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Toxicity testing of “eco-friendly” de-icing formulations using *Chironomus dilutus*[☆]

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ABSTRACT

An influx of chloride ions from road de-icing solutions can result in toxicological effects to organisms in terrestrial and aquatic environments. As such, “eco-friendly” de-icing alternatives are sought to mitigate environmental impacts of de-icing impervious surfaces, while maintaining human safety. While many alternative de-icers are economically impractical for municipal use, the residential commercial market is flooded with de-icing formulations claiming to be “eco-friendly”. Given the little regulation and guidance that surrounds eco-labeling, the meaning of “eco-friendly” remains unclear in the context of biological systems. The objective of the current study was to determine the toxicity of three “eco-friendly” de-icing formulations to *Chironomus dilutus* using 10 d toxicity tests. The toxicity of these three formulations was compared to a traditional formulation composed entirely of chloride salts. Two of the “eco-friendly” de-icers demonstrated LC₅₀s of 6.61 and 6.32 g/L, which were similar in toxicity to the traditional sodium chloride formulation with a LC₅₀ 6.29 g/L. The comparable toxicities of these formulations is likely due to the presence of chloride salts in each of the “eco-friendly” de-icers. The third “eco-friendly” formulation, a urea-based de-icer, demonstrated toxicity an order of magnitude higher than that of the traditional formulation with an LC₅₀ of 0.63 g/L. While *C. dilutus* may not have been the intended endpoint in consideration when marketing these products as “eco-friendly”, consideration of how eco-labeling is utilized and the role of environmental scientists in determining the meaning of such claims must be considered to ensure continued and future protection of the environment.

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1. Introduction

Freshwater salinization due to the de-icing of roadways is a well-documented phenomenon that negatively affects the health of freshwater ecosystems around the world (Mason et al., 1999; Williams et al., 1999; Trombulak and Frissell, 2000; Robidoux and Delisle, 2001; Blasius and Merritt, 2002; Ramakrishna and Viraraghavan, 2005; Kelly et al., 2008; Novotny et al., 2008; Corsi et al., 2010; Findlay and Kelly, 2011; Harless et al., 2011; Hintz et al., 2017; Jones et al., 2017; Schuler et al., 2017; Schuler and Relyea, 2018a,b). As many de-icers consist primarily of chloride salts, runoff and accumulation of chloride ions in freshwater environments causes significant risk to aquatic organisms (Blasius and Merritt, 2002; Sanzo and Hecnar, 2006; Karraker, 2007;

Novotny et al., 2008; Collins and Russell, 2009; Denoël et al., 2010; Gardner and Royer, 2010; Elphick et al., 2011; Harless et al., 2011; Hintz et al., 2017; Jones et al., 2017; Schuler and Relyea, 2018a,b). Indeed, much research on the effects of chloride ions on amphibians, fish, and invertebrates exists within the scientific literature (Williams et al., 1999; Benbow and Merritt, 2004; Soucek and Kennedy, 2005; Sanzo and Hecnar, 2006; Karraker, 2007; Collins and Russell, 2009; Denoël et al., 2010; Gardner and Royer, 2010; Elphick et al., 2011; Soucek et al., 2015; Griffith, 2017; Hintz et al., 2017; Hintz and Relyea, 2017; Jones et al., 2017; Schuler et al., 2017; Schuler and Relyea, 2018a,b). Chloride ions introduced from road de-icers threaten native freshwater species and ecosystems through direct toxicity to more sensitive species, triggering trophic cascades within these ecosystems (Hintz et al., 2017; Jones et al., 2017; Schuler et al., 2017; Schuler and Relyea, 2018b), increased bioavailability of heavy metals (Schuler and Relyea, 2018a), and changes in abiotic factors of freshwater ecosystems that may further the spread of certain invasive species (Coldsnow and Relyea, 2018). Although much attention has been devoted to the toxic

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effects of chloride ions, research demonstrates the cation of the salt can play a major role in determining the toxicity of road de-icing salt runoff to freshwater species (Hintz and Relyea, 2017; Coldsnow and Relyea, 2018). Despite these compelling findings, few proactive measures have been proposed to regulate the use of chloride-based de-icing agents on a large scale due to the need to protect human health during winter months (Ramakrishna and Viraraghavan, 2005). Conversely, the residential de-icing market is flooded with formulations that either enhance the product with other chemical agents to reduce chloride content or completely replace chloride salts with an alternative de-icing substance. These products are consequently marketed to consumers as “eco-friendly” alternatives to traditional formulations.

Eco-friendly de-icing formulations usually consist of one of three chemical additives or chloride replacements, which theoretically decreases risk associated with runoff during spring snowmelt or rainfall events. Calcium magnesium acetate (CMA), a common additive to residential de-icing formulations, serves as a less corrosive and less toxic de-icing alternative to chloride salts, but is less effective as a de-icing agent (Robidoux and Delisle, 2001; Ramakrishna and Viraraghavan, 2005). Therefore, use of CMA often occurs as an additive to reduce the overall chloride content of the formulation without sacrificing efficacy of the product as a de-icer. To this end, some CMA products are marketed as eco-friendly, despite containing upwards of 40% chloride salts by weight (Snow Joe MELT Enviro-Blend Ice Melter w/CMA, Safety Data Sheet, Snow Joe, LLC, Edison, NJ, USA).

