Evaluating the environmental impact of selected chemical de-icers

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Abstract

In this study, the environmental impacts of six commercial chloride-based de-icer products, including Rock Salt and Salt Brine, were evaluated. The nutrients, oxygen demand, heavy metal concentration, corrosion and toxicity of all six de-icers were analysed. With an assumed 500-fold dilution, the test results were compared to the public water-quality criteria. The results show that the selected chemical de-icers have little chance of severely damaging the environment and ecosystem under a normal dilution scenario. However, attention needs to be paid to small water bodies and sensitive receiving water.

Keywords: chemical de-icer; environmental impact; corrosion test; toxicity

1. Introduction

Snow- and ice-control materials (de-icers) are extremely important to winter road safety and mobility in snow-heavy areas, such as high-latitude areas of continents. Large amounts of solid and liquid chemical de-icers are applied during winter in order to get rid of the ice and snow on the roadways and to ensure good friction conditions on roadways [1]. Chloride-based salts are the most commonly seen de-icer products used in winter road maintenance applications. Among all the chloride-based salts, sodium chloride (NaCl) is the most widely used due to its abundance and low cost. Calcium chloride (CaCl2) and magnesium chloride (MgCl2) have better
ice-melting performance at low temperatures, but are more expensive than NaCl. Granular CaCl₂ can be combined with NaCl to increase its effectiveness in cold conditions. In addition to chloride-based salts, potassium acetate (KAc) and calcium magnesium acetate (CMA) are more effective, less corrosive and less damaging to the environment than chloride-based salts, but they are generally much more expensive. Agriculturally based additives provide improved performance, reduced de-icer corrosivity and improved lifespan compared to standard salt de-icers, but they are also expensive.

The use of chemical de-icers on US roads has dramatically increased over the last 50 years, which has the potential to lead to serious environmental issues [2–6]. The release of de-icing materials in the environment adversely impacts living organisms through direct, toxic effects – through either de-icing components (such as Na⁺ and Cl⁻) or co-contaminants (such as metals or ammonia) – and through indirect effects related to the alteration of their environment (water or soil) or nutrient sources. Chemical de-icers can be transported to the environment in several ways, such as spraying 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 (including surface water streams and lakes, as well as groundwater), which leads to increased concentration of the composing ions in surface water, ground water and soil [7]. The salinity increase can result in a range of potentially negative impacts [8–10]. On the other hand, organically derived de-icers can potentially contribute to nutrients. Nitrogen (N) and phosphorous (P), sulphur (S), and sodium (Na) can stimulate the growth of blue-green algae, leading to eutrophication and oxygen depletion [11]. Moreover, chemical de-icers might be corrosive. The corrosion of the de-icers leads to degradation of automobiles and the roadway infrastructure, reduction of the effective lifespan of the infrastructure, and negative impacts on the health of the ecosystem [12].

There are many types of chemical de-icer products available on the market. However, generally manufacturers will not provide assessments of the environmental impacts of their products. Moreover, in order to improve de-icing performance, additives are introduced into the de-icer products, which might not be limited to salts. The potential environmental effect of such unknown components requires further study. Therefore, it is necessary to evaluate the environmental impact of chemical de-icers before they are practically applied to winter roadways. In this study, the environmental impacts of six commercial de-icer products were analysed. The analysis included a chemical analysis (of the nutrients, oxygen demand and heavy metal concentration), a corrosion test and a toxicity test. This work could provide guidance on the selection of chemical de-icers for winter road-maintenance operations and environmental protection.

2. Experiment method
2.1 Sample preparation

Six commercial de-icer products, including rock salt and salt brine, were studied. These six de-icers included three solid de-icers and three liquid de-icers. The formulas of some de-icers are undisclosed for reasons of business confidentiality. The manufacturers only provide information about the composition of chloride-based salts, while the exact chemical composition might be unknown.

