration of 25 or 165 salt/L. Only AquaSalina and GreenBlast – the most toxic deicers identified in this study – may represent a concern for invertebrates – the most sensitive aquatic organisms tested – in the highest exposure scenario (dilution 500 times).

1. Introduction:

The release of deicing materials in the environment adversely impacts living organisms through direct, toxic effects, either related to deicing components (e.g., Na^+ and Cl^-) or to co-contaminants (e.g., metals, ammonia), and indirect effects related to the alteration of their environment (i.e., water or soil) or nutrient sources.

In this study, we conducted laboratory toxicity tests to assess the direct effects of the five deicing materials on living organisms. Because toxicants impact differently different organisms, a battery of tests, utilizing organisms from different trophic levels were used. Because deicers salts are highly soluble in water and are typically applied on impervious pavement, they are washed by running water and mostly impact the aquatic environment. Consequently, this study used a majority of model aquatic species, including a green alga, an aquatic invertebrate (daphind), a fish (fathead minnow, larval and embryonic stage), and an aquatic plant (duckweed). In addition, because deicer salts are known to impact vegetation, a model terrestrial plant, soybean, was included in the study.

2. Objectives of the Study:

Deicer material toxicity and ecotoxicity testing were conducted to assess their potential environmental impacts using a suite of model organisms from different trophic levels, as suggested by PNS (2010). Toxicity testing was conducted, employing appropriate quality controls & quality assurance measures, to determine the deicer dose-response curves, which were used to derive various toxicity endpoints, such as lethal and inhibitory concentration 50% (EC50 or IC50) and the non- and lowest-observed-effect concentration (NOEC & LOEC).

These toxicity endpoints were used (1) to establish a ranking of the deicer materials based on their relative toxicity and (2) to succinctly assess the environmental risk potentially associated with the deicer materials.

The following tests were conducted:

- Freshwater alga, *Pseudokirchneriella subcapitata* (formerly known as *Selenastrum capricornutum*), algal growth assay - EPA-821-R-02-013.
- Aquatic daphnid (invertebrate), *Ceriodaphnia dubia*, survival and reproductive assays - EPA-821-R-02-013.
- Fathead minnow (*Pimephales promelas*), larval toxicity test - EPA-821-R-02-013.
- Fathead minnow (*Pimephales promelas*), embryo-larval survival and teratogenicity test - EPA-821-R-02-013.
- Duckweed (*Lemna minor*), aquatic plant toxicity test using *Lemna* spp. - OCSPP 850.4400.
- Soybean (*Glycine max*), germination and root elongation tests - EPA OPPTS 850.4200.

3. Experimental Methods:

3.1. General:

All toxicity tests were conducted in a dedicated, light- and temperature-controlled growth/incubation room equipped with incubators, orbital shakers, and lighted shelves. Unless otherwise stated, the room was operated at 25 °C under a 16-h/8-h light/dark photoperiod or continuous illumination. The room temperature was monitored daily and was always in the range 23 – 26 °C, which is in compliance with the test requirements. The light intensity was shown to vary significantly depending on the position of the test chambers on the lighted shelves (by approx. 100 – 200 ft-c). When using photosynthetic organisms, these variations were averaged by using a daily or bi-daily random block design for the arrangement of the test chambers on the shelves.

Major equipment used in this study includes the following:

- Spectrophotometer: UV-Vis spectrophotometer PDA, Agilent 8453
- Analytical Balance: Mettler-Toledo ME203E
- Light-meter: Fisher Scientific

- pH-meter: Fisher Scientific AB15
- DO-meter: Hach HQ40d Multi with IntelliCAL LDO101 Optical DO Probe
- Autoclave: 32-L vertical-loading autoclave, Yamato SM300
- Laminar hood: 4-foot Class II Biosafety Cabinet
- Bright-field/fluorescence microscope: Vanguard IS500
- Stereoscopic microscope: Fisher Magnifier 133-8002
- Illuminated plate counter with magnification lens: Fisher Scientific
- Orbital shakers: Thermo Scientific MaxQ2000
- Incubators/ovens: Fisher Scientific Precision Incubator 3EM
- Water bathes: Fisher Scientific Isotemp 2340

All procedure were applied following good laboratory practices and performed by trained personnel under the direct supervision of Dr. Van Aken. All personnel were requested to receive appropriate safety training and wear personal protection equipment. All reagents and chemicals were analytical grade or higher. Analytical equipment, including pH-meter, DO-meter, light-meter, and analytical balance were calibrated and operated according to the manufacturer instructions. The pH-meter, DO-meter, and light-meter were calibrated daily or prior to utilization.

The tests were conducted according to widely accepted guidelines as listed below. These guidelines list recommended and requested conditions, as well as test result acceptability criteria. Requested elements of the tests were always followed and met. We also largely followed recommendations as meeting these test conditions greatly increase the likelihood that the completed test will be acceptable and valid. However, as stated in OCSPP 850.4000, "it is unlikely a study will be rejected when there are slight variations from guideline environmental conditions and study design unless the control organisms are significantly affected […]."

All procedures involving vertebrate animals (i.e., fish larvae and embryos) were described in a detailed protocol that was approved by the Temple University Institutional Animal Care & Use Committee (IACUC) – Protocol ACUP# 4479 – to be compliant with the Federal Animal

Welfare Act. Two administrative amendments were later approved: (1) for personnel addition (08/31/15) and (2) for the extension of the protocol to fish embryos (09/10/15).

3.2. Deicer Materials:

The toxicants tested include the following deicing agents: salt brine (23.3%), AquaSalina, BEET HEET, GreenBlast, and Magic Minus Zero.

Because in the proposed toxicity tests, the test organisms – all aquatic except the terrestrial plant soybean – are exposed to toxicants via the liquid medium, all deicers were tested in their liquid form: 23.3% w/w brine was prepared using rock salt (NaCl), Magic Minus Zero and BEET HEET, which are pre-wetting agents, were first mixed with rock salt according to the manufacturers' recommendations (i.e., 10 and 5 gallons per ton of rock salt, respectively) and a 23.3% w/w brine was then prepared. GreenBlast, which is a liquid deicer containing 26 - 29% magnesium chloride ($MgCl_2$), was mixed with 4 volumes of brine (ratio 1:4), as recommended by the manufacturer. AquaSalina, a liquid deicer containing 22.1% w/w of mixed chloride salts, was used as received.

For the determination of the initial exposure concentrations, we assumed that the toxicity of deicers comes primarily from the salt (deicing) component(s) – not from potential corrosion inhibitors and/or other organic or inorganic additives. The organisms were exposed to 5 dilutions of each deicer material, with the highest concentration being equal to approx. 2 times the lethal or inhibitory concentration 100% (LC100 or IC100) reported in the literature, based on the salt content of the material.

For instance, the LC100 of NaCl for fathead minnow, *P. promelas*, has been reported to be approx. 12 g/L. For deicers based on NaCl (i.e., salt brine, BEET HEET), the dilution was calculated to obtain the final highest concentration of approx. 12 g/L x 2 = 24 g NaCl/L. For deicers based on $MgCl_2$ (i.e., GreenBlast, Magic Minus Zero), the calculated dilution led to a final highest concentration equivalent to 12.3 g $MgCl_2$/L. For AquaSalina (containing NaCl, $MgCl_2$, and $CaCl_2$), the dilution was calculated based on the weighted average of LC100/IC100s of the composing salts, leading to an equivalent salt concentration of 14 g/L. Because the calculated highest doses for all deicers fall within the same order of magnitude and in the purpose to facilitate comparisons, we then used the same dilution factors for all deicers.

3.3. Test Solutions:

Five concentrations of deicer were used in each test. The highest concentration tested was obtained by diluting the liquid form of the deicer (see above) 20 times for alga exposure, 40 times for daphnid exposure, 5 times for fathead minnow larva exposure, 10 times for the fathead minnow embryo exposure, and 10 times for plant (duckweed and soybean) exposure (Table 1). The test solutions were then prepared by diluting sequentially the highest concentration by a factor 2. Dilution of the deicers was performed using growth medium (for duckweed and algae), moderately hard synthetic water (for daphnids and flathead minnows), or Nanopure™ water (for soybean). Moderately hard synthetic water consisted in aerated MILLI-Q® water containing reagent-grade salts (1.2 g $MgSO_4$, 1.92 g $NaHCO_3$, 0.08 g KCl, 1.20 g of $CaSO_4.2H_2O$) at pH 7.4 – 7.8. Specific growth media are described in the sections below.

Table 1: Deicer materials tested and exposure concentrations

Deicer	Original Form	Preparation	Final Concentration (g salt/L)
Brine	Solid NaCl	Dilution	233.00
AquaSalina	Liquid (brine)	No preparation, used as it	221.00
Beet Heet	Liquid wetting agent	Mixing with NaCl and dilution	233.00
GreenBlast	Liquid (brine)	Mixing with 4 volumes of 23% brine	241.40
Magic Minus 0	Liquid wetting agent	Mixing with NaCl and dilution	233.00

3.4. Data Processing:

Results from toxicity testing are expressed as the toxicity endpoints, inhibitory concentration 50% (IC50) and lethal concentration 50% (LC50) – which were calculated using point estimation techniques – and lowest-observed-effect level (LOEC) and non-observed-effect level (NOEC) – which were estimated using hypothesis testing. Separate analyses were performed for the estimation of the LC50 & IC50 endpoints and for the estimation of the LOEC & NOEC endpoints. The endpoints were expressed as mass of salt (NaCl, $CaCl_2$, and/or $MgCl_2$) per volume of diluent (g salt/L) and as mass of deicer material – liquid form – per volume of diluent (g liquid product/L). Toxicity data were analyzed following statistical procedures recommended in the US EPA guidelines, when applicable, or equivalent procedures.

The LC50 and IC50 were determined using the Linear Interpolation Method, the Graphical Method, or a non-linear dose-response regression model (based on a 3-parameter sigmoidal model) and were expressed as mean and 95%-confidence intervals. Calculations were performed using Microsoft Excel, Prism v6.0 (GraphPad, Duarte, CA), and SPSS v22 (IBM, Armonk, NY). When using the Linear Interpolation Method, statistical analysis of the trend line between the two points bracketing the 50% lethality/inhibition was conducted to obtain confidence intervals at 95% confidence (Prism v6.0). When the dose-response curves were not monotonously decreasing with the applied dose (in the case of a stimulatory effect of deicers), the mean values of the response were smoothed, i.e., replaced by the values averaged over the non-monotonous portion of the curve.

The LOEC & NOEC were estimated using One-Way ANOVA followed by Dunnett's Procedure (Prism v6.0) or the Fisher's Exact Test (Microsoft Excel). The Dunnett's method was used when the hypotheses of normality and homogeneity of the variance were satisfied. The normality of the distribution was tested using the Shapiro-Wilk's test and the homogeneity of the variance was tested using the Brown-Forsythe's and Bartlett's test (Prims v6.0). In some cases, the data were transformed (e.g., arcsin transformation) prior to be tested and analyzed. In a number of cases, high mortality at high exposure and/or smoothing the mean response values (non-monotonous dose-response curves) led to a reduction of the number of treatment (concentrations) to compare to only two, in which case a non-paired *t*-test was used.

It is noteworthy that NOEC & LOEC are provided without standard deviations and/or confidence intervals as they are based on hypothesis testing (at 95% confidence) and represent concentrations actually tested resulting in non-significant (NOEC) and significant differences by comparison with the controls (LOEC). The dilution factor selected for the test is therefore essential as it determines the width of the NOEC-LOEC interval and the inherent maximum precision of the test. As the dilution factor decreases, the width of the NOEC-LOEC interval increases, and the inherent maximum precision of the test decreases. With this respect, the US EPA recommends the use of a dilution factor of no less than 0.5.

4. Green Alga, *Selenastrum capricornutum*, Growth Test:

The test was conducted according to the EPA method EPA 2002 Green Alga, *Selenastrum capricornutum*, Growth Test, Method 1003.0, *In* Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th Edition, October 2002, EPA-821-R-02-013 (USEPA 2002), which is the current version of the originally proposed method EPA-600/4-91/002.