Another common additive to residential de-icing formulations is beet juice, an organically derived de-icing alternative. Beet juice does not itself act as a de-icing agent, but can help reduce chloride salt usage by enhancing the degree to which the de-icers bind to road surfaces (Schuler et al., 2017). As with other organic compounds, beet juice can influence aquatic communities by lowering dissolved oxygen content due to increased microbial activity and by increasing nutrient flux into the system, resulting in trophic cascades within freshwater ecosystems (Schuler et al., 2017; Schuler and Relyea, 2018b). Similar to CMA-enhanced formulations, beet juice comprises a small percentage of this eco-friendly blend relative to its chloride composition that consists of 85.0–99.9% of the formulation (MELT Beet-IT, Safety Data Sheet, Snow Joe[®], Carlstadt, NJ, USA).

Urea, commonly used as a de-icing agent on airport runways, is non-toxic to many aquatic and terrestrial species, and is an effective de-icing agent with no added chloride (Turnbull and Bevan, 1995; Ellis et al., 1997; Koryak et al., 1998; Harless et al., 2011). In addition, urea pellets sprinkled on impervious surfaces during winter months are safe for use in households with pets and children, as the urea does not cause dryness of paws or hands, nor consists of sharp crystals that could penetrate skin. As such, urea-based formulations possibly offer the most promise as an eco-friendly de-icer for terrestrial environments, but may pose significant risk to aquatic ecosystems. Hydrolysis of urea to ammonia in aquatic environments can cause significant toxicity and changes to aquatic food webs in waters receiving input from areas of use (Ankley et al., 1995; Turnbull and Bevan, 1995; Schubauer-Berigan et al., 1996; Ellis et al., 1997; Koryak et al., 1998).

Given the way in which these eco-friendly additives are used as only small additions to (e.g., CMA and beet juice) or potentially toxic replacements (e.g., urea) for chloride salts, it is unclear whether these formulations effectively ameliorate the aquatic toxicity resulting from deploying these de-icers on impervious surfaces. Our objectives were to 1) determine the toxicity of three eco-friendly de-icing formulations (CMA-enhanced, beet juice-enhanced, and urea-based) to *Chironomus dilutus* larvae using 10 d toxicity tests, 2) compare these toxicities to that of a traditional

chloride salt de-icing formulation, and 3) explore the meaning of eco-friendly within the context of green marketing and environmental science.

2. Materials and methods

2.1. Chemicals

Four de-icing agents were used to determine the toxicity of these formulations on *Chironomus dilutus*. These formulations represented a traditional road salt formulation (Professional Grade Ice Melter Blend, Morton Salt, Morton International, Inc., Chicago, IL, USA), which uses sodium chloride and calcium chloride as de-icing agents with added anticaking agents, a CMA enhanced blend (Snow Joe MELT Enviro-Blend Ice Melter w/CMA, Snow Joe, LLC, Edison, NJ, USA), a beet juice enhanced blend (Snow Joe MELT Beet-IT, Snow Joe, LLC, Edison, NJ, USA), and a urea-based de-icer (Safe Paw Ice Melter, Gaia Enterprises, Inc., Richboro, PA, USA). The formulations will be abbreviated as sodium chloride (NaCl), calcium magnesium acetate enhanced blend (CMA), beet juice enhanced blend (BJE), and urea-based blend (UB). The CMA, BJE, and UB formulations all claim to be environmentally- or eco-friendly on the packaging, but it is not made clear what portion of the environment these products are intended to be “friendly” towards. Therefore, the results of our study do not represent a challenge to the labeling of these specific products, rather a representation of the potential dangers of eco-friendly labeling in the context of product marketing.

2.2. Toxicity testing

Ten-day acute toxicity tests were conducted using 2nd instar *C. dilutus* obtained from laboratory cultures housed at Penn State Behrend (Erie, PA, USA) using methodologies adapted from Silver et al. (2009) and Lob and Silver (2012). Following a preliminary range-finding test, twenty 2nd instar *C. dilutus* larvae were isolated from laboratory cultures and randomly placed into custom exposure chambers modeled after the design presented by Silver et al. (2009). Briefly, exposure chambers consisted of 15-cm (diameter) x 8-cm (depth) polyvinyl chloride (PVC) chambers with a 1-cm-deep layer of autoclaved silica sand serving as a substrate for test organisms. The temperature of the exposure chambers was maintained at $23 \pm 1^\circ\text{C}$ using a water bath contained in 38 L glass aquaria. The exposure chambers contained either moderately hard water (MHW) (Smith et al., 1997) with no added de-icing agents (i.e. negative controls) or MHW and an added de-icing agent. The traditional road salt formulation, consisting primarily of sodium chloride, represented our baseline toxicity benchmark for evaluating toxicity of “eco-friendly” formulations. All formulations were mixed into MHW in bulk at concentrations determined from preliminary testing and distributed to exposure chambers 24 h prior to addition of *C. dilutus*. Five test concentrations were used with each formulation. The range of concentrations used with each formulation were as follows: NaCl: 3.0, 4.5, 6.0, 7.5, 9.0 g/L; CMA: 3.0, 4.5, 6.0, 7.5, 9.0 g/L; BJE: 3.0, 4.5, 6.0, 7.5, 9.0 g/L; UB: 0.05, 0.65, 1.25, 1.85, 2.45 g/L. Five replicates of each concentration were included during each toxicity test, such that there were 25 chambers for each formulation, as well as 10 replicate chambers containing MHW as a negative control, totaling 60 exposure chambers per test. Toxicity tests were conducted in batches, with NaCl tests included with each evaluation of the three “eco-friendly” formulations in order to ensure that the sensitivity of the cultures did not change over the length of the study and to allow for direct comparisons of median lethal concentration (LC₅₀) benchmarks for each “eco-friendly” formulation relative to toxicity of the traditional formulation