Rock salt is a solid de-icer containing mostly NaCl, and is one of the most commonly used de-icers in the industry. Product A and Product B were liquid products that were added to rock salt as pre-wetting agents according to the manufacturers’ recommendations. The former was composed of 22.4% MgCl₂ and 20% molasses, while the latter was an agricultural-based CaCl₂ de-icer. According to the manufacturers, these pre-wetting agents will enhance the performance of rock salt. Per manufacturer’s recommendation, Product A was mixed with rock salt at 10 gallons per ton of rock salt (rock salt amended with Product A will be simply referred to as Product A hereafter), while Product B was mixed with rock salt at 5 gallons per ton of rock salt (rock salt amended with Product B will be referred to as Product B hereafter).

Salt brine, a liquid de-icer, is an aqueous solution of 20–40% NaCl. In this experiment, 23.3% NaCl salt brine was used. Product C was an MgCl₂-based liquid de-icer containing 26–9% MgCl₂. Before testing, Product C was added to salt brine at 20% of the total volume of the solution (salt brine amended with Product C will be referred to as Product C hereafter). The last liquid de-icer, Product D, was a natural saltwater solution produced from ancient seas according to manufacturers. Product D contained a total of 22.1% chloride salts, including 7.7% Na, 1.5% potassium (K), 10.3%
2.2 Chemical analysis

Ultra-pure water (18 \( \Omega \text{M/cm} \)) was used as the zero concentration calibration curve point, and as the diluent when dilution was needed. Samples and standards were analysed at room temperature. Interference can impact numerical values, either by artificially elevating them or by depressing the analytically derived values. Chloride was a potential interference in some analyses, and is noted in the following methods discussion. Matched-matrix standards, in which the standards are composed in a matrix similar to the samples, can be used to decrease the matrix artefacts if the matrix is causing signal enhancement or suppression (that is, a change in analyte detection). However, a matched matrix (such as a 23.3% NaCl concentration) could also result in an invalid result if the matrix reagents contain impurities of the analyte in question. Because of this, an NaCl matched matrix was employed only when suggested in the method. Each product analysis was conducted in triplicate, and the results are presented as the arithmetic mean along with standard deviation (\( \sigma \)). Analysis of variance (ANOVA) statistical analyses were conducted using R to determine whether differences in treatment means were present; statistical significance was set at \( \alpha = 0.05 \).

Table 1. ICP-MS analysis conditions and calibration

| Element | Mass | Mode | Matrix | R     | DL (\( \mu \text{g/L} \)) |
|---------|------|------|--------|-------|--------------------------|
| Cr      | 52   | He   | 1% HNO\(_3\) | 0.991 | 1.27                     |
| Ni      | 60   | He   | 1% HNO\(_3\) | 0.839 | 1.77                     |
| Cu      | 63   | He   | 1% HNO\(_3\) | 0.993 | 0.75                     |
| Zn      | 66   | He   | 1% HNO\(_3\) | 0.989 | 3.27                     |
| As      | 75   | H\(_2\) | 1% HNO\(_3\) | 0.799 | 0.68                     |
| Ag      | 107  | He   | 1% HNO\(_3\) | 0.993 | 0.00                     |
| Cd      | 111  | He   | 1% HNO\(_3\) | 0.991 | 0.00                     |
| Hg      | 202  | He   | 1% HCl     | 0.996 | 0.05                     |
| Pb      | 206 + 208 | He | 1% HNO\(_3\) | 1.000 | 0.40                     |
2.3 Corrosion test
Corrosion testing was conducted using the Pacific Northwest Snowfighters (PNS) 72-hour cyclic method, which is widely applied in the literature [16–18]. The method specified the steel washers (dimension, materials and hardness) and the pre-cleaning technique. The cleaned washers were then measured to determine individual dimensions and mass. There were three washers per reaction vessel, which contained ~450 mL of solution; the de-icer products were tested at 3% NaCl or equivalent. The washers were completely submerged for 10 minutes, and then held in the headspace above the solution for 50 minutes; this process was repeated for 72 hours. At the conclusion of 72 hours of cycling, the washers were removed, carefully cleaned as specified and re-weighed. The corrosion testing apparatus, during use in one of the analysis rounds, is shown in Fig. 2.