4.1. Summary of the Method:

The method measures the chronic toxicity of effluents and receiving water to the freshwater green alga, *S. capricornutum*, in a 4-day static test. The effects include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components which adversely affect the physiological and biochemical functions of the test organisms. This test method was used as a definitive test – vs. limit or screening test –, consisting of five effluent concentrations and a control. This test is very versatile because it can also be used to identify materials which are biostimulatory and may cause nuisance growths of algae, aquatic weeds, and other organisms at higher trophic levels.

A green alga, *S. capricornutum*, population was exposed in a static system to a series of concentrations of test material, for 96 h. The response of the population was measured in terms of changes in cell density (cell counts per mL), which was determined based on the optical density at 750 nm (OD750) and converted into cell density using a predetermined standard curve.

Algae were exposed to five concentrations of deicer material increasing following a factor two and to algal growth medium (control). The highest concentration was chosen to be fully inhibitory to algal growth, according to a review of the literature and assuming that the toxicity was only attributable to the salt content. For algal tests, the highest concentration of deicer consisted in a dilution 40 times, i.e., a concentration of 2.5% of the liquid deicer or a concentration of 5.825 g NaCl/L for the salt brine. At the onset of the test, the flasks were each inoculated with a small volume of concentrated algal suspension to reach an initial cell density of approx. 10,000 cells/mL.

The algal strain, *S. capricornutum*, was obtained as live slants or cell suspensions from Carolina Biological Supply Company (Burlington, NC). All manipulations were conducted under sterile conditions.

The tests were conducted using 250-mL glass conical flasks containing 100 mL of test solution or algal growth medium (control). The test solution consisted in test material – deicer, liquid form – diluted in Algal Growth Medium. The Algal Growth Medium was prepared as directed in USEPA (2002). The pH was adjusted to 7.5 and the medium was sterilized by autoclaving. Four replicate flasks were used per treatment, i.e., 24 flasks per deicer or 120 flasks in total. Flasks were incubated at 25 °C on an orbital shaker at 100 rpm under continuous 'cool white' fluorescent lighting (approx. 400 ft-c). OD750 was recorded at the beginning of the test and after 96 h of incubation. pH and temperature were recorded daily in one of the replicate of each treatment.

To calculate the cell number of the inoculum and at the end of the test, a standard curve was established by recording the OD750 of serial dilutions of a cell suspension whose cell density was counted using a microscope and a hemocytometer. The following linear relationship was determined: cell density (cells/mL) = OD750 x 2.92 ± 0.49 10^7 (r^2 = 0.99).

The endpoints of toxicity tests using the green alga, *S. capricornutum*, are based on the adverse effects on cell growth, measured as the number of cells/mL – estimated by the OD750. For the determination of the NOEC & LOEC, inhibition growth data were analyzed by hypothesis testing using the Dunnett's Method (normal distribution, homogeneous variance) using Prism v6.0 (α = 0.05; Graphpad, Duarte, CA), as recommended by US EPA guidelines. The normality of data distribution was tested using the Shapiro-Wilk test (α = 0.01; Prism v6.0). The homogeneity of the variance was tested using both the Brown-Forsythe's and Bartlett's test (α = 0.01; Prism v6.0). Because parametric hypothesis tests – e.g., Dunnett's test – are preferred to non-parametric alternatives, we choose to accept the hypothesis of variance homogeneity if at least one of the two tests passed.

For the determination of the IC50 and the associated confidence intervals, inhibition growth data were analyzed by point estimate using the Linear Interpolation Method using Prism v6.0, as recommended by US EPA guidelines. Non-monotonous dose-response curves were corrected by smoothing the mean response values, as previously described. Processing was performed on non-transformed data.

4.2. Results:

4.2.1. Acceptability of the test:

For the test results to be acceptable, the mean algal cell density in the control flasks must exceed 10^6 cells/mL at the end of the test and the coefficient of variation (CV) must not exceed 20%. The mean algal cell densities in the controls for all deicers fell within these requirements with final concentrations ranging from 1.18 to 2.25 10^6 cells/mL and CVs ranging from 9.77 to 14.47%.

4.2.2. Toxicity Endpoints:

For all deicers, the centered data are normally distributed (Shapiro-Wilk test). For all deicers, at least one of the variance homogeneity test passes (Brown-Forsythe's or Bartlett's test). We therefore assumed that the Bennett's hypothesis test could be used for the determination of the NOEC & LOEC (Table 2). For the calculation of the IC50 by the Linear Interpolation Method, the mean values of the response (OD750) were smoothed for the non-monotonous portion of the dose-response curve as described above.

The 4-day IC50 based on algal growth, as calculated by Linear Interpolation, ranges from 3.68 g salt/L (BEET HEET, most toxic) to 4.94 g salt/L (Magic Minus Zero, least toxic) (Table 2). The NOEC & LOEC, as determined by the Bennett's hypothesis test, ranges from 1.46 (BEET HEET) to 3.02 g salt/L (GreenBlast) and from 2.91 (BEET HEET) to 6.04 g product/L (GreenBlast), respectively (Table 2). BEET HEET IC50 is significantly lower than all others, except the salt brine IC50 (95% confidence) (Table 2).

Table 2: Endpoints of toxicity testing of *Selenastrum capricornutum* exposed to the five deicer materials.

Deicer	Maximum Dose		Normality	Variance Homogeneity		Hypothesis Tests - Bennett				Point Estimate - Linear Interpolation			
	Dilution 20x		Shapiro-Wilk	Brown-Forsythe	Bartlett	NOEC		LOEC		IC50			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	11.66	60.06	Y	Y	N	2.91	3.76	5.83	7.49	4.02	3.68-4.34	20.71	18.96-22.36
Aquasalina	10.50	60.50	Y	Y	Y	2.63	3.58	5.25	7.19	4.58	4.28-4.96	25.05	23.42-27.14
Beet Heet	11.66	60.06	Y	Y	Y	1.46	1.88	2.91	3.76	3.68	3.16-4.10	18.96	16.28-21.12
GreenBlast	12.08	60.86	Y	Y	N	3.02	3.80	6.04	7.61	4.70	4.42-4.98	23.68	22.26-25.08
Magic Minus 0	11.66	60.06	Y	Y	Y	2.91	3.76	5.83	7.49	4.94	4.54-5.44	25.45	23.38-28.02

(1) Expressed as g of NaCL/L for brine, Beet Heet, and Magic Minus Zero; as g of total salt/L for Aquasalina and GreenBlast

(2) Expressed as g of liquid form of deicer/L

4.3. Discussion:

The IC50 values obtained in this study are in generally good agreement with data reported in the literature. A recent study conducted on several deicers showed 4-day IC50 for *S. capricornutum* ranging from 1.15 to 5.36 g salt/L (Clear Roads 2013). Another publication showed 3-day IC50 of 2.70-2.90 g $CaCl_2$, which is more toxic than other salts (Ball et al.. 2008).

Based on the IC50, the toxicities of all deicers are rather similar – except for BEET HEET – and seem therefore to be related primarily to the salt content. The higher observed toxicity for BEET HEET – which is significantly lower than all others except the brine (95% confidence level) – may be related to the presence of specific organic compounds (proprietary composition).

5. Daphnid, *Ceriodaphnia dubia*, Survival and Reproduction Test:

The test was conducted according to the US EPA method 1002.0, Daphnid, *Ceriodaphnia Dubia*, Survival and Reproduction Test, *In* Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th Edition, October 2002, EPA-821-R-02-013 (US EPA 2002), which is the current version of the originally proposed method EPA-600/4-91/002.

5.1. Summary of the Method:

This method measures the chronic toxicity of effluents and receiving water to the daphnid, *C. dubia*, using less than 24-hour old neonates during a three-brood (7-day), static renewal test. The effects include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components which adversely affect the physiological and biochemical functions of the test organisms. The test method was used as a definitive test, consisting of 5 deicer concentrations and a control.

C. dubia neonates were exposed in a static renewal system to different concentrations of the test solutions, until 60% or more of surviving control females had three broods of offspring. Test results are based on survival and reproduction.

Daphinds were exposed to 5 concentrations of deicer material increasing following a factor two and to dilution water (control). The highest concentration was chosen to be fully lethal to daphnids, according to a review of the literature and assuming that the toxicity was only attributable to the salt content. For daphnid tests, the highest concentration of deicer consisted in a dilution 40 times, i.e., a concentration of 2.5% of the liquid deicer or a concentration of 5.825 g NaCl/L for the salt brine.

C. dubia, '3rd brood' neonates, less 24-hour old, were shipped live from MBL Aquaculture (Sarasota, FL) by overnight shipment.

The tests were conducted using disposable 30-mL polypropylene cups containing 15 mL of test solution or dilution water (control). The test solution consisted in test material – deicer, liquid form – diluted in dilution water. Ten replicate cups were used per treatment, i.e., 60 cups per deicer or 300 flasks in total. Each cup contained one neonate. Ten brood vials, each with 8 or more young, were randomly selected and distributed to each test chamber in the test board (one per test chamber). Test organisms were assigned to test chambers using a block randomization procedure, such that offspring from a single female were distributed evenly among the treatments, appearing once in every test concentration ('blocking by known parentage').

Test cups were incubated at 25 °C under static conditions and under day/night cycles – photoperiod of 16-h of light and 8-h of darkness, light intensity 50 to 100 ft-c. Neonates were fed daily with a combination of yeast, Cerophyll®, trout chow (YCT), and fresh *S. capricornutum* cell suspension. YCT and *S. capricornutum* cell suspension were purchased from MBL Aquaculture (Sarasota, FL). Neonates were transferred daily into fresh test solution.

The pH of the tests solutions was measured at the beginning and the end of each 24-hour period. Aeration is not recommended during the test. Test solutions were aerated by manual agitation before to be added to test cups prior to daphnid transfer. The DO was randomly measured in cups at the end of 24-hour periods.

Three or four broods are usually obtained in the controls in a 7-day test – a brood is a group of offspring released from the female over a short period of time when the carapace is discarded during molting. The total number of young produced by a healthy control organism in three broods often exceeds 30 per female. Each day, the live adults are transferred to fresh test solutions, and the numbers of live young are recorded. Observations were conducted using a lighted plate counter equipped with a magnification lens.

The endpoints of toxicity tests using the daphnid, *C. dubia*, are based on the adverse effects on adult survival and reproduction (estimated by the total youth production). For survival data, the LC50 was determined by the Linear Interpolation Method (Prism v6.0) and the LOEC & NOEC were estimated using the Fisher's Exact test (Microsoft Excel), as recommended by the US EPA guidelines.

For reproduction data, the IC50 was determined using the Linear Interpolation Method (Prism v6.0) and the LOEC & NOEC were estimated using the Dunnett's Procedure, as recommended by the US EPA guidelines.

5.2. Results:

5.2.1. Acceptability of the test:

For the test results to be acceptable, at least 80% of all control organisms must survive, and 60% of surviving control females must produce at least three broods, with an average of 15 or more young per surviving female. One hundred % of the organisms survived and produced 3 broods in the controls for all deicers. The total average number of youngs per female in the controls ranged from 18.7 to 32.2.

5.2.2. Toxicity Endpoints:

Based on 7-day survival data, GreenBlast is shown to be the most toxic deicer (NOEC = 0.75 g salt/L, LOEC = 1.51 g salt/L, IC50 = 1.09 g salt/L), while less differences are observed between four other deicer materials (NOEC = 1.38 – 1.46 g salt/L, LOEC = 2.76 – 2.91 g salt/L, IC50 = 1.70 – 2.84 g salt/L) (Table 3).

For all deicers, the reproduction data are normally distributed (Shapiro-Wilk test) and both variance homogeneity tests pass (Brown-Forsythe's and Bartlett's test). We therefore considered that the Bennett's hypothesis test could be used for the determination of the NOEC & LOEC for reproduction. Based on 7-day reproduction data, AquaSalina and GreenBlast are shown to be the most toxic deicers (NOEC = 0.35 and 0.38 g salt/L, LOEC = 0.69 and 0.75 g salt/L, IC50 = 1.01 and 0.61 g salt/L for AquaSalina and GreenBlast, respectively). GreenBlast IC50 is significantly lower than all others (95% confidence) (Table 3).

Table 3: Endpoints of toxicity testing of *Ceriodaphnia dubia* exposed to the five deicer materials.