(NaCl).

Test organisms were held within exposure chambers for 10 d with a 16:8 h light:dark photoperiod. Water quality, including dissolved oxygen, conductivity, pH, and temperature were monitored three times (i.e. initial, midpoint, final) over a 10 d exposure period and averaged to ensure compliance with ASTM Standards (2010) using a Yellow Springs Incorporated 6820 multi-parameter water quality meter (YSI Inc., Yellow Springs, OH, USA). No aeration was provided to the chambers unless dissolved oxygen in overlying water dropped below 2.5 mg/L, which was not documented to occur in any of the toxicity tests (ASTM, 2010). To ensure that the de-icer concentration did not change significantly over the course of the exposures, any water lost due to evaporation was replenished daily with deionized water to the original water volume added to each chamber. Larvae were fed 0.5 mL of well-blended TetraMin® (Spectrum Brands – Pet, Blacksburg, VA, USA) slurry (52 g/L) each day for the duration of testing.

Following the 10 d exposure period, *C. dilutus* were removed from the exposure chambers using a 500 µm sieve, and were subsequently counted as either alive or dead. Missing and unresponsive larvae were scored as mortalities.

2.3. Statistical analysis

Data collected from toxicity tests were analyzed to determine LC₅₀ values using a Probit analysis in IBM SPSS Statistics software, Version 25 (IBM, Armonk, NY, USA). Nominal concentrations (g/L) of each formulation were used to determine the LC₅₀ values for each test. The LC₅₀s of the “eco-friendly” formulations were compared to LC₅₀s of NaCl included with each test using the 95% confidence intervals of the LC₅₀ estimates achieved from each data set. Although this comparison does not represent a robust statistical analysis, significant overlap of confidence intervals suggests statistical similarity and relates to the biological similarities or differences resulting from exposure to each of the four de-icing formulations used in our study (Cumming et al., 2007).

3. Results and discussion

3.1. Quality control

Water quality parameters were maintained within acceptable limits for the duration of the 10 d exposures for each toxicity test (ASTM, 2010). Average temperature and pH were 23.53 ± 0.928 °C (mean ± standard deviation) and 8.31 ± 0.627, respectively across the three water quality measurements made over the course of the three toxicity tests. Average dissolved oxygen was 5.03 ± 2.463 mg/L for the CMA and BJE tests. Average control mortality of *C. dilutus* was equal to 12.00 ± 9.775% (mean ± standard deviation), 19.00 ± 10.750%, and 9.50 ± 8.960% for CMA, BJE, and UB toxicity tests, respectively. Dissolved oxygen readings obtained during the definitive UB test were not reported due to the dissolved oxygen meter malfunctioning during the course of the experiment. Average dissolved oxygen from the preliminary range finding test with UB was 6.35 ± 1.651 mg/L, suggesting the presence of UB in the water did not significantly affect the dissolved oxygen. As average control mortality was <20% for the UB test and lower than that reported for either the CMA or BJE tests, the data were retained despite unclear dissolved oxygen measurements. Furthermore, the reported LC₅₀ (Table 1) was similar to that obtained from preliminary testing data (0.194 g/L (0.102–0.306 g/L); 95% Confidence Interval (CI)), such that the data from the definitive test was deemed acceptable despite the malfunctioning probe.

Table 1

Ten-day lethal concentration 50s (LC₅₀s) for calcium magnesium acetate (CMA) enhanced de-icing formulation, beet juice extract (BJE) enhanced de-icing formulation, and urea-based de-icing formulation (UB) for *Chironomus dilutus*, including LC₅₀s for traditional road de-icing salt (NaCl) included with each toxicity test of eco-friendly de-icers to allow for direct comparison of toxicity. Values in parenthesis represent 95% confidence intervals (n = 25).

	LC ₅₀ (g/L)		
NaCl ^a	6.29 (5.740–6.908)	6.11 (5.057–7.740)	6.44 (6.101–6.795)
CMA	6.61 (5.720–7.876)	–	–
BJE	–	6.32 (5.574–7.233)	–
UB	–	–	0.63 (0.247–1.25)

^a NaCl was included with each toxicity test evaluating the effects of CMA, BJE, and UB on *C. dilutus*, such that the resulting LC₅₀s of NaCl from these individual tests are reported for direct comparison to “eco-friendly” blends.

