Ice formation and the risk of chloride toxicity in shallow wetlands and lakes

Hilary A. Dugan 1,* Greta Helmueller, 1,2 John J. Magnuson 1

1Center for Limnology, University of Wisconsin – Madison, Madison, Wisconsin; 2University of South Florida, College of Marine Science, St. Petersburg, Florida

Abstract

The process of ice formation in shallow waterbodies can increase chloride to toxic levels in waterbodies already impacted by chloride loading from road salt (NaCl deicer) application. Chloride concentrations were measured bi-weekly in a shallow, urban wetland in Madison, Wisconsin. We found that in this shallow waterbody, ice thickening doubled chloride concentrations from ion exclusion as the water froze. To understand the role of ice formation and ion exclusion, we constructed a numerical model to predict chloride concentrations beneath the ice resulting from ion exclusion. Where chloride levels already are elevated above background and flushing rates are low, ice thickening can push concentrations well above toxicity thresholds for much of the winter. The compounding effects of road salt runoff and ice formation should be considered in the management of water quality and ecosystem health in shallow urban water bodies or waterbodies receiving road salt runoff from nearby roadways.

In north temperate ecosystems, a major threat to freshwater quality is chloride runoff from road salt (specifically sodium chloride, NaCl) application (Findlay and Kelly 2011). Road salt runoff impacts wetlands (Richburg et al. 2001; Hill and Sadowski 2016), streams (Thunqvist 2004; Kaushal et al. 2005; Corsi et al. 2010), lakes (Novotny et al. 2008; Chapra et al. 2009; Dugan et al. 2017), and groundwater (Williams et al. 2000; Panno et al. 2006), and affects most lakes surrounded by impervious surfaces in areas of the U.S. Midwest and Northeast (Dugan et al. 2017).

Long-term increases in chloride concentrations in lakes has been shown across North America (Dugan et al. 2017), but these long-term trends are found in deeper lakes with medium to long residence times. The residence time of a lake is considered the mean time water or a dissolved substance (like chloride) spends in the lake before being flushed.
out. Longer residence times allow chloride concentrations to build up in a lake. For example, Lake Mendota in Madison, Wisconsin, has a mean depth of 12.8 m and a residence time of 4 yr. Chloride concentrations have risen from background levels of <3 mg L⁻¹ in 1940 to 50 mg L⁻¹ in 2016 (Fig. 1) (Center for Limnology; NTL LTER 2012). In recent years, this equates to an increase of over 700 tons of chloride per year in Lake Mendota. Streams and shallow lakes may not experience long term increases in chloride concentrations owing to the short residence time of the system, but they are much more susceptible than larger lakes to rapid increases (and decreases) in chloride concentrations and the influence of chloride contaminated groundwater (Panno et al. 1999; Williams et al. 2000; Marsalek 2003). Shallow wetlands and lakes may be more vulnerable to disturbances, akin to river systems, than lake systems with longer water residence times (Resh et al. 1988).

Elevated chloride levels in wetlands and lakes can harm biological function (Corsi et al. 2010; Van Meter and Swan 2014; Hintz et al. 2017), and lead to decreased survival and impaired reproduction in a range of aquatic species and inhibition of plant growth (EPA 1988). We have used 230 mg L⁻¹ as a conservative concentration below which there is likely to be relatively low chloride toxicity based on published criteria by the U.S. Environmental Protection Agency (EPA) and the Wisconsin Department of Natural Resources (WI DNR). The chronic and acute chloride criteria are set at 230 mg L⁻¹ and 860 mg L⁻¹ by the EPA (EPA 1988), and 395 mg L⁻¹ and 757 mg L⁻¹ by the WI DNR (Wisconsin DNR 2008). The “chronic” threshold is defined as the concentration that should not be exceeded by a 4-d average chloride concentration more than once every 3 yr. The “acute” threshold should not be exceeded by a 1-h average concentration more than once every 3 yr (EPA 1988). These criteria are recommended guidelines, and, in reality, specific aquatic plants and animals display a range of tolerances to chloride loading.