Corrosion as miles penetration per year (MPY), adjusted corrosion (corrected for same-test Nanopure water corrosion MPY (Equations (1–3)) and NaCl normalized (referred to as ‘% NaCl’) were calculated according to the following equations:

$$MPY = \frac{(m_{\text{initial}} - m_{\text{final}}) \times 100 \text{ mg}}{\text{Area} \times 72 \text{ h} \times 7.85 \text{ g/mL}} \times 534$$ (1)

$$MPY_{\text{corrected}} = MPY_{\text{treatment}} - MPY_{\text{nanopure}}$$ (2)

$$\%\text{NaCl} = \frac{MPY_{\text{corrected, treatment}}}{MPY_{\text{corrected, NaCl}}} \times 100\%$$ (3)

2.4 Toxicity test
All assays used in this study were standardized toxicity tests that were conducted following published EPA guidelines [19–21]. The tests included a freshwater alga (Selenastrum capricornutum) algal growth assay, aquatic daphnid (Ceriodaphnia dubia) survival and reproductive assays, a fathead minnow (Pimephales promelas) larval toxicity test, a fathead minnow (Pimephales promelas) embryo-larval survival and teratogenicity test, a duckweed (Lemna minor) aquatic plant toxicity test using Lemna spp, and soybean (Glycine max) germination and root elongation tests.

In the proposed toxicity tests, the test organisms, all aquatic except the terrestrial plant soybean, were exposed to toxicants via the liquid medium. Therefore, the de-icers were tested in liquid form. Five concentrations and a control were used for each de-icer in each test. The highest concentration tested was obtained by diluting the liquid form of the de-icers five 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 of 2.

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 de-icers per volume of diluent (g/L). Toxicity data was analysed following statistical procedures recommended in the US EPA guidelines when applicable or equivalent procedures.

3. Results and discussion
3.1 Chemical analysis
De-icer product chemical analysis and corrosion testing are important, as they identify potential
Table 2. Chemical composition of de-icer products

| Materials | Rock salt | Salt brine | Product A | Product B | Product C | Product D |
|-----------|-----------|------------|-----------|-----------|-----------|-----------|
| Physical State | Solid | Liquid | Liquid | Liquid | Liquid | Liquid |
| Composition | Proprietary | Proprietary | Proprietary | Proprietary | Proprietary | Proprietary |
| NaCl | 90–100% | NA | 7.7% | 7.7% | 7.7% | 7.7% |
| KCl | NA | NA | NA | NA | NA | NA |
| CaCl₂ | NA | NA | NA | NA | NA | NA |
| MgCl₂ | NA | NA | 22.4% | 22.4% | 22.4% | 22.4% |
| Organic | NA | NA | Molasses 20% | Agricultural base organic | NA | NA |
| Other | NA | NA | NA | Chloride | Performance enhancer 0.2% | NA |

Note: Specific gravity: g/mL.

direct environmental and infrastructure effects associated with using de-icer products. In this part of the study, 10 chemical analyses were conducted, including pH, BOD, COD, ammonia, nitrate, nitrite, organic N, total N, P and metals (Table 2). Additionally, corrosion testing was conducted. These analyses have been thematically grouped as follows: pH, oxygen demand (BOD and COD), nutrients (P, ammonia, nitrate, nitrite, organic N and total N) and metals.

Environmental pH has a large effect on both biotic and abiotic conditions. Fig. 3 shows sample pH triplicate analysis results. It should be noted here that the products were not diluted for analysis. The Pennsylvania Department of Environmental Protection (DEP) has set a pH criterion of 6.0–9.0 [22]. As can be seen, only Product D exceeded the lower limit, which means Product D contained not only chloride-based salts but also other acidic chemicals. Generally, after sufficient dilution, the effect of de-icers on environmental pH is negligible. However, it should be noted that a de-icer product’s effect on the receiving water body’s pH will depend on the dilution and the receiving water body’s buffering capacity, with small water bodies with minimal buffering capacity at the greatest risk of substantial pH changes.

Elevated nutrient inputs are often associated with increased oxygen demand, and thus result in depleted dissolved oxygen (DO) concentrations. Low DO concentrations have been associated with widespread fish kills. Eutrophication-induced hypoxic water bodies (very low DO) are referred to as ‘dead zones’ when they can no longer support aquatic life. Two examples are the Chesapeake Bay and the Mississippi Delta into the Gulf of Mexico. For nutrients, the following nutrient endpoints were analysed: P, ammonia, nitrate, nitrite, organic N and total N. Nutrient results are summarized in Table 3. In order to compare with relevant Pennsylvania DEP criteria [22], a 500-fold dilution of de-icers was assumed from road application to environmental waters [1].