3.2. Toxicity of enhanced de-icing formulations

Toxicity of NaCl was consistent over the duration of the testing period, as evidenced by the 10 d LC₅₀ values (Table 1). Toxicity of both the CMA and BJE formulations were comparable to each other as well as the NaCl formulation, with LC₅₀ values that were not different as evidenced by overlapping 95% confidence intervals (Table 1, Fig. 1). As the exact amounts of each chemical included in the formulations is proprietary, it is not possible to definitively interpret how much of the toxicity of these formulations was attributed solely to the chloride ions, as opposed to other chemicals which may have been present (i.e. anticaking agents, CMA, beet juice). Previous research evaluating the toxicity of chloride ions to *C. dilutus*, however, revealed the 96 h LC₅₀ to be 5.87 g/L Cl⁻ (5.452–6.313 g/L Cl⁻; ± 2 standard deviations) (Elphick et al., 2011), which may suggest the toxicity of these three formulations was due primarily to chloride ions. Considering the differences in the duration of the toxicity tests used in these two studies, direct comparisons of the LC₅₀ values is difficult (Elphick et al., 2011, Table 1). Our objective, however, was to compare eco-friendly de-icing formulations to traditional formulations. As the toxicity of both the CMA and BJE blends were similar to that of NaCl, these results suggest a similar chloride content within both the NaCl and CMA/BJE formulations. Therefore, the eco-friendly formulations offer little in the way of environmental protection when considering aquatic invertebrates likely to exist in areas receiving high amounts of de-icing runoff. Furthermore, in comparison to other aquatic invertebrates and amphibians, *C. dilutus* demonstrate rather high tolerance for chloride pollution, such that the effects of these eco-friendly formulations on other aquatic species may be quite pronounced (Benbow and Merritt, 2004; Sanzo and Hecnar, 2006; Collins and Russell, 2009; Elphick et al., 2011). In comparison to traditional road salt formulations, both CMA and BJE did not offer any advantage in terms of reducing toxicity to *C. dilutus* during the 10-d toxicity tests, such that it is unclear what is meant by the eco-friendly labels on these products (Table 1, Fig. 1). This conclusion was further strengthened after comparing the toxicity of the UB formulation to that of NaCl.

3.3. Toxicity of urea de-icing formulation

Toxicity of UB was an order of magnitude greater to *C. dilutus* than NaCl (Table 1, Fig. 1). Urea is a naturally produced waste product that demonstrates relatively low toxicity in aquatic systems (Harless et al., 2011). In aquatic conditions, however, urea hydrolyzes to form ammonia, which is significantly more toxic to aquatic life (Turnbull and Bevan, 1995; Koryak et al., 1998). The rate of this conversion is dependent on temperature, time, and microbial population density (Evans et al., 1973; Turnbull and Bevan,