In northern climates, waterbodies (including lakes, ponds, and wetlands) are susceptible to high chloride loading from anthropogenic road salt runoff. In shallow waterbodies, this loading can be exacerbated by chloride exclusion during ice cover thickening. When water begins to crystallize into ice, dissolved ions are rejected into the surrounding water, and not incorporated into the ice lattice (Notz and Worster 2009). We hypothesize that ice cover formation in shallow water bodies with high chloride concentrations from anthropogenic inputs can raise chloride levels to toxic levels during winter. In cold climates, ice formation can freeze half the volume of a shallow waterbody, thereby potentially doubling ion concentrations. The process of ion exclusion from freshwater ice has only been documented in a few lakes (see Table 1).

**Table 1.** Ion and solute exclusion rates from lake ice.

| Site     | Solute | Exclusion rate (%) | Citation          |
|----------|--------|--------------------|-------------------|
| Wisconsin| Chloride| 60, 89, 99         | This study        |
| Laboratory| Conductivity| 95          | Bluteau et al. (2017) |
| Canada   | Conductivity| 87–99         | Pieters and Lawrence (2009) |
| Canada   | Conductivity| 80–97*         | She et al. (2016) |
| China    | TDS     | 80                | Zhang et al. (2012) |
| Canada   | Ions    | 63–99†           | Belzile et al. (2002) |
| Canada   | CDOM    | 29–99†           | Belzile et al. (2002) |

* Calculated from pond and ice core concentrations.
† Converted from exclusion factor (ef: water column concentration : ice cover concentration) by 1–(1/ef). Biased rates, as pre-ice water concentrations are unknown.
Here we focus on the role of ice formation and thickening in elevating chloride levels in a shallow, open-water marsh already impacted by road salt runoff in Madison, Wisconsin. We use observational data and a numerical model to assess changes in chloride concentration based on chloride exclusion and dilution from changes in ice thickness.

Research site

The Class of 1918 Marsh is part of the Lakeshore Nature Preserve on the campus of the University of Wisconsin - Madison (Fig. 1). Surface water sources include runoff from parking lots, building roofs, sidewalks, a large area of undeveloped playing fields, and a snow storage pile for snow removed from campus streets, sidewalks, and parking lots (Fig. 1). Water plumbed from the roof of the hospital was added to the south-inlet storm sewer to dilute contaminants in the runoff from streets and parking lots. Presently the outlet waters are pumped into a storm sewer that passes under University Bay Drive and enters Lake Mendota’s University Bay. Shallow groundwater likely contributes some inflow; however, both shallow ground- and surface water flows are reduced significantly owing to freezing conditions during the winter. The marsh in 2015 had a total area including the cattails of \( \sim 74,000 \text{ m}^2 \), and open water area of 23,400 m². On 12 Dec 2012, water depths at 18 locations across the open water averaged 0.2 m and ranged from 0.1 m to 0.44 m.