P, presented as phosphorus (not as phosphate), was found to be significantly greater in the rock salt than in salt brine, therefore comparisons are made to the separate reference products (rock salt and salt brine for solid and liquid formulas, respectively). In general, solid formulas had higher P concentrations than did liquid formulas. Among the solid de-icers, both of the pre-wetting agents resulted in statistically significant increases in P compared to the rock salt. For liquid de-icers, Product D was found to have significantly elevated P concentrations compared to salt brine; Product C was statistically equivalent to salt brine.

Ammonia was found to be significantly greater in the rock salt than in salt brine (by around a factor of 2). Comparisons were made to the separate reference products (rock salt and salt brine for solid and liquid formulas, respectively). Product A and Product B both had nominal ammonia values that were statistically significantly lower than their
Table 3. Nutrient summary for triplicate analysis of de-icer products

| Sample       | P (mg/L) Mean ± σ | NH₃-N (mg/L) Mean ± σ | NO₃⁻ – N (mg/L) Mean ± σ | NO₂⁻ – N (mg/L) Mean ± σ | Total N (mg/L) Mean ± σ |
|--------------|-------------------|-----------------------|--------------------------|--------------------------|-------------------------|
| Rock salt    | 0.89 ± 0.01       | 1.05 ± 0.13           | 0.01 ± 0.01              | 0.01 ± 0.00              | 3.26 ± 0.42             |
| Product A    | 1.31 ± 0.04       | 0.29 ± 0.01           | 0.04 ± 0.07              | 0.01 ± 0.01              | 3.67 ± 0.27             |
| Product B    | 1.08 ± 0.03       | 0.84 ± 0.09           | 0.02 ± 0.03              | 0.01 ± 0.00              | 7.10 ± 0.60             |
| Salt brine   | 0.17 ± 0.10       | 0.58 ± 0.14           | 0.92 ± 0.96              | 0.00 ± 0.00              | 1.67 ± 0.12             |
| Product C    | 0.09 ± 0.03       | 0.05 ± 0.01           | 75.27 ± 115.2           | 0.03 ± 0.01              | 2.54 ± 0.27             |
| Product D    | 1.10 ± 0.05       | 53.04 ± 5.46          | 454.03 ± 773.8          | 0.04 ± 0.00              | 6.72 ± 0.60             |

Analysis was conducted for organic N, but owing to necessary dilution, all samples were below the detection limit.

appropriate reference (rock salt). Product C was equivalent to the salt brine reference, but Product D’s ammonia values were significantly elevated. The ammonia criterion set by the Pennsylvania DEP is temperature-related pH values [22] For an assumed pH of 7 and temperature of 0°C, the freshwater criterion is 0.017 mg/L for un-ionized ammonia. With an assumed 500-fold dilution, all in-stream ammonia values would be at least an order of magnitude below the criterion, with the exception of Product D, which would be around eight times higher than the criterion. However, the measured value of ammonium is suspect, as it is substantially higher than the measured total N value. If the measured total N value for Product D is used, and all of the total N is assumed to be ammonia, then in-stream ammonia concentrations were below the criterion.

Nitrite was also 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, but nitrite concentrations were significantly elevated in Product A, Product C and Product D; Product B was equivalent to salt. The Pennsylvania DEP provides a criterion of 10 mg/L as N for combined nitrate and nitrite [22]; as total N was less than this criterion for all de-icers in their undiluted form, this is not a concern.

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, 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. The results of COD and BOD are summarized in Fig. 4. Among the chemical de-icers, Product C had the largest COD value; Product D and Product B had significantly higher COD values than rock salt, but lower than Product C. Product A had a COD value statistically similar to that of 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 salt have non-detectable BOD. Product C had the largest BOD value, followed by Product B, then Product D, with Product A having the lowest BOD value.