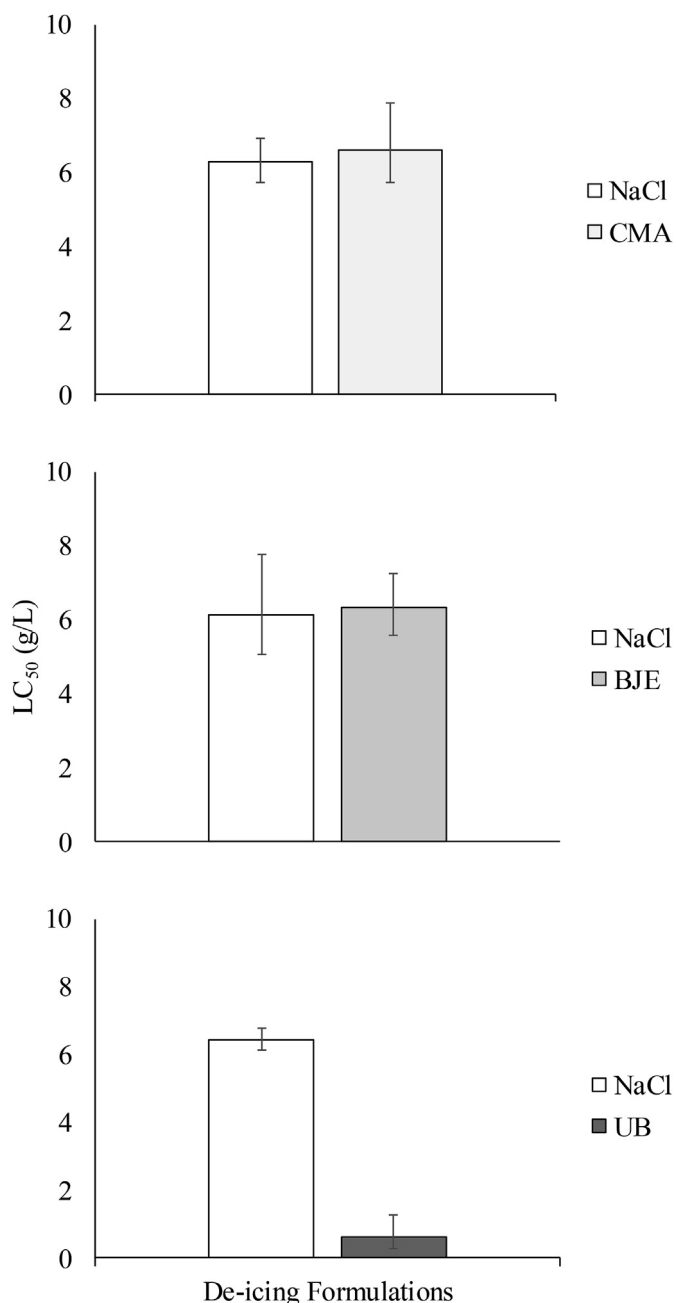


Fig. 1. Lethal concentration 50 (LC₅₀) benchmarks determined for traditional road salt (NaCl), calcium magnesium acetate enhanced formulation (CMA), beet juice enhanced formulation (BJE), and urea-based formulation (UB). Toxicity tests with the traditional road salt formulation were conducted with each “eco-friendly” formulation to allow for direct comparison of LC₅₀s. Error bars represent 95% confidence intervals (n = 25).

1995). Previous research evaluating the ecosystem health of tributaries in close proximity to airports—where urea is commonly used as a de-icing agent—found that spikes in urea coincided with rain or snowmelt events, suggesting that urea is capable of moving across terrestrial landscapes to fresh waters (Turnbull and Bevan, 1995; Koryak et al., 1998). In fact, ammonia concentrations due to urea contamination reached 53.5 mg/L in a Pennsylvania stream in close proximity to the Pittsburgh International Airport during the winter months of 1995–1996 (Koryak et al., 1998). This accumulation of urea, and thus ammonia, in the waterways was deemed responsible for severe degradation of invertebrate communities

downstream of the pollution sources (Koryak et al., 1998). Similarly, significant toxicity associated with urea contamination to *Gammarus pulex* housed within the receiving stream did not occur until approximately 8 d after the spike in urea (Turnbull and Bevan, 1995); this is consistent with the observations made about urea toxicity to *C. dilutus* in our study. *Chironomus dilutus* recovered at the end of the 10 d test from UB test chambers appeared to have reached the 4th instar over the course of the test and retained the vibrant red color associated with this species. Yet, the recovered individuals were clearly dead, suggesting mortality had occurred shortly before the conclusion of the test (personal observation). As the substrate used in the tests was autoclaved prior to its addition to exposure chambers, the delayed toxicity may be associated with the slow hydrolysis of urea to ammonia due to i) the establishment of a thermodynamic equilibrium in the water, or ii) a reestablished microbial community within the experimental chambers (Evans et al., 1973).

In a worst-case scenario (i.e. high water temperatures and aeration), urea would be expected to hydrolyze to ammonia at a daily rate of 3–6% of the original urea concentration in the water (Evans et al., 1973). Assuming the UB de-icer used in our study was composed of 100% urea, and that the hydrolysis rate of the original urea concentration was 6% per day, the highest rate estimated to occur in natural systems (Evans et al., 1973), the calculated ammonia LC₅₀ for *C. dilutus* based on the mass of UB de-icer used in the test would equal 0.378 g/L. *Chironomus dilutus* exposed to ammonia for 10 d demonstrated LC₅₀s of 6.60–390 mg/L total ammonia, depending on pH (Schubauer-Berigan et al., 1996). These LC₅₀s are significantly lower than that calculated for *C. dilutus* based on data from our study using the nominal UB concentration (Table 1, Fig. 1). However, using the hydrolysis rate of 6% estimated by Evans et al. (1973), and transforming the LC₅₀ based on the UB concentration to ammonia, the estimated ammonia LC₅₀ of our study (0.378 g/L) is similar to previous research (0.390 g/L) (Schubauer-Berigan et al., 1996). This may suggest that a majority of the toxicity associated with the UB formulation is due to the conversion of urea to ammonia.

Ammonia toxicity to aquatic invertebrates is interesting in that LC₅₀ values, at least for some species, are dependent upon pH and how the ammonia concentration is represented (Ankley et al., 1995; Schubauer-Berigan et al., 1996). Ammonia toxicity to *C. dilutus*, when expressed as total ammonia, demonstrated a marked increase in LC₅₀s with increasing pH; however, when represented as un-ionized ammonia, increases in pH resulted in a decrease in LC₅₀s (Schubauer-Berigan et al., 1996). The same trend holds true for the aquatic oligochaete, *Lumbriculus variegatus*, except that the effect of pH was more pronounced for this species (Schubauer-Berigan et al., 1996). Acute toxicity tests evaluating the effects of total ammonia on the amphipod, *Hyalella azteca*, demonstrated relative consistency in LC₅₀s over a range of two pH units, yet when LC₅₀s were expressed as un-ionized ammonia, lethal concentrations varied by over 50-fold across the same pH range (Ankley et al., 1995). Therefore, the role of the ionization state of ammonia in water, whether ionized (ammonium ion) or un-ionized (ammonia), in determining toxicity to aquatic invertebrates is species-dependent (Ankley et al., 1995; Schubauer-Berigan et al., 1996). Given the pH range of the water in the current study (7.76–8.76), there was likely a higher concentration of un-ionized ammonia in the water than ionized ammonia, possibly contributing to the elevated LC₅₀ of the UB de-icing blend in comparison to pure ammonia (Table 1) (Ankley et al., 1995; Schubauer-Berigan et al., 1996). Future research investigating the rate of conversion of the UB formulation to ammonia, the influence of microbial communities on this conversion, and the resulting effects on toxicity of urea-based de-icers would aid in determining the role of ammonia in the toxicity