Methods

Routine sampling sites (Fig. 1) included the south-inlet storm sewer (South Bridge) and three open water locations (South Marsh, Mid Marsh, and North Marsh). Water flows from South Marsh, to Mid Marsh, to North Marsh and eventually into Lake Mendota. Sampling was conducted every 2 weeks from Nov 2014 through the summer of 2015. Samples could not be obtained on 14 March 2015 because ice conditions were too dangerous for access. In 2014–2015, total winter precipitation (Dec–Mar) was 50% less than the climatological average (1960–2015) (Lawrimore et al. 2011). All samples were collected at the surface of the marsh. If ice was present, a hole was first drilled with an ice drill or ice chisel (spud) or spud. Water was collected via syringes, ice was present, a hole was first drilled with an ice drill or spud. Water was collected via syringes, and filtered through a 25 mm 0.45 μm GMF filter into plastic scintillation vials in the field. All samples were stored at 4°C and analyzed at the University of Wisconsin’s Center for Limnology on an ion chromatograph (Dionex ICS 2100) using an electro-chemical suppressor. For each sampling event, water temperature, water depth, ice thickness, and snow depth were recorded. Water depth was measured from the water surface to the marsh bottom. Of the three open-water sites, no site was consistently the deepest or shallowest. The full range of water depths was between 0.12 m and 0.65 m; however, we suspect the shallower measurements were prone to error owing to soft bottom sediments and benthic macrophytes as well as by missing the narrow deep site at the South Marsh site. Given missing data and the uncertainty in water depths, we ran the numeric model using individual water depth measurements as well as minimum, mean, median, and maximum water depths across the three sites. Using maximum water depths across the three sites returned the lowest root mean square error (RMSE) in model fit.

Numerical model

We wrote a numerical model to predict the concentration of chloride in 1918 Marsh resulting from ice formation at three sites (South Marsh, Mid Marsh, and North Marsh) using measurements of water depth, ice thickness, and inflowing chloride concentrations. Because we had no flow data, our model does not include outflow. Therefore, it is only applicable for a system with a residence time greater than the model time step, otherwise any ion exclusion from ice cover formation would be flushed quickly downstream. During winter, the assumptions of no outflow and no evaporation/sublimation are acceptable, as freezing temperatures and short days minimize these fluxes.

Thus, we assumed that increased water depth in a two-week period was the result of inflow from the upstream area. The proportion of water depth attributed to inflowing water \( \text{Pinflow} \) was calculated as:

\[
\text{Pinflow} = \frac{\text{water depth}_t - \text{water depth}_{t-1}}{\text{water depth}_t} \tag{1}
\]

The inflow concentration was taken as the mean of the chloride concentration measured at time \( t \) and \( t-1 \). The proportion of the water column beneath the ice attributed to new ice formation \( \Delta \text{Ice} \) was calculated as the change in ice thickness divided by the average water depth:

\[
\Delta \text{Ice} = \frac{0.9 \times (\text{Icethickness}_t - \text{Icethickness}_{t-1})}{0.5 \times (\text{Waterdepth}_t + \text{Waterdepth}_{t-1})} \tag{2}
\]

Ice thickness was converted to water equivalents by multiplying by 0.9, the normal density ratio of freshwater ice to water.

Chloride concentration was calculated differently based on whether ice was thickening or melting:

Ice thickening

Chloride concentration at time \( t \) \( \text{Marsh}[\text{Cl}]_t \) was calculated as the weighted average of two water parcels, (i) new water flowing into the marsh \( \text{Inflow}[\text{Cl}] \times \text{Pinflow} \) and (ii) water already present in the marsh \( (1-\text{Pinflow}) \times \text{Marsh}[\text{Cl}]_{t-1} \). The concentration of the latter increases from additional chloride due to ion exclusion \( [(1-\text{Pinflow}) \times \text{Marsh}[\text{Cl}]_{t-1} \times \Delta \text{Ice} \times \text{Pexc}] \). The new concentration of chloride is divided by \( (1-\Delta \text{Ice}) \) to reflect the smaller volume of water present beneath the ice cover. \( \text{Pexc} \) represents the proportion of ions excluded from the
ice, as some chloride ions are likely trapped between ice crystals. Since \( P_{\text{exc}} \) is not well constrained for freshwater systems, we ran the model 100 times for each site using \( P_{\text{exc}} \)

\[
\frac{\text{Marsh}[\text{Cl}]_t}{(1 - \text{Pinflow})} = \frac{[\text{Marsh}[\text{Cl}]_{t-1} \times (1 - P_{\Delta \text{Ice}})] + [\text{Marsh}[\text{Cl}]_{t-1} \times P_{\Delta \text{Ice}} \times P_{\text{exc}}]}{1 - P_{\Delta \text{Ice}}}
\]