As expected, the COD values for each product were greater than the BOD values. This indicates that the products contain some material that is chemically oxidizable, but is not readily bioavailable to be biologically oxidized in a timely manner. The lack of consistence among BOD/COD ratios can similarly be attributed to differences in labile readily biodegradable material (the BOD/COD range was 0.2–0.3 for non-reference products). Taken together, Product C is likely to exert the greatest oxygen demand in both the short and the longer term. The Pennsylvania DEP does not have BOD or COD criteria. However, a range of DO criteria do exist that depend on flowing status (flowing or lake), monitoring duration, season and whether the ecosystem is naturally used for early life stages; in all cases, the minimum DO concentration is greater than 5.0 mg/L, and in sensitive cases is
The greatest oxygen depletion would be up to 9.0 mg/L. Under a 500-fold dilution scenario, the greatest oxygen depletion would be ~2.4 mg/L for Product C, which would possibly be harmful to sensitive receiving waters.

Several metals are required in trace amounts to support biological growth (including Zn), while others are not needed (such as Cd, Hg and Pb). At elevated concentrations, many metals can become toxic to aquatic biota. The results of the metals analysis of the selected chemical de-icers are shown in Table 4, including the elemental concentrations of the following metals (and the mass-to-charge value at which the analysis was conducted): Cr (52), Ni (60), Cu (63), Zn (66), As (75), silver (Ag, 107), Cd (111), Hg (202) and Pb (206). Among the nine measured metals, Zn was usually the most abundant metal, with Cu and As also abundant. Ni, Ag and Hg were the least abundant elements. Pre-wetting agents generally resulted in elevated metal concentrations, compared to the rock salt reference, as would be expected, since they are rock salt amendments; the increase was often greater for Product A than for Product B. Among all liquid de-icers, Product D had lower metal concentrations than the salt brine reference; this was notably the case for Cu and As, though the Pb concentration of Product D was greater than that of the salt brine. Product C had metal concentrations greater than the salt brine, which was generally expected as it consisted of 80% salt brine. Noteworthy increases in metal concentrations in Product C compared to the salt brine included Cr, Ni and As.

Metals criteria are often set for dissolved metal concentrations (that is, 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 has been well discussed in the literature [23]. Pennsylvania DEP criteria equations can be found in Table 5, and in [22]. The following metals have hardness-dependent criteria (calculated nominal maximum and continuous criteria assuming 100 mg/L as CaCO3): 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 (that is, they are not water quality–specific) at 340 and 150 μg/L maximum and continuous criteria. Hg criteria are also set nominal values (that is, they 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). Assuming a 500-fold dilution in the receiving water and a receiving-water body hardness of 100 mg/L as CaCO3, none of the de-icers would exceed continuous, maximum or drinking-water criteria, and generally expected concentrations were over an order of magnitude below all criteria (expected concentrations were less than 10% of the criteria). However, it should be noted that roadway runoff metals have been demonstrated to be another source of contamination, such as the reflection contributions from roadway-associated sources, including tyres, brakes and roadside soil (particularly for Pb as a legacy from leaded gasoline use) [24–6]. While the stormwater runoff metals may originate from sources other than the de-icer products, the presence of elevated salt concentrations may change the metals’ fate, transport and toxicity.

### Table 4. Metals results for triplicate analysis of de-icer products

| Sample          | Cr (52) | Ni (60) | Cu (63) | Zn (66) | As (75) |
|-----------------|---------|---------|---------|---------|---------|
| Rock salt       | Mean ± σ | Mean ± σ | Mean ± σ | Mean ± σ | Mean ± σ |
| Product A       | 31.35 ± 0.85 | 50.66 ± 0.93 | 49.38 ± 0.38 | 78.08 ± 110.7 | 51.77 ± 0.77 |
| Product B       | 18.46 ± 0.77 | 20.55 ± 0.48 | 16.15 ± 41.43 | 32.84 ± 65.32 | 11.37 ± 0.37 |
| Salt brine      | 2.17 ± 0.67 | 27.46 ± 0.27 | 5.18 ± 153.9 | 30.59 ± 4.29 | 1.41 ± 0.41 |
| Product C       | 8.44 ± 3.13 | 44.30 ± 3.29 | 18.58 ± 281.9 | 137.7 ± 100.8 | 9.98 ± 0.98 |
| Product D       | 1.34 ± 0.59 | 2.67 ± 0.24 | 0.29 ± 81.19 | 7.54 ± 0.57 | 0.19 ± 0.19 |