attributed to this de-icing formulation. In comparison to NaCl, however, the UB de-icer offers the most environmentally harmful formulation to *C. dilutus*, and casts serious doubt on the claims and use of eco-friendly labels and green marketing tactics within the context of de-icing formulations. As such, the role of scientists in determining the validity of eco-friendly products and green marketing requires further evaluation if such labeling and claims are to meaningfully influence the perception of consumers.

3.4. Green marketing and environmental scientists

Green marketing was originally conceptualized in the 1970s and then revitalized in the 1990s as a strategy for businesses to adapt to changes in public perception of the environment and the sustainability of business and societal expansion (Peattie and Charter, 2003). With an emphasis on sustainability, green marketing is summarized as a holistic management process that minimizes environmental impacts and pollution of businesses at all levels of production, from manufacturing to product use and disposal (Peattie and Charter, 2003). As understanding the impacts of pollution on the environment is the role of environmental scientists and toxicologists, science is thoroughly integrated with the green marketing process through development and enforcement of regulations, risk assessment and management, and the development of innovative means for controlling and remediating pollution. Despite this integration, it appears, at least based on our results, that there is a lack in understanding between these two groups about what constitutes the “environment,” and therefore, what should be deemed eco-friendly.

The three brands of de-icing formulation we tested, MELT Enviro-Blend (CMA), MELT Beet-IT (BJE), and Safe Paw (UB), all claim on the packaging to be “eco-friendly.” While it is not clear what is meant by this specifically, a consumer may reasonably conclude that this claim should extend past the “environment” of an urban landscape (e.g., lawns, flowerbeds, and landscaping), and include surrounding wild areas, such as aquatic environments. This is not the case, however, as all three of the eco-friendly formulations demonstrated equal or increased toxicity to *C. dilutus* in comparison to NaCl (Table 1, Fig. 1). Possibly the eco-friendly labeling referred to an increased efficacy as an ice-melter, such that less product would be needed to achieve the same level of traffic safety. This does not appear to be the case, however, as the effective temperatures of the NaCl, CMA, BJE, and UB formulations are -26°C , -22°C , -20°C , and -2°C , respectively. As such, equal or more of these formulations would need to be applied to achieve the same level of de-icing, suggesting increased toxicity to *C. dilutus* may be expected based on the use of these products. Perhaps, then, these claims are focused on protecting more charismatic aquatic species, such as fish, reptiles, and amphibians. While this is likely untrue for the chloride-based de-icers (Williams et al., 1999; Benbow and Merritt, 2004; Sanzo and Hecnar, 2006; Karraker, 2007; Collins and Russell, 2009; Denoël et al., 2010; Gardner and Royer, 2010; Elphick et al., 2011; Hintz et al., 2017; Hintz and Relyea, 2017; Jones et al., 2017; Schuler et al., 2017; Schuler and Relyea, 2018a,b), for urea-based formulations these claims may hold value as at least some vertebrate species are relatively unaffected by urea contamination (Harless et al., 2011). Danger lies in this line of thinking, however. As discussed above, in aquatic environments, urea converts rather rapidly to ammonia (Evans et al., 1973), which is harmful to not only aquatic invertebrates, but many vertebrate species as well (Ankley et al., 1995; Schubauer-Berigan et al., 1996; Turnbull and Bevan, 1995; Ellis et al., 1997; Koryak et al., 1998; Randall and Tsui, 2002). Furthermore, basing eco-friendly labeling on protecting only large, enigmatic vertebrate species threatens to doom wild places faster than failing to

incorporate eco-labeling into the manufacturing and marketing of these products. *Chironomus dilutus* are representative of the more tolerant end of the spectrum in considerations of pollution by chloride salt and urea de-icers (Schubauer-Berigan et al., 1996; Benbow and Merritt, 2004; Sanzo and Hecnar, 2006; Collins and Russell, 2009; Elphick et al., 2011), such that it is likely these eco-friendly blends will have an even more significant impact on other members of aquatic ecosystems than the effects reported here (Table 1, Fig. 1). With loss of aquatic invertebrates from waterways comes significant changes in food webs, energy transfer, and nutrient cycling (Hintz et al., 2017; Jones et al., 2017; Schuler and Relyea, 2018b). Indeed, the worldwide distribution of Chironomidae means members of this invertebrate family help form the basis of food webs in a large diversity of habitats (Tokeshi, 1995). Eco-labeling that is protective of only species that catch the attention and adoration of the public eye fails to capture the real threat posed by failure to balance economic and societal growth with environment consciousness and protection.