Survival Data									
Deicer	Maximum Dose		Hypothesis Tests - Fisher Exact				Point Estimate - Graphical	
	Dilution 40x		NOEC		LOEC		IC50	
	g salt/L(1)	g liq/L(2)	g salt/L	g liq/L	g salt/L	g liq/L	g salt/L	g liq/L
Brine	5.83	30.03	1.46	7.51	2.91	15.01	2.10	10.85
Aquasalina	5.53	30.25	1.38	7.56	2.76	15.13	1.99	10.91
Beet Heet	5.83	30.03	1.46	7.51	2.91	15.01	1.70	8.77
GreenBlast	6.04	30.43	0.75	3.80	1.51	7.61	1.09	5.49
Magic Minus 0	5.83	30.03	1.46	3.75	2.91	7.51	2.84	14.63

Reproduction Data														
Deicer	Maximum Dose		Normality	Variance Homogeneity		Hypothesis Tests - Bennett				Point Estimate - Linear Interpolation			
	Dilution 40x		Shapiro-Wilk	Brown-Forsythe	Bartlett	NOEC		LOEC		IC50			
	g salt/L(1)	g liq/L(2)	Y/N	Y/N	Y/N	g salt/L	g liq/L	g salt/L	g liq/L	g salt/L	CI (95%)	g liq/L	CI (95%)
Brine	5.83	30.03	Y	Y	Y	0.73	3.75	1.46	7.51	1.38	1.18-1.80	7.12	6.10-9.26
Aquasalina	5.53	30.25	Y	Y	Y	0.35	1.89	0.69	3.78	1.01	0.92-1.11	5.55	5.01-6.07
Beet Heet	5.83	30.03	Y	Y	Y	0.73	3.75	1.46	7.51	1.04	0.77-1.27	5.38	3.95-6.57
GreenBlast	6.04	30.43	Y	Y	Y	0.38	1.90	0.75	3.80	0.61	0.55-0.67	3.06	2.75-3.40
Magic Minus 0	5.83	30.03	Y	Y	Y	0.73	3.75	1.46	7.51	1.25	0.98-1.79	6.42	5.07-9.21

(1) Expressed as g of NaCL/L for brine, Beet Heet, and Magic Minus Zero; as g of total salt/L for Aquasalina and GreenBlast
(2) Expressed as g of liquid form of deicer/L

5.3. Discussion:

The IC50 values obtained in this study are in generally good agreement with data reported in the literature. A recent study conducted on several deicers showed 7-day IC50 for *C. dubia* ranging from 0.10 to 1.55 g salt/L based on survival and 0.02 to 1.03 g salt/L based on reproduction (Clear Roads 2013). Another reports showed 7-day IC50 ranging from 1.51 to 2.34 g NaCl/L and 7-day IC50 of 1.44 g $CaCl_2$/L (Evans and Frick 2001, DeGraeve et al. 1992). Another publication reported a 7-day reproduction EC50 of 1.76 g NaCl/L (Cowgill and Milazzo 1990). A 4-day survival LC50 of 2.63 g NaCl was also reported (WI SLOH 1995).

The higher toxicity of GreenBlast observed in this study seems to match the generally higher toxicity of $MgCl_2$ by comparison to NaCl and $CaCl_2$ for *C. dubia*, as it was reported in the literature: 2-day LC50 = 0.88-0.96 g $MgCl_2$/L (Mount et al. 1997).

6. Fathead minnow, *Pimephales promelas*, Larval Survival and Growth Test:

The test was conducted according to the US EPA method 1000.0, Fathead Minnow, *Pimephales promelas*, Larval Survival and Growth Test, *In* Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th Edition, October 2002, EPA-821-R-02-013 (USEPA 2002), which is the current version of the originally proposed method EPA-600/4-91/002.

6.1. Summary of the Method:

The method estimates the chronic toxicity of effluents and receiving water to the fathead minnow, *P. promelas*, using newly hatched larvae in a 7-day, static renewal test. The effects include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components which adversely affect the physiological and biochemical functions of the test organisms. The method was used as a definitive test, consisting of a minimum of 5 effluent concentrations and a control.

Fathead minnow larvae were exposed in a static renewal system for seven days to increasing concentrations of deicer materials. Test results were based on the survival and weight of the larvae.

Fathead minnow larvae, less 24-hour old, were shipped live from MBL Aquaculture (Sarasota, FL) by overnight shipment. Upon arrival at the test site, 15 larvae were transferred to each 250-mL test chamber containing control or test medium. Four test chambers were used per treatment, i.e. 24 chambers per deicers and 120 chambers for the all test.

The larvae were fed as much as they could eat twice a day with live, less than 24-hour old, brine shrimp. Egg shrimps, Argentemia Grade I Gold Label (hatch out %: 90%; naupli size: 450 - 475 μm), were obtained from Argent Chemical Laboratories (Redmond, WA) and produced daily by incubation in artificial sea water at 28 °C, under aeration and continuous lighting. Every day, all but a small volume of the holding water (approximately 5%) was removed by siphoning and replaced slowly with control or test medium.

The larvae were held in a controlled temperature room at 25 °C under ambient laboratory lighting with day/night cycles – photoperiod of 16-h of light and 8-h of darkness, light intensity 50 to 100 ft-c. The DO was maintained at a minimum of 5.0 mg/L by alternate aeration in all test chambers over each 24-hour period. The DO and pH of the test solutions was be checked at the beginning and the end of each 24-hour period. Wide-bore (approx. 5-mm diameter), smooth plastic pipette was used for transferring smaller larvae. Larvae were observed carefully each day for signs of disease, stress, physical damage, and mortality. Dead larvae were removed as soon as observed.

When the toxicity test(s) were concluded, all live test larvae (including controls) were humanely euthanized by immersion in 2% (v/v) ethanol (i.e., 10-30 mL of 95% ethanol/L) as per 2013 AVMA Guidelines for the Euthanasia of Animals.

The endpoints of toxicity tests using fathead minnow, *P. promelas*, larvae are based on the adverse effects on survival and growth. For survival data, the LOEC & NOEC were estimated using the Dunnett's Procedure (Prism v6.0), as recommended by the US EPA guidelines. The Dunnett's Procedure was applied on arcsin-transformed survival percentage. The IC50 was determined using a 3-parameter sigmoidal dose-response model (Prism v6.0). The analysis was performed on directly survival percentage data. The US EPA guidelines recommend using the Probit Analysis – or Logistic Regression Analysis –, which follows a similar approach based on a logistic model (the US EPA software for Probit Analysis could not be downloaded as it is not compatible with current Windows OS).

For growth data, the LOEC & NOEC were estimated using the Dunnett's Procedure (Prism v6.0), as recommended by the US EPA guidelines. The IC50 was determined using the linear Interpolation Method (Prism v6.0), as recommended by the US EPA guidelines. Both analyses were conducted on the fish dry weight per test chamber (i.e., biomass).

6.2. Results:

6.2.1. Acceptability of the test:

For the test results to be acceptable, survival in the controls must be at least 80%. The average dry weight per surviving control larvae at the end of the test must equal or exceed 0.25 mg. The survival rates of control organisms ranged between 93.3% to 100%. The average weight of control organisms ranged from 0.296 to 0.506 mg.

6.2.2. Toxicity Endpoints:

For all deicers, the survival data were normally distributed (Shapiro-Wilk test) and at least one variance homogeneity tests passed (Brown-Forsythe's and Bartlett's test). We therefore considered that the Bennett's hypothesis test could be used for the determination of the NOEC & LOEC. Based on 7-day survival data, AquaSalina was shown to be the most toxic deicer (NOEC = 2.76 g salt/L, LOEC = 5.53 g salt/L, IC50 = 4.68 g salt/L). AquaSalina IC50 is significantly lower than others, except GreenBlast (95% confidence). Besides, not much difference was observed between deicers based on NOEC & LOEC (NOEC = 2.76 – 3.02 and LOEC = 5.53 – 6.04) (Table 4).

The growth data were normally distributed (Shapiro-Wilk test), except for the brine. In this case, we still decided to use the Bennett's test, which is more reliable than alternative non-parametric tests. Based on the 7-day growth IC50, GreenBlast was shown to be the most toxic deicer (IC50 = 4.80 g salt/L vs. higher or equal to 5.09 for the other deicers). GreenBlast IC50 is not significantly lower than the IC50 of other deicers except BEET HEET (95% confidence). Based on the NOEC & LOEC, both GreenBlast and Magic Minus Zero exhibited a higher toxicity (NOEC = 2.91 – 3.02 and LOEC = 5.83 – 6.04) than other materials (NOEC ≥ 5.53 and LOEC ≥ 11.05) (Table 4).

Table 4: Endpoints of toxicity testing of *Pimephales promelas* larvae exposed to the five deicer materials.

Survival Data													
Deicer	**Maximum Dose**		**Normality**	**Variance Homogeneity**		**Hypothesis Tests - Bennett**				**Point Estimate - Sigmoidal Dose-Response**			
	Dilution 5x		**Shapiro-Wilk**	**Brown-Forsythe**	**Bartlett**	**NOEC**		**LOEC**		**IC50**			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	46.60	240.20	Y	Y	Y	2.91	15.01	5.83	30.03	5.92	5.80-6.03	30.50	29.91-31.09
Aquasalina	44.20	242.00	Y	Y	Y	2.76	15.13	5.53	30.25	4.68	4.28-5.08	25.62	23.44-27.79
Beet Heet	46.60	240.20	Y	Y	Y	2.91	15.01	5.83	30.03	6.20	6.08-6.32	31.95	31.33-32.58
GreenBlast	48.28	243.46	Y	Y	Y	3.02	15.18	6.04	30.44	5.44	5.21-5.67	27.42	26.25-28.58
Magic Minus 0	46.60	240.20	Y	Y	N	2.91(3)	15.01	5.83	30.03	6.12	5.92-6.32	31.55	30.50-32.58

Growth Data													
Deicer	**Maximum Dose**		**Normality**	**Variance Homogeneity**		**Hypothesis Tests - Bennett**				**Point Estimate - Linear Interpolation**			
	Dilution 5x		**Shapiro-Wilk**	**Brown-Forsythe**	**Bartlett**	**NOEC**		**LOEC**		**IC50**			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	46.60	240.20	N	Y	N	5.83(4)	30.50	11.65	60.05	5.09	3.92-8.35	26.24	20.21-43.04
Aquasalina	44.20	242.00	Y	Y	Y	5.53	30.28	11.05	60.50	5.36	3.49-	29.35	19.11-
Beet Heet	46.60	240.20	Y	Y	N	5.83	30.50	11.65	60.05	7.07	5.64-15.06	36.44	29.07-77.63
GreenBlast	48.28	243.46	Y	Y	N	3.02	15.23	6.04	30.46	4.80	4.42-5.21	24.20	22.29-26.27
Magic Minus 0	46.60	240.20	Y	N	Y	2.91	15.00	5.83	30.05	5.51	5.03-6.21	28.40	25.93-32.01

(1) Expressed as g of NaCL/L for brine, Beet Heet, and Magic Minus Zero; as g of total salt/L for Aquasalina and GreenBlast

(2) Expressed as g of liquid form of deicer/L

(3) The Bennett's test was in this case performed on raw data as sinarc transformed data did not allow estimating the NOEC

(4) The data do not pass the normality test; we still use Bennett's test to compare the treatments

6.3. Discussion:

The IC50 and LC50 values obtained in this study are in generally good agreement with data reported in the literature. A recent study conducted on several deicers showed 7-day survival LC50 for *P. promelas* ranging from 0.54 to 6.29 g salt/L and 7-day growth IC50 ranging from 0.56 to

7.35 g salt/L (Clear Roads 2013). Other reports showed 7-day survival LC50 = 5.49 - 5.74 g NaCl/L, 7-day survival LC50 = 4.63 g $CaCl_2$/L, and 4-day survival LC50 = 2.12 g $MgCl_2$/L (Aquatic Toxicity Group 1998, Ball et al.. 2008, Beak International 1999, Evans and Frick 2001, Mount et al.. 1997). Our 7-day growth IC50 also fall within the range of the values reported in the literature: 7-day growth EC50 = 7.21 g NaCl/L and 9.52 g $CaCl_2$/L (Evans and Frick 2001). Another publication reported a 7-day growth EC50 = 4.99 g NaCl/L (Beak International 1999).