| Sample          | Ag (107) | Cd (111) | Hg (202) | Pb (206) |
|-----------------|---------|---------|----------|----------|
| Rock salt       | Mean ± σ | Mean ± σ | Mean ± σ | Mean ± σ |
| Product A       | 8.06 ± 1.61 | 23.60 ± 3.71 | 0.69 ± 3.56 | 0.10 ± 0.10 |
| Product B       | 38.40 ± 56.28 | 105.4 ± 153.8 | 0.05 ± 13.80 | 2.60 ± 0.60 |
| Product C       | 10.53 ± 9.23 | 38.34 ± 37.38 | 0.19 ± 17.23 | 0.58 ± 0.58 |
| Product D       | 0.20 ± 0.10 | 0.44 ± 0.93 | 0.13 ± 0.82 | 0.10 ± 0.10 |

Up to 9.0 mg/L. Under a 500-fold dilution scenario, the greatest oxygen depletion would be ~2.4 mg/L for Product C, which would possibly be harmful to sensitive receiving waters.
Table 5. Corrosion testing results (de-icer products were tested at 3% NaCl and equivalent)

| Sample                  | Mean MPY ± σ | Corrected MPY Mean ± σ | % of NaCl Mean ± σ |
|-------------------------|--------------|------------------------|--------------------|
| Ultra-pure H₂O          | 95 ± 69      | 36 ± 13                | 117 ± 225          |
| 3% NaCl ref.            | 130 ± 63     | 84 ± 144               | 321 ± 219          |
| 0.78% MgCl₂ ref.        | 64 ± 63      | 22 ± 23                | 321 ± 80           |
| 0.93% CaCl₂ ref.        | 50 ± 110     | 27 ± 26                | 326 ± 98           |
| 3% MgCl₂ ref.           | 60 ± 22      | 22 ± 22                | 321 ± 80           |
| 3% CaCl₂ ref.           | 58 ± 27      | 27 ± 27                | 326 ± 98           |
| MgCl₂ chloride eq.      | 142 ± 69     | 9 ± 5                  | 24 ± 14            |
| CaCl₂ chloride eq.      | 33 ± 11      | 11 ± 11                | 283 ± 32           |
| Rock salt               | 60 ± 29      | 63 ± 111               | 205 ± 206          |
| Product A               | 46 ± 17      | 65 ± 175               | 210 ± 220          |
| Product B               | 64 ± 40      | 65 ± 125               | 220 ± 209          |
| Salt brine              | 46 ± 9       | 68 ± 173               | 209 ± 206          |
| Product C               | 29 ± 23      | 65 ± 227               | 232 ± 232          |
| Product D               | 41 ± 23      | 60 ± 189               | 206 ± 206          |

Table 6. Summary of toxicity testing results of de-icer products using algae, daphnids, duckweed, soybean and fathead minnows

| De-icer (g salt/L)       | Selenastrum (growth) NOEC | LOEC | IC₅₀ | Daphnids (survival) NOEC | LOEC | IC₅₀ | Daphnids (reproduction) NOEC | LOEC | IC₅₀ | Minnow larvae (survival) NOEC | LOEC | IC₅₀ | Minnow larvae (growth) NOEC | LOEC | IC₅₀ |
|-------------------------|---------------------------|------|------|--------------------------|------|------|----------------------------|------|------|----------------------------|------|------|----------------------------|------|------|
| Brine                   | 2.91                      | 5.83 | 4.02 | 1.46                     | 2.91 | 2.1  | 0.73                       | 1.46 | 1.38 | 2.91                       | 5.83 | 5.92 | 5.83                       | 11.65| 5.09 |
| Product D               | 2.63                      | 5.25 | 4.58 | 1.38                     | 2.76 | 1.99 | 0.35                       | 0.69 | 1.01 | 2.76                       | 5.83 | 4.68 | 5.83                       | 11.05| 5.36 |
| Product B               | 1.46                      | 2.91 | 3.68 | 1.46                     | 2.91 | 1.7  | 0.73                       | 1.46 | 1.04 | 2.91                       | 5.83 | 6.2  | 5.83                       | 11.65| 7.07 |
| Product C               | 3.02                      | 6.04 | 4.7  | 0.75                     | 1.51 | 1.09 | 0.38                       | 0.75 | 0.61 | 3.02                       | 6.04 | 5.44 | 3.02                       | 6.04 | 4.8 |
| Product A               | 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 |