This study, and the literature that precedes it, highlight the importance of our role as scientists in defining appropriate criteria for the designation of eco-friendly product labeling. Unclear or false claims of eco-friendly products not only undermine the advancement of production of green products and marketing, but also pose greater long-term risks to the environment due to the illusion of environmental protection. In order for green marketing to truly serve as a holistic approach to reducing the environmental footprint of businesses, there needs to be 1) greater transparency regarding the composition of eco-friendly formulations and consumer expectations, 2) improved communication/collaboration between businesses and the scientific community, and 3) defined regulations and guidelines for eco-labeling.

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References

- Ankley, G.T., Schubauer-Berigan, M.K., Monson, P.D., 1995. Influence of pH and hardness on toxicity of ammonia to the amphipod *Hyaella azteca*. *Can. J. Fish. Aquat. Sci.* 52, 2078–2083.
- ASTM Standard E1706-05, 1995 (2010), 2010. Standards Test Method for Measuring the Toxicity of Sediment-associated Contaminants with Freshwater Invertebrates. ASTM International, West Conshohocken, PA. <https://doi.org/10.1520/E1706-05R10>.
- Benbow, M.E., Merritt, R.W., 2004. Road-salt toxicity of select Michigan wetland macroinvertebrates under different testing conditions. *Wetlands* 24 (1), 68–76.
- Blasius, B.J., Merritt, R.W., 2002. Field and laboratory investigations on the effects of road salt (NaCl) on stream macroinvertebrate communities. *Environ. Pollut.* 120, 219–231.
- Coldsnow, K.D., Relyea, R.A., 2018. Toxicity of various road-deicing salts to Asian clams (*Corbicula fluminea*). *Environ. Toxicol. Chem.* 37 (7), 1839–1845.
- Collins, S.J., Russell, R.W., 2009. Toxicity of road salt to Nova Scotia amphibians. *Environ. Pollut.* 157, 320–324.
- Corsi, S.R., Graczyk, D.J., Geis, S.W., Booth, N.L., Richards, K.D., 2010. A fresh look at road salt: aquatic toxicity and water-quality impacts on local, regional, and national scales. *Environ. Sci. Technol.* 44, 7376–7382.
- Cumming, G., Fidler, F., Vaux, D.L., 2007. Error bars in experimental biology. *JCB (J. Cell Biol.)* 177 (1), 7–11.
- Denoël, M., Bichot, M., Ficetola, G.F., Delcourt, J., Yliff, M., Kestemont, P., Poncin, P.,