The relatively higher toxicity of GreenBlast (based on the growth IC50) could again be related to the presence of $MgCl_2$, known to be more toxic than Ca or Na-based salts.

7. Fathead minnow, *Pimephales promelas*, Embryo-Larval Survival and Teratogenicity Test:

The test was conducted according to the US EPA method 1001.0, Fathead Minnow, *Pimephales promelas*, Embryo-Larval Survival and Teratogenicity Test, *In* Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th Edition, October 2002, EPA-821-R-02-013 (USEPA 2002), which is the current version of the originally proposed method EPA-600/4-91/002.

7.1. Summary of the Method:

The method estimates the chronic toxicity of effluents and receiving water to the fathead minnow, *P. promelas*, using embryos in a 7-day, static renewal test. The effects include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components which adversely affect the physiological and biochemical functions of the test organisms. The test is useful in screening for teratogens because organisms are exposed during embryonic development. The method was used as a definitive test, consisting of a minimum of 5 effluent concentrations and a control.

Fathead minnow embryos were exposed in a static renewal system to five different concentrations of deicer materials for seven days, starting shortly after fertilization of the eggs.

Test results are based on the total frequency of both mortality and gross morphological deformities (terata).

Fathead minnow embryos, less 48-hour old, were shipped live from Aquatic Biosystems (Fort Collins, CO) by overnight shipment. Upon arrival at the test site, 10 healthy embryos were transferred to each 75-mL test chamber (100 x 25 Petri dishes) containing control or test medium. Four test chambers were used per treatment, i.e. 24 chambers per deicers and 120 chambers for the all test.

The embryos and larvae were not fed during the test. Every day, all but a small volume of the holding water (approximately 5-10%) was removed by siphoning and replaced slowly with control or test medium. Embryos started to hatch after 2 days of incubation in our facility (3-4 days after egg fertilization).

The embryos/larvae were held in a controlled temperature room at 25 °C under ambient laboratory lighting with day/night cycles – photoperiod of 16-h of light and 8-h of darkness, light intensity 50 to 100 ft-c.

The DO was maintained at a minimum of 5.0 mg/L by alternate aeration in all test chambers over each 24-hour period. The DO and pH of the test solutions was be checked at the beginning and the end of each 24-hour period. Wide-bore (approx. 2.5-mm diameter), smooth plastic pipette was used for transferring embryos. After the hatching begun, dead and live embryos, and hatched, dead, live, and deformed larvae were counted daily. Deformed larvae are those with gross morphological abnormalities (e.g., lack of appendages, lack of fusiform shape, lack of mobility, or other characteristics that preclude survival). Dead embryos and larvae were removed. Upon hatching, deformed larvae are counted as dead.

When the toxicity test(s) were concluded, all live test larvae (including controls) were humanely euthanized by immersion in 2% (v/v) ethanol (i.e., 10-30 mL of 95% ethanol/L) as per 2013 AVMA Guidelines for the Euthanasia of Animals.

The endpoints of toxicity tests using fathead minnow, *P. promelas*, embryos-larvae are based on total mortality – combined number of dead embryos and larvae, and deformed larvae – in each test chamber at the termination of the test. The LOEC & NOEC were estimated using the Dunnett's Procedure (Prism v6.0), as recommended by the US EPA guidelines. The Dunnett's Procedure was applied on arcsin-transformed survival percentage. The IC50 was determined using a 3-parameter sigmoidal dose-response model (Prism v6.0). The analysis was performed on directly survival percentage data. The US EPA guidelines recommend using the Probit Analysis – or Logistic Regression Analysis –, which follows a similar approach based on a logistic model (the US EPA software for Probit Analysis could not be downloaded as it is not compatible with current Windows OS).

7.2. Results:

7.2.1. Acceptability of the Test:

For the test results to be acceptable, survival in the controls must be at least 80%. The average number of survivors in the controls after the 7 days of the test ranges from 95 to 100%.

7.2.2. Toxicity Endpoints:

For all deicers, the survival data were normally distributed (Shapiro-Wilk test) and at least one variance homogeneity tests passed (Brown-Forsythe's and Bartlett's test; Table 5). We therefore considered that the Bennett's hypothesis test could be used for the determination of the NOEC & LOEC.

Based on NOEC & LOEC, GreenBlast was shown to be the most toxic deicer (NOEC = 0.19 g salt/L, LOEC = 1.51 g salt/L. The especially low value of GreenBlast NOEC is explained by the fact that it was estimated by the LC05 as the actual NOEC could be determined using hypothesis testing (i.e., the lowest dose does not result in a significant difference as compared with controls). Based on the LC50, the brine was shown to be the more toxic (LC50 = 2.52). brine IC50 is significantly lower than others, except BEET HEET and Magic minus Zero (95% confidence) (Table 5).

Table 5: Endpoints of toxicity testing of *Pimephales promelas* embryos exposed to the five deicer materials.

Deicer	Maximum Dose		Normality	Variance Homogeneity		Hypothesis Tests - Bennett				Point Estimate - Sigmoidal Dose-Response			
	Dilution 5x		Shapiro-Wilk	Brown-Forsythe	Bartlett	NOEC		LOEC		LC50			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	23.30	120.10	Y	Y	Y	1.46	7.53	2.91	15.00	2.52	2.24-2.81	13.01	11.54-14.48
Aquasalina	22.10	121.00	Y	Y	Y	5.53	30.28	11.05	60.50	5.97	5.69-6.25	32.70	31.17-34.22
Beet Heet	23.30	120.10	Y	Y	Y	1.46	7.53	2.91	15.00	2.92	2.63-3.22	15.05	13.53-16.58
GreenBlast	24.14	121.73	Y	Y	Y	0.19(3)	0.96	1.51	7.61	3.52	3.13-3.90	17.74	15.80-19.68
Magic Minus 0	23.30	120.10	Y	Y	N	1.46(4)	7.53	2.91	15.00	2.76	2.58-2.94	14.22	13.29-15.15

(1) Expressed as g of NaCL/L for brine, Beet Heet, and Magic Minus Zero; as g of total salt/L for Aquasalina and GreenBlast

(2) Expressed as g of liquid form of deicer/L

(3) The NOEC could not be calculated and was evaluated by the EC05

(4) The Bennett's test was in this case performed on log-transformed data as arcsin-transformed data are not normally distributed

7.3. Discussion:

Limited data are available in the literature about the toxicity of salt or deicers for *P. promelas*. The only report that we found mention a 7-day LC50 for *P. promelas* embryos of 1.44 g NaCl/L Beak International 1999), which is lower, but close to the values obtained in this study ranging from 2.52 to 5.97.

The relatively higher toxicity of GreenBlast (based on the growth NOEC & LOEC) could again be related to the presence of $MgCl_2$, known to be more toxic than Ca or Na-based salts.

8. Duckweed, *Lemna minor*, Aquatic Plant Toxicity Test:

The test was conducted according to the EPA method, Aquatic Plant Toxicity Test Using *Lemna* spp. Ecological Effects Test Guidelines OCSPP 850.4400 (USEPA 2012). The protocol was slightly modified according to Brain and Solomon (2007).

8.1. Summary of the Method:

This guideline is intended for use in developing data on the toxicity of chemical substances and mixtures subject to environmental effects test regulations. This guideline prescribes test procedures and conditions using the freshwater vascular aquatic plant, *L. minor*, to develop data on the phytotoxicity of test substances.

Duckweed plants, *L. minor*, were maintained in test vessels containing nutrient medium alone and nutrient medium to which the test substance has been added. Over an exposure period of 7 days, data on population growth are obtained. In addition to measurements of effects on frond number, effects on frond size (dry weight) were determined. The test is designed to determine the quantity of test substance that results in a 50 percent inhibition (IC50) in yield and average growth rate based on number of fronds and yield, and average growth rate based on frond size (dry weight), and to determine the no observed effect concentration (NOEC) for these effect measures.

The test was conducted as definitive test to determine for *L. minor* the concentration-response curve for yield and growth rate, and the median inhibition concentration (IC50) value for each of these responses. The full concentration-response curve (curve between IC05 and IC90) is determined using a minimum of 5 concentrations of the test chemical, plus appropriate controls.

Live *L. minor* plants were obtained from Carolina Biological Supply Company (Burlington, NC). Plants used the test were randomly selected from cultures which were between 7 and 12 days old. Plants were exposed in disposable – 100 mm x 25 mm – deep culture dishes, each containing 50 mL of test solution and 3 - 5 plants (consisting of 3 - 4 fronds per plant), with a total of 12 - 16 fronds per test vessel. Before introduction in test vials, selected plants were sterilized by immersion in 0.1% NaClO for 1 min, following immersion in sterile DI water for approx. 30 min. The test solution consisted in test material – deicer, liquid form – diluted in plant growth medium. The growth medium was the Swedish Standard (SIS) *Lemna* growth medium. All manipulations were conducted under sterile conditions. Four replicate test vials were used per treatment, i.e., 24 flasks per deicer or 120 flasks in total. Test vials were incubated at 25 °C under continuous 'cool white' fluorescent lighting (approx. 400 ft-c).

After 7 days of incubation, the plants were observed under a magnification lens. The number of fronds in each test vial were recorded (discolored fronds were counted as dead). The plants were then rinse by immersion in an abundant volume of DI water and transferred into pre-weighted weighting dishes. The plants were dried at 60 °C until constant weight and weighted.

The endpoints of toxicity tests using the duckweed, *L. minor*, are based on the adverse effects on growth as measured by the change in fronds numbers and biomass (dry weight) over the time of the experiment – 7 days. The IC50s were determined using the Linear Interpolation method and the LOECs and NOECs were estimated using the Dunnett's Procedure, as previously described.

8.2. Results:

8.2.1. Acceptability of the test:

For the test results to be acceptable, the doubling time of number of fronds in the control must exceed 2.5 days and the lowest test concentration level must be not less than the 7-day yield and average specific growth rate IC50 values based on number of fronds and dry weight. The calculated doubling times (based on the number of fronds) in the controls were lower than 2.5 days, except for the test using GreenBlast which was 2.59 days. However, we decide to accept the GreenBlast test results as this value is only 3.6% over the requested 2.5 days.

8.2.2. Toxicity Endpoints:

For all deicers, the centered data were normally distributed (Shapiro-Wilk test). For all deicers, at least one of the variance homogeneity test passed (Brown-Forsythe's or Bartlett's test; Table 6). We therefore assumed that the Bennett's hypothesis test could be used for the determination of the NOEC & LOEC.

Based on the 7-day IC50 calculated using the number of fronds, two deicers, AquaSalina and Magic Minus Zero are found to be significantly more toxic (95% confidence) than the others: 2.42 and 2.53 g salt/L, respectively, vs. 5.14, 5.40, and 7.63 g salt/L for the others (Table 6). These results are confirmed by the NOEC & LOEC, also showing a higher toxicity of AquaSalina and Magic Minus Zero toward duckweed (Table 6).

Results based on the biomass growth roughly confirmed results based on the number of fronds. Based on the 7-day IC50 calculated using the biomass growth, AquaSalina and Magic Minus Zero are found to be significantly more toxic (95% confidence) than the others: 2.26 and

4.42 g salt/L, respectively, vs. 8.27, 8.86, and 10.62 g salt/L for the others (Table 6). These results are confirmed by the NOEC & LOEC, also showing a higher toxicity of AquaSalina and Magic Minus Zero toward duckweed (Table 6).

Table 6: Endpoints of toxicity testing of *Lemna minor* exposed to the five deicer materials.