3.2 Corrosion test

Table 5 shows the results of the corrosion test. Generally, all reference solutions and de-icer products were found to be less corrosive than the 3% NaCl standard. The exception was that equivalent Cl from MgCl₂ (2.44% MgCl₂) was found to be slightly more corrosive than 3% NaCl, as can be seen in the positive value for NaCl. By contrast, equivalent Cl from CaCl₂ 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 studied due to elevated variance values, but general trends were discussed. The de-icers salts (rock salt and salt brine) were also found to be less corrosive than the 3% NaCl reference, which was potentially due to impurities present in the salt sources. Rock salt and Product B had similar average corrosion-rate values, while Product A had a lower average corrosion rate. Among liquid de-icers, Product C was consistently less corrosive than Product D. However, the relative corrosivity of salt brine was more variable, making comparisons challenging. It should be noted that field corrosion results are often different than those observed in the laboratory.

3.3 Toxicity test

A summary of toxicity testing results is presented in Table 6 in the form of a matrix containing the relevant toxicity endpoints for the different tests. Based on the animal toxicity endpoints, the most toxic de-icer was Product C. Based on the plant/algae test, the most toxic de-icer was Product D. Considering that the toxicity endpoints were presented
Table 7. RQs calculated for invertebrates, fish, algae and plants using the lowest NOEC and LC50 recorded in the present study and predicted environmental concentrations of 25, 165 and 470 mg/L

| De-icer         | Invertebrates | Fish | Algae | Aquatic plants |
|-----------------|---------------|------|-------|----------------|
|                 | 25mg/L        | 165mg/L | 470mg/L | 25mg/L        | 165mg/L | 470mg/L | 25mg/L        | 165mg/L | 470mg/L       |
| Salt brine      | 0.02          | 0.23  | 0.64  | 0.01          | 0.11    | 0.32    | 0            | 0.04    | 0.12 | 0 | 0.02 | 0.05 |
| Product D       | 0.04          | 0.47  | 1.34  | 0             | 0.03    | 0.08    | 0            | 0.04    | 0.1  | 0.01 | 0.07 | 0.21 |
| Product B       | 0.02          | 0.23  | 0.64  | 0.01          | 0.11    | 0.32    | 0            | 0.04    | 0.13 | 0    | 0.02 | 0.04 |
| Product C       | 0.04          | 0.43  | 1.24  | 0.08          | 0.87    | 0.05    | 0            | 0.04    | 0.1  | 0    | 0.02 | 0.06 |
| Product A       | 0.02          | 0.23  | 0.64  | 0.01          | 0.11    | 0.32    | 0            | 0.03    | 0.1  | 0    | 0.04 | 0.11 |

as g salt/L, this observation may be explained by the nature of salt and composing ions. The relative toxicity of salts is known to vary with the anion and cation combinations present in the material [27]. A large amount of experimental research has shown that the relative toxicity of the cationic component is as follows: K > magnesium (Mg) > Na/Ca [28–30]. This observation may explain the relative higher toxicity of Product D, which contained potassium chloride (1.5% w/v) and MgCl₂ (2.6% w/v), and Product C, which contained MgCl₂ (5.2–5.8% w/v).

These toxicity endpoints were used to assess the environmental risk associated with the de-icer materials. The US EPA frequently uses a deterministic approach – the quotient method – to compare toxic levels to the environment. The risk quotient (RQ) is calculated by dividing the level of exposure by the toxicity endpoint. This ratio allows for the identification of high-risk and low-risk situations. In risk assessments based on chronic toxicity to aquatic animals, the lowest NOECs for freshwater fish and invertebrates are used to calculate the RQ. For risk assessments based on chronic toxicity to aquatic vascular plants and algae, the RQ is based on the lowest IC/LC50. We thus calculated the RQs for invertebrates, fish, algae and plants. Three environmental exposure scenarios were considered: low exposure (25 mg salt/L), high exposure (165 mg salt/L) and exposure to a 500-fold dilution of the de-icers (470 mg salt/L). The results are shown in Table 7.