2010. Cumulative effects of road de-icing salt on amphibian behavior. *Aquat. Toxicol.* 99, 275–280.
- Ellis, J.B., Revitt, D.M., Llewellyn, N., 1997. Transport and the Environment: effects of organic pollutants on water quality. *Water Environ. J.* 11 (3), 170–177.
- Elphick, J.R.F., Bergh, K.D., Bailey, H.C., 2011. Chronic toxicity of chloride to freshwater species: effects of hardness and implications for water quality guidelines. *Environ. Toxicol. Chem.* 30 (1), 239–246.
- Evans, W.H., David, E.J., Patterson, S.J., 1973. Biodegradation of urea in river waters under controlled laboratory conditions. *Water Res.* 7, 975–985.
- Findlay, S.E.G., Kelly, V.R., 2011. Emerging indirect and long-term road salt effects on ecosystems. *Ann. N. Y. Acad. Sci.* 1223, 58–68.
- Gardner, K.M., Royer, T.V., 2010. Effect of road salt application on seasonal chloride concentrations and toxicity in south-central Indiana streams. *J. Environ. Qual.* 39, 1036–1042.
- Griffith, M.B., 2017. Toxicological perspective on the osmoregulation and ionoregulation physiology of major ions by freshwater animals: teleost fish, Crustacea, aquatic insects, and Mollusca. *Environ. Toxicol. Chem.* 36 (3), 576–600.
- Harless, M.L., Huckins, C.J., Grant, J.B., Pypker, T.G., 2011. Effects of six chemical deicers on larval wood frogs (*Rana sylvatica*). *Environ. Toxicol. Chem.* 30 (7), 1637–1641.
- Hintz, W.D., Mattes, B.M., Schuler, M.S., Jones, D.K., Stoler, A.B., Lind, L., Relyea, R.A., 2017. Salinization triggers a trophic cascade in experimental freshwater communities with varying food-chain length. *Ecol. Appl.* 27 (3), 833–844.
- Hintz, W.D., Relyea, R.A., 2017. Impacts of road deicing salts on the early-life growth and development of a stream salmonid: salt type matters. *Environ. Pollut.* 223, 409–415.
- Jones, D.K., Mattes, B.M., Hintz, W.D., Schuler, M.S., Stoler, A.B., Lind, L.A., Cooper, R.O., Relyea, R.A., 2017. Investigation of road salts and biotic stressors on freshwater wetland communities. *Environ. Pollut.* 221, 159–167.
- Karraker, N.E., 2007. Are embryonic and larval green frogs (*Rana clamitans*) insensitive to road deicing salt? *Herpetol. Conserv. Biol.* 2 (1), 35–41.
- Kelly, V.R., Lovett, G.M., Weathers, K.C., Findlay, S.E.G., Strayer, D.L., Burns, D.J., Likens, G.E., 2008. Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. *Environ. Sci. Technol.* 42, 410–415.
- Koryak, M., Stafford, L.J., Reilly, R.J., Hoskin, R.H., Haberman, M.H., 1998. The impact of airport deicing runoff on water quality and aquatic life in a Pennsylvania stream. *J. Freshw. Ecol.* 13 (3), 287–298.
- Lob, D.W., Silver, P., 2012. Effects of elevated salinity from road deicers on *Chironomus riparius* at environmentally realistic springtime temperatures. *Freshw. Sci.* 31 (4), 1078–1087.
- Mason, C.F., Norton, S.A., Fernandez, I.J., Katz, L.E., 1999. Deconstruction of the chemical effects of road salt on stream water chemistry. *J. Environ. Qual.* 28 (1), 82–91.
- Novotny, E.V., Murphy, D., Stefan, H.G., 2008. Increase of urban lake salinity by road deicing salt. *Sci. Total Environ.* 406, 131–144.
- Peattie, K., Charter, M., 2003. Green marketing. In: Baker, M.J. (Ed.), *The Marketing Book*, fifth ed. Butterworth-Heinemann, Burlington, Massachusetts, pp. 726–756.
- Ramakrishna, D.M., Viraraghavan, T., 2005. Environmental impact of chemical deicers: a review. *Water Air Soil Pollut.* 166, 49–63.
- Randall, D.J., Tsui, T.K.N., 2002. Ammonia toxicity in fish. *Mar. Pollut. Bull.* 45, 17–23.
- Robidoux, P.Y., Delisle, C.E., 2001. Ecotoxicological evaluation of three deicers (NaCl, NaFo, CMA): effect on terrestrial organisms. *Ecotoxicol. Environ. Saf.* 48, 128–139.
- Sanzo, D., Hecnar, S.J., 2006. Effects of road de-icing salt (NaCl) on larval wood frogs (*Rana sylvatica*). *Environ. Pollut.* 140, 247–256.
- Schubauer-Berigan, M.K., Monson, P.D., West, C.W., Ankley, G.T., 1996. Influence of pH on the toxicity of ammonia to *Chironomus tentans* and *Lumbriculus variegatus*. *Environ. Toxicol. Chem.* 14 (4), 713–717.
- Schuler, M.S., Hintz, W.D., Jones, D.K., Lind, L.A., Mattes, B.M., Stoler, A.B., Sudol, K.A., Relyea, R.A., 2017. How common road salts and organic additives alter food webs: in search of safer alternatives. *J. Appl. Ecol.* 54, 1353–1361.
- Schuler, M.S., Relyea, R.A., 2018a. A review of the combined threats of road salts and heavy metals to freshwater systems. *Bioscience* 68 (5), 327–335.
- Schuler, M.S., Relyea, R.A., 2018b. Road salt and organic additives affect mosquito growth and survival: an emerging problem in wetlands. *Oikos* 127 (6), 866–874.
- Silver, P., Rupprecht, S.M., Stauffer, M.F., 2009. Temperature-dependent effects on road deicing salt on chironomid larvae. *Wetlands* 29 (3), 942–951.
- Smith, M.E., Lazorchak, J.M., Herrin, L.E., Brewer-Swartz, S., Thoeny, W.T., 1997. A reformulated, reconstituted water for testing the freshwater amphipod, *Hyalella azteca*. *Environ. Toxicol. Chem.* 16 (6), 1229–1233.
- Soucek, D.J., Kennedy, A.J., 2005. Effects of hardness, chloride, and acclimation on the acute toxicity of sulfate to freshwater invertebrates. *Environ. Toxicol. Chem.* 24 (5), 1204–1210.
- Soucek, D.J., Mount, D.R., Dickinson, A., Hockett, J.R., McEwen, A.R., 2015. Contrasting effects of chloride on growth, reproduction, and toxicant sensitivity in two genetically distinct strains of *Hyalella azteca*. *Environ. Toxicol. Chem.* 34 (10), 2354–2362.
- Tokeshi, M., 1995. Species interactions and community structure. In: Armitage, P., Cranston, P.S., Pinder, L.C.V. (Eds.), *The Chironomidae: the Biology and Ecology of Non-biting Midges*, first ed. Chapman & Hall, London, pp. 297–331.
- Trombulak, S.C., Frissell, C.A., 2000. Review of ecological effects of roads on terrestrial and aquatic communities. *Conserv. Biol.* 14 (1), 18–30.
- Turnbull, D.A., Bevan, J.R., 1995. The impact of airport de-icing on a river: the case of the Ouseburn, Newcastle upon Tyne. *Environ. Pollut.* 88, 321–332.
- Williams, D.D., Williams, N.E., Cao, Y., 1999. Road salt contamination of groundwater in a major metropolitan area and development of a biological index to monitor its impact. *Water Res.* 34 (1), 127–138.