Frond Number													
Deicer	**Maximum Dose**		**Normality**	**Variance Homogeneity**		**Hypothesis Tests - Bennett**				**Point Estimate - Linear Interpolation**			
	Dilution 10x		**Shapiro-Wilk**	**Brown-Forsythe**	**Bartlett**	**NOEC**		**LOEC**		**IC50**			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	23.30	120.10	Y	N	Y	2.91	15.00	5.83	30.05	5.40	4.18-11.24	27.83	21.55-57.94
Aquasalina	22.10	121.00	Y	N	Y	1.38	7.56	2.76	15.11	2.42	1.99-3.28	13.25	10.90-17.96
Beet Heet	23.30	120.10	Y	Y	Y	2.91	15.00	5.83	30.05	7.39	7.03-8.16	39.33	36.24-42.06
GreenBlast	24.14	121.73	Y	Y	Y	3.02	15.23	6.04	30.46	5.14	4.76-5.59	25.92	24.00-28.19
Magic Minus 0	23.30	120.10	Y	N	Y	0.34(3)	1.75	1.46	7.53	2.53	2.18-3.08	13.04	11.24-15.88

Biomass Growth													
Deicer	**Maximum Dose**		**Normality**	**Variance Homogeneity**		**Hypothesis Tests - Bennett**				**Point Estimate - Linear Interpolation**			
	Dilution 10x		**Shapiro-Wilk**	**Brown-Forsythe**	**Bartlett**	**NOEC**		**LOEC**		**IC50**			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	23.30	120.10	Y	Y	Y	5.83	30.05	11.65	60.06	8.86	6.75-11.32	45.67	34.79-58.35
Aquasalina	22.10	121.00	Y	N	Y	1.38	15.11	2.76	60.50	2.26	1.98-2.62	12.37	10.84-14.34
Beet Heet	23.30	120.10	Y	Y	Y	5.83	30.05	11.65	60.06	10.62	8.49-17.06	54.74	43.76-87.94
GreenBlast	24.14	121.73	Y	Y	Y	3.02	15.23	12.07	60.87	8.27	wide	41.70	wide
Magic Minus 0	23.30	120.10	Y	N	Y	2.91	15.00	5.83	30.05	4.42	1.98-5.34	22.78	10.21-27.53

(1) Expressed as g of NaCL/L for brine, Beet Heet, and Magic Minus Zero; as g of total salt/L for Aquasalina and GreenBlast

(2) Expressed as g of liquid form of deicer/L

(3) The NOEC could not be calculated and was evaluated by the IC05

8.3. Discussion:

Several studies have been conducted on the effect of salts on duckweed plants, showing toxic effects of the same order of magnitude as observed in this investigation. A publication from Sikorski et al. (2012) reported significant inhibition of duckweed fresh biomass (by 44%) exposed to 3.66 g NaCl/L. Two other publications reported 7-day IC50 based on the number of fronds = 6.87 and 4.80-5.50 g NaCl/L, respectively (Buckley et al. 1996, Keppeler 2009).

9. Soybean, *Glycine max*, germination and root elongation tests:

The test was conducted according to the EPA method, Seed germination/Root Elongation Toxicity Test (public draft), Ecological Effects Test Guidelines OPPTS 850.4200 (USEPA 1993). The protocol was slightly modified according to Adhikari et al. (2012).

9.1. Summary of the Method:

This guideline is intended for use in developing data on the acute toxicity of chemical substances and mixtures subject to environmental effects test regulations. This guideline prescribes test procedures and conditions using seeds of commercially important terrestrial plants to develop data on the phytotoxicity of chemicals.

Fresh test solution (7.5 mL) was added to Petri dishes that have been filled with two paper filters. The seed were then positioned on the substrate allowing adequate room for anticipated growth. A filter paper was added on top of the seeds and Petri dish lids were be used to hold the seed in place, and the dishes sealed with Parafilm. (ii) The dishes were incubated in the dark in a controlled-temperature growth facility at a slight angle to facilitate linear root growth. Seed were incubated until at least 65 percent of the control seed have germinated and developed roots that are at least 20 mm long.

The number of seeds that germinated was counted, and root lengths measured. Concentration response curves, EC10s, and EC50s for seed germination and root elongation were determined.

The test was conducted as definitive test to determine the concentration-response curves, the EC10s and EC50s for seed germination and root elongation. The full concentration-response curve (curve between IC05 and IC90) was determined using a minimum of 5 concentrations of the test chemical, plus appropriate controls. Four replicate dishes, each with 10 seeds were tested for each concentration and the control.

Soybean seeds, *Glycine max*, cv. Enrei, were obtained from the Missouri Foundation Seed at the University of Missouri (Columbia, MO). Before introduction in test vials, selected plants were sterilized by immersion in 1% NaClO for 5 min, following by rinsing 3 times in sterile water and immersion in 500 mL sterile DI water for approx. 30 min. The test solution consisted in test material – deicer, liquid form – diluted in DI water. All manipulations were conducted under sterile conditions. Four replicate test vials were used per treatment, i.e., 24 flasks per deicer or 120 flasks in total. Test vials were incubated at 25 °C in the dark.

After 5 days of incubation, the seeds and seedlings were observed visually. Seeds showing a radicle of at least 5 mm were considered as germinated. The germination percentages were recorded and the root length – in the case of germinated seeds – was measured using a rule.

The endpoints of germination and root elongation tests using soybean, *glycine max*, are based on the adverse effects on germination percentages and root elongation (length) over the time of the experiment – 5 days. The IC50s were determined using the Linear Interpolation method and the LOECs and NOECs were estimated using the Dunnett's Procedure, as previously described.

9.2. Results:

9.2.1. Toxicity Endpoints:

For all deicers, the centered data were normally distributed (Shapiro-Wilk test). Because of the need to smooth the mean values to achieve monotonous decrease of the dose-response curves, the number of treatments to compare was only two in a number of cases. A *t*-test was then used for the determination of NOEC & LOEC. For all deicers with three or more treatments to be compared, at least one of the variance homogeneity test passed (Brown-Forsythe's or Bartlett's test and the Bennett's hypothesis test was used for the determination of the NOEC & LOEC (Table 7).

Based on the 5-day IC50 calculated using the germination percentages, two deicers, the brine and GreenBlast are found more toxic than the others based on NOEC & LOEC: 5.83 and 11.65 g salt/L for the brine and 6.04 and 12.07 g salt/L for GreenBlast, respectively, vs. over 11 and 22 g salt/L for the others, respectively. No significant differences are observed between the 5 deicers based on the IC50 ranging from 16.47 to 18.89 g salt/L (Table 7).

Results based on the biomass growth roughly confirmed results based on the number of fronds. Based on the 7-day IC50 calculated using the biomass growth, AquaSalina and Magic Minus Zero are found to be significantly more toxic (95% confidence) than the others: 2.26 and 4.42 g salt/L, respectively, vs. 8.27, 8.86, and 10.62 g salt/L for the others. These results are confirmed by the NOEC & LOEC, also showing a higher toxicity of AquaSalina and Magic Minus Zero toward duckweed (Table 7).

Table 7: Endpoints of toxicity testing of *Glycine max* exposed to the five deicer materials.

Germination													
Deicer	Maximum Dose		Normality	Variance Homogeneity		Hypothesis Tests - Bennett or t-test				Point Estimate - Linear Interpolation			
	Dilution 10x		Shapiro-Wilk	Brown-Forsythe	Bartlett	NOEC		LOEC		IC50			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	23.30	120.10	Y	N/A(3)	N/A(3)	5.83	30.05	11.65	60.05	17.03	15.53-18.46	87.78	80.05-95.15
Aquasalina	22.10	121.00	Y	N/A(3)	N/A(3)	11.05	60.50	22.10	121.00	16.47	15.88-17.05	90.18	86.94-93.35
Beet Heet	23.30	120.10	Y	Y	N	11.65	60.05	23.30	120.10	17.86	16.91-18.84	92.06	87.16-97.11
GreenBlast	24.14	121.73	Y	N/A(3)	N/A(3)	6.04	30.46	12.07	60.87	18.89	16.63-21.39	95.26	83.86-107.86
Magic Minus 0	23.30	120.10	Y	N/A(3)	N/A(3)	11.65	60.05	23.30	120.10	16.88	16.11-17.62	87.01	83.04-90.82
Root Length													
Deicer	Maximum Dose		Normality	Variance Homogeneity		Hypothesis Tests - Bennett				Point Estimate - Linear Interpolation			
	Dilution 10x		Shapiro-Wilk	Brown-Forsythe	Bartlett	NOEC		LOEC		IC50			
	g salt/L(1)	*g liq/L(2)*	*Y/N*	*Y/N*	*Y/N*	*g salt/L*	*g liq/L*	*g salt/L*	*g liq/L*	*g salt/L*	*CI (95%)*	*g liq/L*	*CI (95%)*
Brine	23.30	120.10	Y	Y	N	2.91	15.00	5.83	30.02	9.52	9.16-9.91	49.07	47.22-51.08
Aquasalina	22.10	121.00	Y	Y	Y	5.53	30.30	11.05	60.60	8.94	7.79-10.35	48.95	42.65-56.67
Beet Heet	23.30	120.10	Y	N	Y	5.83	30.02	11.65	60.05	10.92	9.25-14.62	56.29	47.68-75.36
GreenBlast	24.14	121.73	Y	N	Y	6.04	30.46	12.07	60.87	9.19	8.76-9.62	46.34	44.17-48.51
Magic Minus 0	23.30	120.10	Y	Y	Y	5.83	30.02	11.65	60.05	9.03	7.67-10.51	46.55	39.54-54.17

(1) Expressed as g of NaCL/L for brine, Beet Heet, and Magic Minus Zero; as g of total salt/L for Aquasalina and GreenBlast

(2) Expressed as g of liquid form of deicer/L

(3) The number of treatments to be compared was reduced to two, requiring a t-test instead of ANOVA/Bennett's test

9.3. Discussion:

Several studies have been conducted on the effect of salts on crop plants, including soybean. In a widely-cited study, Maas & Hoffman (1977) reported the threshold of yield reduction in a large number of crop species, showing toxicity threshold ranging from 6.4 to 51.2 g NaCl/L, which is within the range of the results obtained in our study (germination NOEC = 5 – 12 g salt/L, germination IC50 = 16 – 19 g salt/L, root length NOEC = 3 – 6 g salt/L, root length IC50 = 9 - 11 g salt/L). In particular, soybean was shown to exhibit negative effects on yield at exposure of approx. 32 g NaCl/L. Although this value is above the LOEC and IC50 observed in the present study, this discrepancy is likely due to the exposure of plants in the early stage. In accordance with prior reports on the toxicity of salt on crop species, the effect of deicers was less marked on the seed germination (higher NOEC, LOEC, and IC50) than on root growth (Chachar et al. 2008).

10. Conclusions:

A summary of toxicity testing results is presented in Table 8 in the form of a matrix containing the relevant toxicity endpoints (i.e., IC50, LC50, NOEC, and LOEC) for the different tests: algae, daphnids, fathead minnows, duckweed, and soybean, and for the five deicer materials.

Table 8: Summary of the toxicity testing using algae, daphnids, duckweed, soybean, and fathead minnows for the five deicer materials. The endpoints NOEC, LOEC, and IC/LC50 are presented (expressed as g salt/L).

Deicer	Selenastrum - Growth			Daphnids - Survival			Daphnids - Reproduction			Minnow Larvae - Survival			Minnow Larvae - Growth		
g Salt/L	NOEC	LOEC	IC50	NOEC	LOEC	LC50	NOEC	LOEC	IC50	NOEC	LOEC	LC50	NOEC	LOEC	IC50
Brine	2.91	5.83	4.02	1.46	2.91	2.10	0.73	1.46	1.38	2.91	5.83	5.92	5.83	11.65	5.09
Aquasalina	2.63	5.25	4.58	1.38	2.76	1.99	0.35	0.69	1.01	2.76	5.53	4.68	5.53	11.05	5.36
Beet Heet	1.46	2.91	3.68	1.46	2.91	1.70	0.73	1.46	1.04	2.91	5.83	6.20	5.83	11.65	7.07
GreenBlast	3.02	6.04	4.70	0.75	1.51	1.09	0.38	0.75	0.61	3.02	6.04	5.44	3.02	6.04	4.80
Magic Minus 0	2.91	5.83	4.94	1.46	2.91	2.84	0.73	1.46	1.25	2.91	5.83	6.12	2.91	5.83	5.51
Deicer	Minnow Embryos - Survival			Duckweed - Fronds			Duckweed - Growth			Soybean - Germination			Soybean - Root Length		
g Salt/L	NOEC	LOEC	IC50	NOEC	LOEC	IC50	NOEC	LOEC	IC50	NOEC	LOEC	IC50	NOEC	LOEC	IC50
Brine	1.46	2.91	2.52	2.91	5.83	5.40	5.83	11.65	8.86	5.83	11.65	17.03	2.91	5.83	9.52
Aquasalina	5.53	11.05	5.97	1.38	2.76	2.42	1.38	2.76	2.26	11.05	22.10	16.47	5.53	11.05	8.94
Beet Heet	1.46	2.91	2.92	2.91	5.83	7.39	5.83	11.65	10.62	11.65	23.30	17.86	5.83	11.65	10.92
GreenBlast	0.19	1.51	3.52	3.02	6.04	5.14	3.02	12.07	8.27	6.04	12.07	18.89	6.04	12.07	9.19
Magic Minus 0	1.46	2.91	2.76	0.34	1.46	2.53	2.91	5.83	4.42	11.65	23.30	16.88	5.83	11.65	9.03

These toxicity endpoints were used (1) to establish a ranking of the deicer materials based on their relative toxicity and (2) to succinctly assess the environmental risk associated with the deicer materials.