The US EPA considers that the level of concern for chronic risk for aquatic organisms corresponds to an RQ of 1.0 – in other words, there is no concern for RQs lower than 1.0 [20]. Based on this standard, none of the de-icers tested seemed to pose a significant threat to the environment concentrations of 25 or 165 salt/L. Product D and Product C, identified as the most toxic de-icers in the previous toxicity endpoints study, may represent a concern for invertebrates, which were the most sensitive aquatic organisms tested, in the highest-exposure scenario (500-fold dilution).

4. Conclusions

Overall, it seems unlikely that use of any of the de-icer products tested would result in direct negative environmental impacts to typical receiving water bodies, assuming adequate dilution. Direct negative environmental impacts might occur for small water bodies, where there is likely to be less dilution, or sensitive receiving waters. In particular, Product D might reduce the pH. For receiving waters that are sensitive to nutrients or low DO concentrations, Product B and Product D generally had the highest nutrient concentrations, but Product C exerted the greatest oxygen demand. None of the products exceeded metals criteria for the given dilution and receiving-water hardness assumptions, though Product A was near the Cd criterion. Toxicity testing data suggests that only Product D and Product C might 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, corrosion and toxicity) associated with the six de-icers tested could be expected to be minimal; indirect effects were not tested in this study. However, the effects on water quality and toxicity should be carefully re-evaluated in small watersheds, where dilution may be minimal, or in sensitive receiving water bodies.

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References

1. Fay L, Shi X. Environmental impacts of chemicals for snow and ice control: state of the knowledge. Water Air Soil Poll 2012; 223:2751–70.
2. Buttle JM, Labadia CF. Deicing salt accumulation and loss in highway snowbanks. J Environ Qual 1999; 28:155–64.
3. McFarland BL, O’Reilly KT. Environmental impact and toxicological characteristics of calcium magnesium acetate. In:
4. Albright M. Changes in water quality in an urban stream following the use of organically derived deicing products. Lake Reserv Manage 2005; 21:119–24.
5. Backman L, Folkeson L. Influence of deicing salt on vegetation, groundwater, and soil along two highways in Sweden.
6. Bang SS, Johnston D. Environmental effects of sodium acetate/formate deicer, Ice Shear™. Arch Environ Cont Tox 1998; 35:580–7.
7. Marsalek J. Road salts in urban stormwater: an emerging issue in stormwater management in cold climates. Water Sci Technol 2003; 48:61–70.
8. Novotny EV, Murphy D, Stefan HG. Increase of urban lake salinity by road deicing salt. Sci Total Environ 2008; 406:131–44.
9. Ruth O. The effects of de-icing in Helsinki urban streams, southern Finland. Water Sci Technol 2003; 48:33–43.
10. Smith DW, Facey RM, Novotny V, et al. Management of winter diffuse pollution from urban areas: effect of drainage and deicing operations. In: Ninth International Conference on Cold Regions Engineering, Duluth, MN, USA, 1998, 243–57.
11. Ramakrishna DM, Viraraghavan T. Environmental impact of chemical deicers – a review. Water Air Soil Poll 2005; 166:49–63.
12. Shi X, Fay L, Yang Z, et al. Corrosion of deicers to metals in transportation infrastructure: introduction and recent developments. Corros Rev 2009; 27:23–52.
13. Eaton AD, Cliesceri LS, Rice EW, et al. (eds) Standard Methods for the Examination of Water and Wastewater, 21st edn. Washington, DC: American Public Health Association; American Water Works Association; Water Pollution Control Federation, 2005.
14. Eaton AD, Cliesceri LS, Greenberg AE, et al. (eds) Standard Methods for the Examination of Water and Wastewater, 19th edn. Washington, DC: American Public Health Association; American Water Works Association; Water Pollution Control Federation, 1995.
15. US Environmental Protection Agency. EPA method 200.8: determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry. Technical report. EPA 1994.
16. Fischel M. Evaluation of selected deicers based on a review of the literature. Technical report. Colorado Department of Transportation Research Branch 2001.