For each material, a toxicity score was calculated using a weighted average of the different toxicity endpoints – referred to as *overall score*. In the absence of further rationale, the same weighting factor was used for all endpoints. Specific scores were also calculated for the plant and algal tests – referred to as *plant/algal score* – and animal tests –referred to as *animal score*. The deicers were then be ranked based on their relative toxicity score. In order to avoid giving higher weight to tests using less sensitive organisms (higher endpoints), the endpoints, NOEC, LOEC, and IC/LC50, were also divided by the highest value recorded in each test, resulting in adjusted endpoint from 0.0 to 1.0. The score are calculated for all endpoints (NOEC, LOEC, and IC50) and for the IC/LC50 endpoints only. The corresponding ranks of deicers (1 = most toxic, 5 = least toxic) are then calculated based on the scores (Table 9).

Table 9: Ranking of the five deicer materials based on the toxicity endpoints from testing using algae, daphnids, duckweed, soybean, and fathead minnows: 1 = most toxic, 5 = least toxic. Ranks were calculated based on the normalized toxicity endpoints. The red highlight depicts the most toxic deicers.

Deicer	Overall Score				Plant/Algal Score				Animal Score			
	NOEC, LOEC, IC/LC50	Rank	IC/LC50	Rank	NOEC, LOEC, IC/LC50	Rank	IC/LC50	Rank	NOEC, LOEC, IC/LC50	Rank	IC/LC50	Rank
Brine	1.00	2.5	1.00	4.0	1.00	2.0	1.00	3.0	1.00	3.0	1.00	2.0
Aquasalina	1.16	5.0	0.96	2.5	0.97	1.0	0.75	1.0	1.34	5.0	1.18	5.0
Beet Heet	1.13	4.0	1.08	5.0	1.25	5.0	1.14	5.0	1.01	4.0	1.03	3.0
GreenBlast	0.90	1.0	0.93	1.0	1.14	4.0	1.03	4.0	0.67	1.0	0.84	1.0
Magic Minus 0	1.00	2.5	0.96	2.5	1.03	3.0	0.83	2.0	0.96	2.0	1.09	4.0

Based on the *overall score* and *animal score*, the most toxic deicer is GreenBlast. Based on the plant/algal score, the most toxic deicer is AquaSalina. Considering that the toxicity endpoints were presented as g salt/L, this observation may be explained by the nature of salt and composing ions. The effect of salts on aquatic life is well documented and the relative toxicity of salts is known to vary with the anion and cation combinations present in the material (Clear Roads 2013). A large body of experimental research has shown that the relative toxicity of the cationic component is as follows: potassium (K) > magnesium (Mg) > sodium (Na)/calcium (Ca). This observation may explain the relative higher toxicity of AquaSalina, which contains KCl (1.5% w/v) and $MgCl_2$ (2.6% w/v), and GreenBlast, which contains $MgCl_2$ (5.2-5.8% w/v).

Besides ranking the deicer materials, toxicity endpoints, such as NOEC and LC50/IC50, are also used by public agencies to conduct environmental risk assessment. When conducting risk assessment studies, US EPA frequently uses a deterministic approach – the quotient method – to compare toxic levels to environmental levels. The *risk quotient* (RQ) is calculated by dividing the level of exposure by the toxicity endpoint. This ratio allows identifying high- and low-risk situations.

Risk Quotient = Exposure/Toxicity

For risk assessments based on chronic toxicity to aquatic animals, the lowest NOEC for freshwater fish and invertebrates are used to calculate the risk quotient. For risk assessments based on chronic toxicity to aquatic vascular plants and algae, the risk quotient is based on the lowest EC50.

The determination of the risk of deicers for the aquatic environment also depends of the average concentration in the environment, which is highly variable depending on numerous factors, including application level, precipitation, flow regime, distance from the source, etc. Chloride (Cl^-) concentrations in surface freshwater generally range from 0 to 100 mg/L (0 to 165 mg NaCl/L), with most concentrations lower than 20 mg/L (33 mg NaCl/L). According the Environment Canada (2000), many studies showed that salt in highway runoff is typically quickly diluted in receiving waters resulting in concentrations lower than 15 mg Cl^-/L (25 mg NaCl/L). As a guideline, it is also usually considered that deicer salts are diluted 500 times from road application to environmental waters (approx. 470 mg NaCl/L in the case of the liquid deicers) (Fay and Shi 2012).

We have then calculated the risk quotient for invertebrates, fish, algae, and plants using the NOEC and EC50 of the most sensitive test and the predicted environmental concentrations of 25, 165, and 470 mg salt/L (the last one representing a dilution approx. 500 times of the liquid deicer) (Table 10).

Table 10: Risk quotients (RQs) calculated for invertebrates, fish, algae, and plants using the lowest NOEC and EC50 recorded in the present study and predicted environmental concentrations of 25, 165, and 470 mg/L. The pink color depicts the deicer of potential environmental concern

Deicer	Invertebrates				Fish			
	Lowest NOEC	Risk Quotient			Lowest NOEC	Risk Quotient		
	mg/L	15 mg/L	165 mg/L	470 mg/L	mg/L	15 mg/L	165 mg/L	470 mg/L
Brine	730.00	0.02	0.23	0.64	1460.00	0.01	0.11	0.32
Aquasalina	350.00	0.04	0.47	1.34	5530.00	0.00	0.03	0.08
Beet Heet	730.00	0.02	0.23	0.64	1460.00	0.01	0.11	0.32
GreenBlast	380.00	0.04	0.43	1.24	190.00	0.08	0.87	2.47(1)
Magic Minus 0	730.00	0.02	0.23	0.64	1460.00	0.01	0.11	0.32
Deicer	**Algae**				**Aquatic Plants**			
	Lowest EC50	**Risk Quotient**			**Lowest EC50**	**Risk Quotient**		
	mg/L	**15 mg/L**	**165 mg/L**	**470 mg/L**	**mg/L**	**15 mg/L**	**165 mg/L**	**470 mg/L**
Brine	4020.00	0.00	0.04	0.12	8860.00	0.00	0.02	0.05
Aquasalina	4580.00	0.00	0.04	0.10	2260.00	0.01	0.07	0.21
Beet Heet	3680.00	0.00	0.04	0.13	10620.00	0.00	0.02	0.04
GreenBlast	4700.00	0.00	0.04	0.10	8270.00	0.00	0.02	0.06
Magic Minus 0	4940.00	0.00	0.03	0.10	4420.00	0.00	0.04	0.11

(1) The risk quotient was calculated based on the EC05 because the NOEC could not be determined. Consequently, it cannot be used for comparison with others.

US EPA considers that the *level of concern* for chronic risk for aquatic organisms correspond to a risk quotient of 1.0 – i.e., there is no concern for risk quotients lower than 1.0. Based on this value, none of the deicers tested seem to pose a significant threat to the environment at the concentration of 25 or 165 salt/L. Only AquaSalina and GreenBlast – the most toxic deicers identified in this study – may represent a concern for invertebrates – the most sensitive aquatic organisms tested – in the highest exposure scenario (dilution 500 times). The high risk quotient calculated for GreenBlast with fish does not compare well with other deicers as the NOEC was estimated by the EC05, resulting in a very low value.

References:

Adhikari T, Kundu S, Biswas AK, Tarafdar JC, Rao AS (2012). Effect of copper oxide nano particle on seed germination of selected crops. *J. Agricul. Sci. Technol. A* **2**:815-823.

Ball GFA, Herrington PR, Patrick JE (2008). Environmental effects of emulsions. Land Transport New Zealand Research Report 343. 46 pp.

Brain RA, Solomon KR (2007). A protocol for conducting 7-day daily renewal tests with *Lemna gibba*. *Nature Protocols* **2**:979-987.

Buckley JA, Rustangi KP, Laughlin JD (1996). Response of *Lemna minor* to sodium chloride and a statistical analysis of continuous measurements for EC50 and 95% confidence limits calculation. *Bulletin of Environmental Contamination and Toxicology* **57**:1003-1008.

Chachar QI, Solangi AG, Verhoef A (2008). Influence of sodium chloride on seed germination and seedling root growth of cotton (*Gossypium hirsutum* L.). *Pak. J. Bot.* **40**:183-197.

Clear Roads (2013). Determining the Aquatic Toxicity of Deicing Materials. Project 99083/CR11-02, December 2013, www.clearroads.org.

Cowgill UM, Milazzo DP (1990). The sensitivity of two cladocerans to water quality variables: salinity and hardness. *Archiv. Hydrobio.* **120**:185-196.

DeGraeve GM, Cooney JD, Marsh BH, Pollock TL, Reichenbach NG (1992). Variability in the performance of the 7-d *Ceriodaphnia dubia* survival and reproduction test: An intra and interlaboratory study. *Environ. Toxicol. Chem.* **11**:851-866.

Environment Canada (2000). Canadian Environmental Protection Act, 1999 Priority Substance List Assessment Report – Road Salts, Draft for Public Comments, Environment Canada, Health Canada, August 2000.

Evans MS, Frick C (2001). The Effects of Road Salts on Aquatic Ecosystems. Technical report, Environment Canada Health Canada, 2001.

Fay L, Shi X (2012). Environmental Impacts of Chemicals for Snow and Ice Control: State of the Knowledge. *Water Air and Soil Pollution* **223**:2751-2770.

Keppeler EC (2009). Toxicity of sodium chloride and methyl parathion on the macrophyte *Lemna minor* (Linnaeus, 1753) with respect to frond number and chlorophyll. *Biotemas* **22**:27-33.

Maas EV, Hoffman GJ (1977). Crop Salt Tolerance – Current Assessment. *Journal of the Irrigation and Drainage Division* **103**:115-134.

Mount DR, Gulley DD, Hockett JR, Garrison TD, Evans JM (1997) .Statistical models to predict the toxicity of major ions to *Ceriodaphnia dubia*, *Daphnia magna* and *Pimephales promelas* (fathead minnows). *Environ. Toxicol. Chem.* **16**:2009-2019.

Pacific Northwest Snowfighters – PNS (2010). Snow and Ice Control Chemical Products Specifications and Test Protocols for the PNS Association of British Columbia, Colorado, Idaho, Montana, Oregon and Washington, Revision 10-12. Pacific Northwest Snowfighters.

Sikorski L, Piotrowicz-Cieslak AI, Adomas B (2013). Phytotoxicity of sodium chloride towards common duckweed (*Lemna minor* L.) and yellow lupin (*Lupinus luteus* L.). *Archives of Environmental Protection* 39:117-128.

US Environmental Protection Agency – USEPA (1993). Seed Germination/Root Elongation Toxicity Test (Public draft). Ecological Effects Test Guidelines OPPTS 850.4200. Prevention, Pesticides and Toxic Substances – 7101. EPA 712–C–96–154, April 1996.

US Environmental Protection Agency – USEPA (2002). Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th Edition. October 2002, EPA-821-R-02-013.

US Environmental Protection Agency – USEPA (2012). Aquatic Plant Toxicity Test Using *Lemna* spp. Ecological Effects Test Guidelines OCSPP 850.4400. Agency Office of Chemical Safety and Pollution Prevention – 7101. EPA 712-C-008, January 2012.

Wisconsin State Laboratory of Hygiene – WI SLOH (1995). Unpublished data on chloride toxicity to aquatic species. From A. Letts (Technical Manager, Morton International Inc. Chicago, Illinois) to M.S. Evans (National Hydrology Research Institute, Environment Canada), August 11, 1998.

Appendix: Dose-Response Curves:

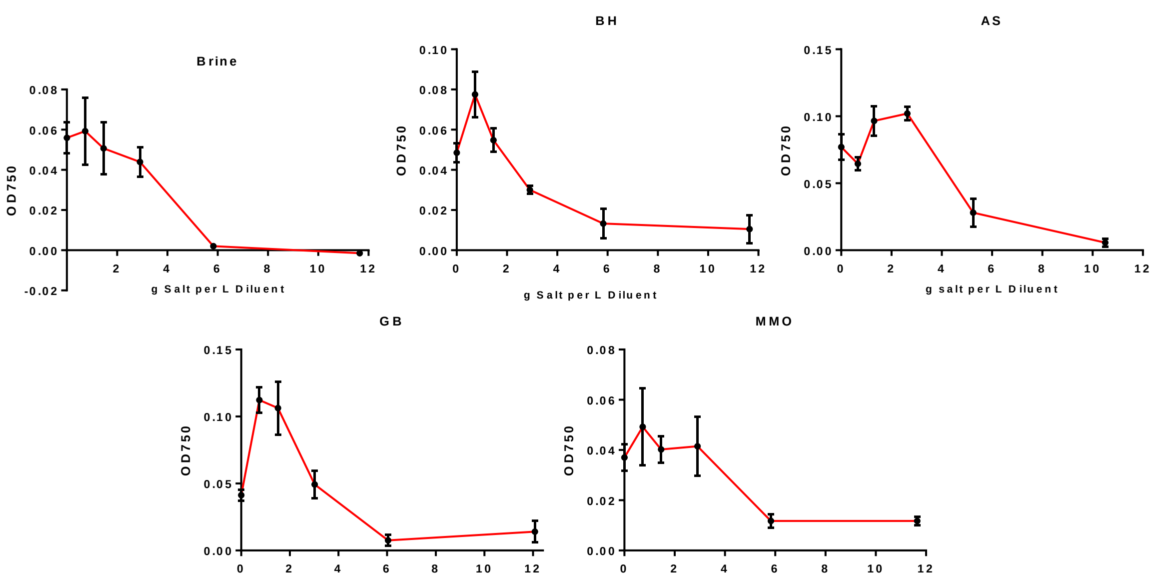

Figure 1: Dose-response curves of *Selenastrum capricornutum* exposed to the five deicer materials. The graphs represent the response – average cellular growth measured by the optical density at 750 nm (OD750) – as a function of the deicer concentration expressed in g salt/L of

diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates.

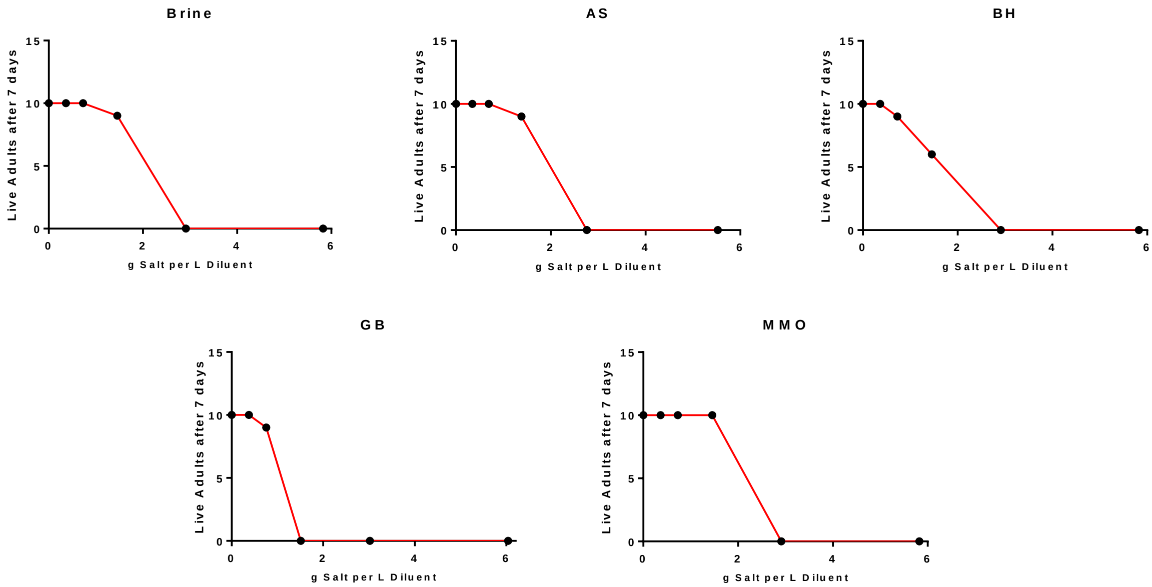

Figure 2: Dose-response curves of *Ceriodaphnia dubia* exposed to the five deicer materials. The graphs represent the response – number of survival adults after 7 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero.

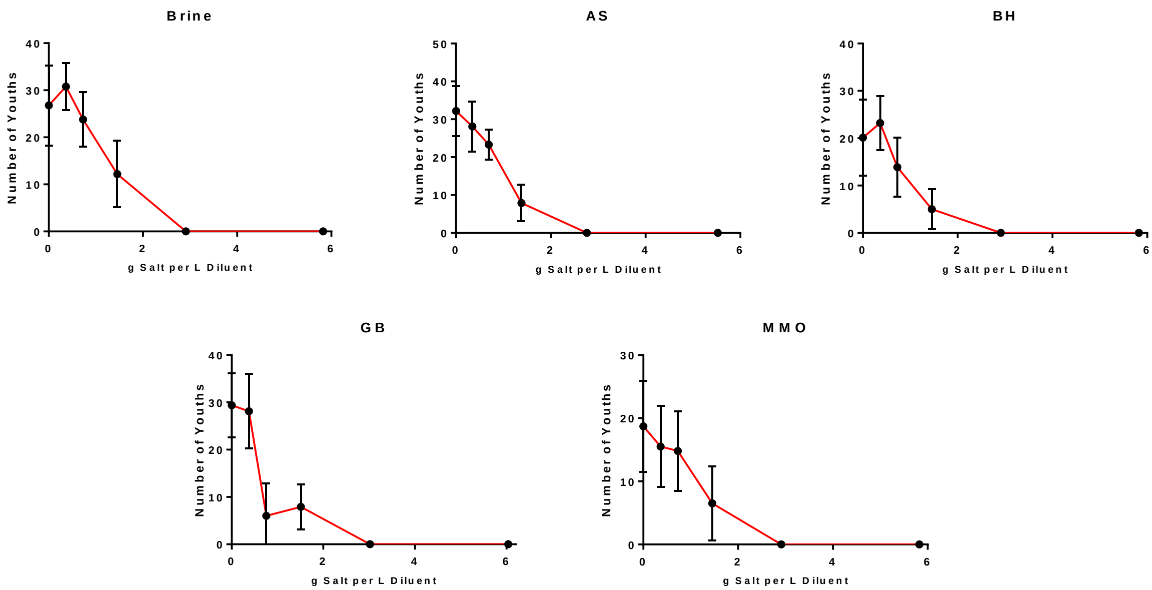

Figure 3: Dose-response curves of *Ceriodaphnia dubia* exposed to the five deicer materials. The graphs represent the response – average number of youths produced per adult over 7 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates.

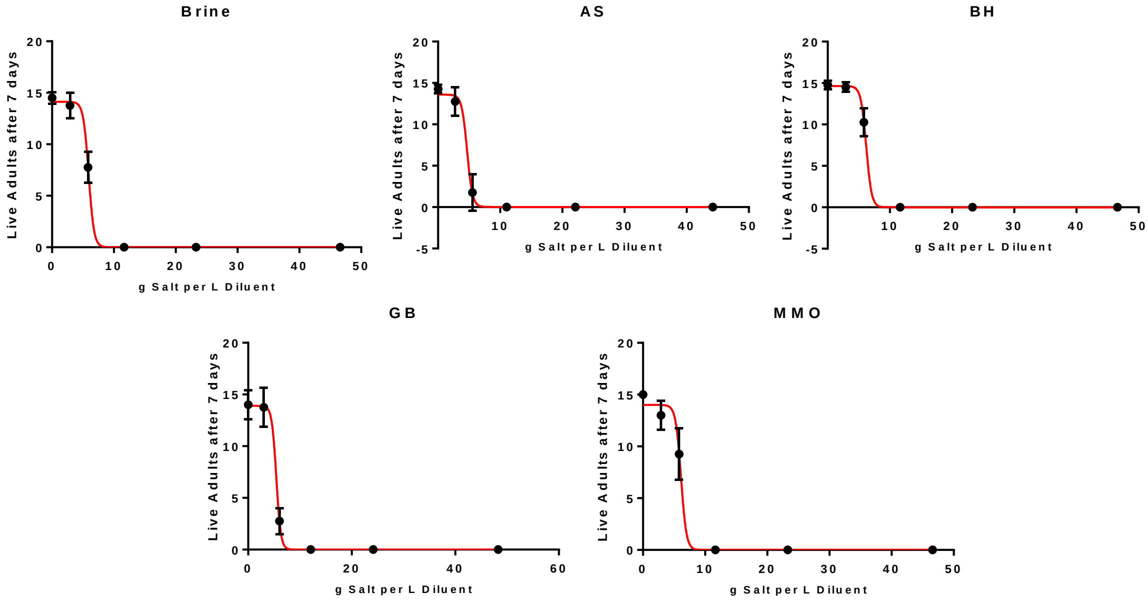

Figure 4: Dose-response curves of *Pimephales promelas* larvae exposed to the five deicer materials. The graphs represent the response – average number of adult survivor over 7 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates. The solid line represent a fitting according to a 3-parameter sigmoidal dose-response model.

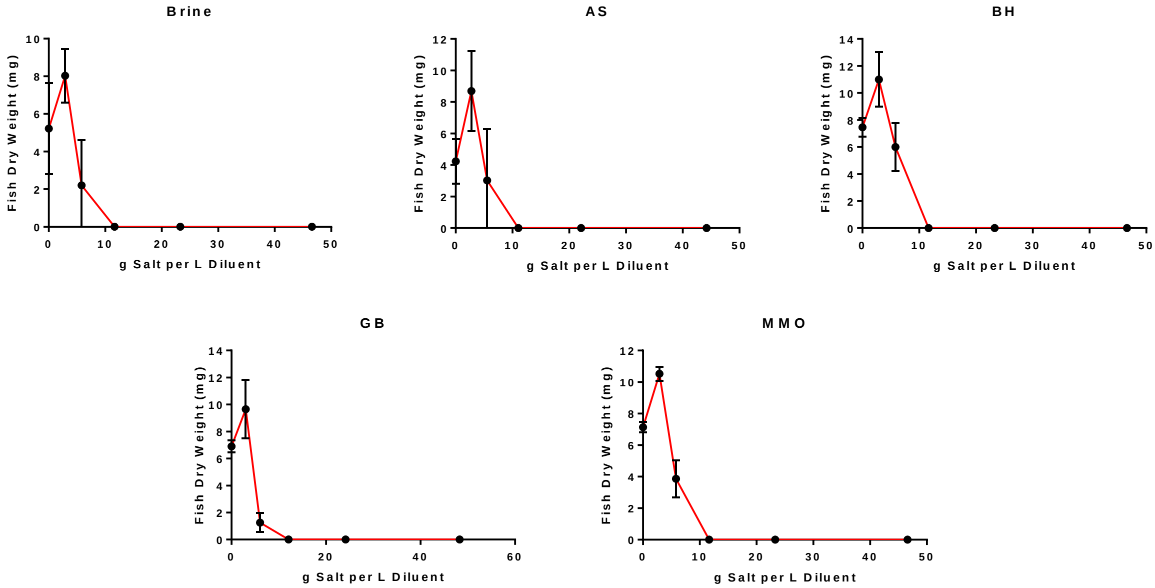

Figure 5: Dose-response curves of *Pimephales promelas* larvae exposed to the five deicer materials. The graphs represent the response – average fish growth rate (dry weight) over 7 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates.

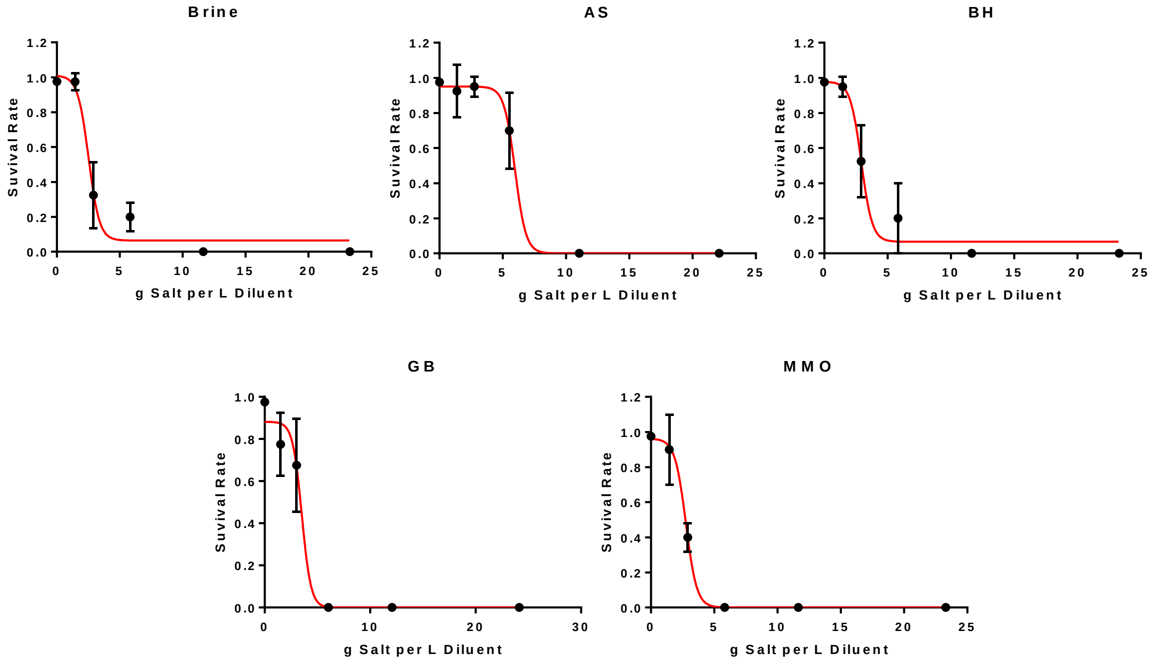

Figure 6: Dose-response curves of *Pimephales promelas* embryos exposed to the five deicer materials. The graphs represent the response – average embryo and larva survival and larva deformation fraction observed over 7 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates. The solid line represent a fitting according to a 3-parameter sigmoidal dose-response model.

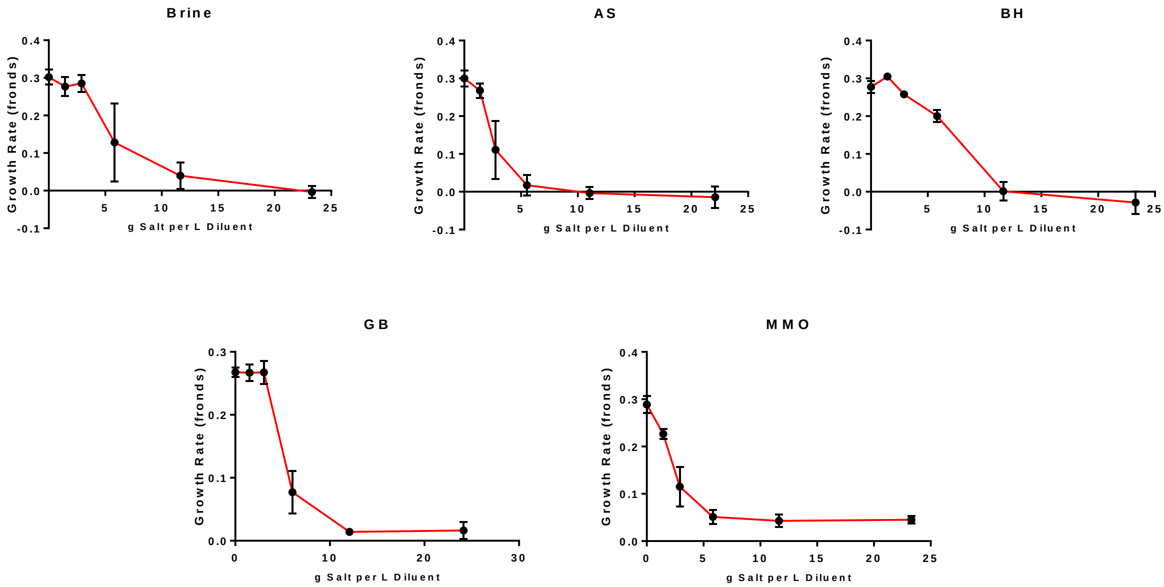

Figure 7: Dose-response curves of *Lemna minor* exposed to the five deicer materials. The graphs represent the response – growth rate based on the frond number over 7 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates.

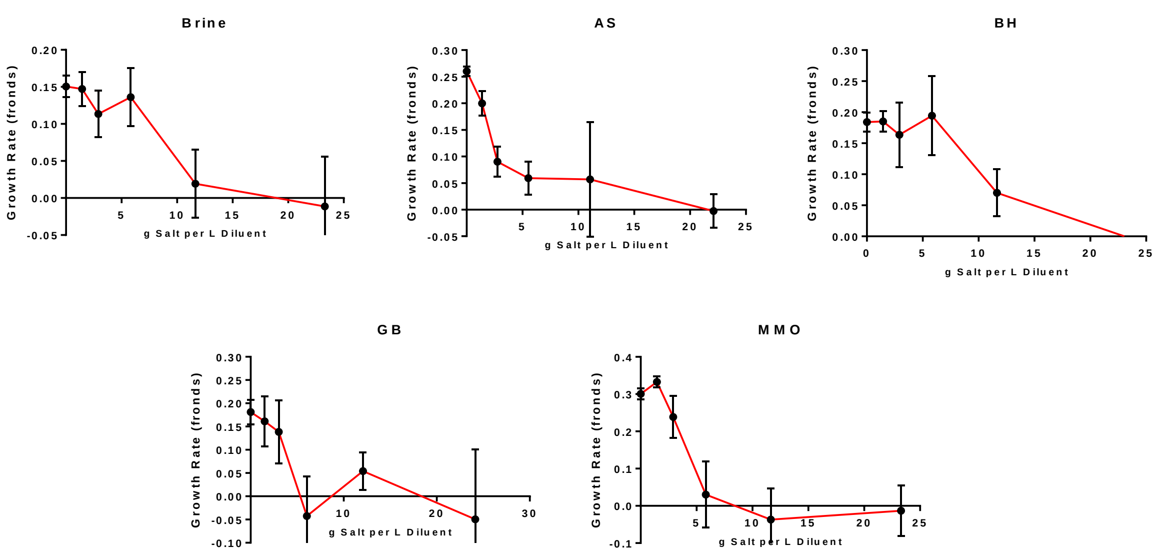

Figure 8: Dose-response curves of *Lemna minor* exposed to the five deicer materials. The graphs

represent the response – growth rate based on biomass (dry weight) over 7 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates.

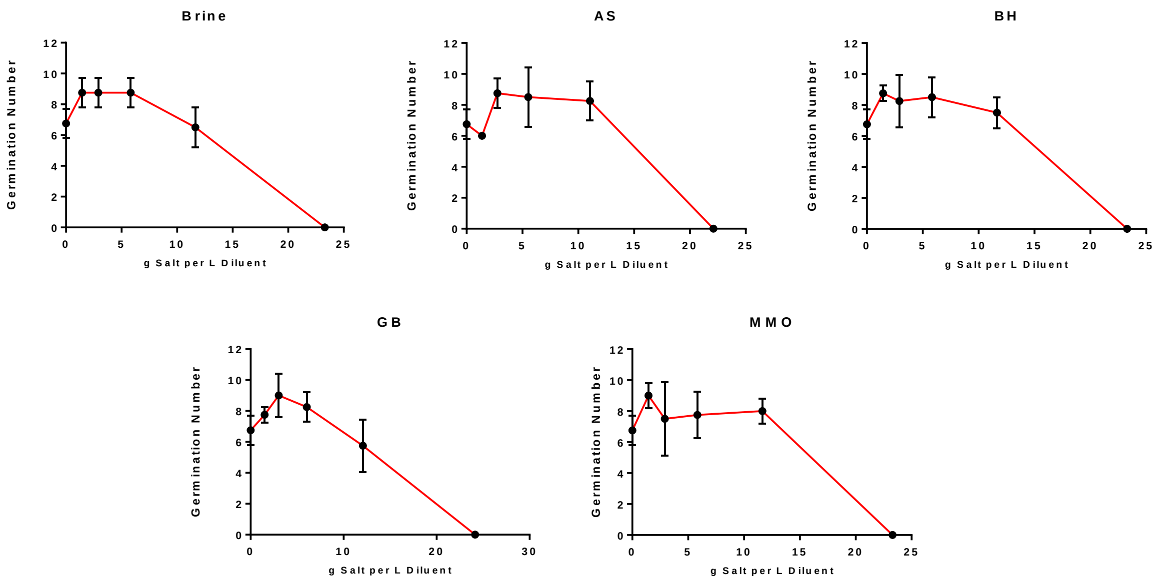

Figure 9: Dose-response curves of *Glycine max* exposed to the five deicer materials. The graphs represent the response – germination rate over 5 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates.

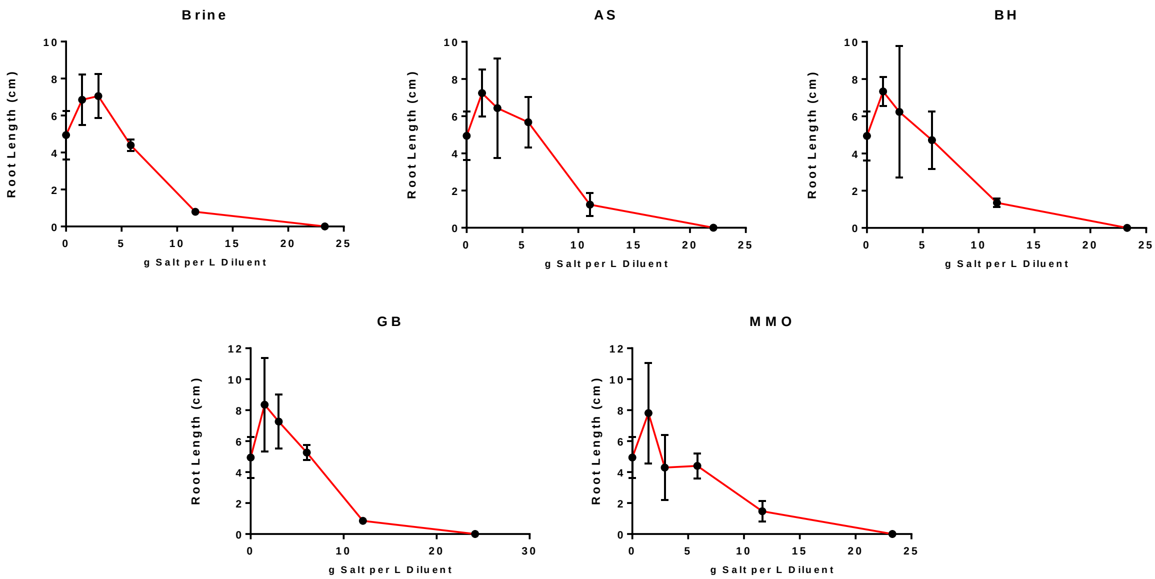

Figure 10: Dose-response curves of *Glycine max* exposed to the five deicer materials. The graphs represent the response – root length over 5 days – as a function of the deicer concentration expressed in g salt/L of diluent. brine: Salt brine, AS: AquaSalina, BH: BEET HEET, GB: GreenBlast, and MMO: Magic Minus Zero. The response is presented as mean and standard deviation between 4 replicates.