Decreases in water depth were either the result of outflow or evaporation/sublimation, and were not taken into account in our model. Therefore, when Pinflow = 0, and Eq. 3 is simplified to:

\[
\frac{\text{Marsh}[\text{Cl}]_t}{1 - P_{\Delta \text{Ice}}} = [\text{Marsh}[\text{Cl}]_{t-1} \times (1 - P_{\Delta \text{Ice}})] + [\text{Marsh}[\text{Cl}]_{t-1} \times P_{\Delta \text{Ice}} \times P_{\text{exc}}]
\]

**Ice melt**

When ice melt leads to a decrease in ice thickness, \( P_{\Delta \text{Ice}} \) is negative. \( \text{Marsh}[\text{Cl}]_t \) is the weighted average of inflowing water, water already present, and ice melt:

\[
\frac{\text{Marsh}[\text{Cl}]_t}{(1 - \text{Pinflow})} = \frac{[\text{Marsh}[\text{Cl}]_{t-1} \times (1 + P_{\Delta \text{Ice}})]}{1 - P_{\Delta \text{Ice}}}
\]

When Pinflow = 0, and Eq. 5 is simplified to

\[
\frac{\text{Marsh}[\text{Cl}]_t}{1 - P_{\Delta \text{Ice}}} = [\text{Marsh}[\text{Cl}]_{t-1} \times (1 + P_{\Delta \text{Ice}})] + [\text{Marsh}[\text{Cl}]_{t-1} \times -P_{\Delta \text{Ice}} \times (1 - P_{\text{exc}})]
\]

The assumptions of this model, includes:

- A constant ion exclusion rate from ice cover thickening.
- The chloride concentration in the water remains the same during the time step.
- Surface and groundwater discharge over the time step is negligible.

For the 1918 Marsh, we ran the model at two-week time steps based on the availability of observational data. The inflow chloride concentrations (\( \text{Marsh}[\text{Cl}]_{t-1} \)) to South Marsh were taken from the South Bridge sampling site. South Marsh was then considered the inflow to the Mid Marsh site, and likewise Mid Marsh was taken as the inflow to the North Marsh. Observation data were used for initial chloride concentrations (\( \text{Marsh}[\text{Cl}]_{t-1} \)).

Alternatively, the model can be run independently for each time step, by using observational data for \( \text{Marsh}[\text{Cl}]_{t-1} \) at each time step (as opposed to only setting initial conditions) and allowing the exclusion rate to change. At each time step, \( P_{\text{exc}} \) was chosen as the lowest calculated RMSE.

**Results**

Chloride concentrations in the 1918 Marsh increased from \( \sim \) 240 mg L\(^{-1} \) on 26 Oct 2014 to a maximum of 1250 mg L\(^{-1} \) on 1 March 2015. Following ice melt, concentrations in the marsh decreased and declined slowly from April to December, 2015 (Fig. 2a,b, Helmueller et al. pers. comm.). Overall, the mean concentration at the three open-water sites of 307 mg L\(^{-1} \) is approximately 6 times higher than the 2015 concentration of neighboring Lake Mendota, and 100 times above likely background concentrations (< 3 mg L\(^{-1} \)) based on early Lake Mendota values (Fig. 1b).

Chloride concentrations were similar at all open-water sites, except for 1 Mar 2015 when concentrations at North Marsh spiked to 1251 mg L\(^{-1} \), compared to 894 mg L\(^{-1} \) at Mid Marsh, and 619 mg L\(^{-1} \) at South Marsh (Fig. 2a). Maximum chloride concentrations coincided with the maximum ice thickness (0.41 m) recorded on the marsh on 1 Mar 2015. At all open-water sites (South-, Mid-, and North Marsh), the change in chloride over a 2-week time step was correlated positively with the change in ice thickness ($r^2 = 0.69$, Supporting Information Fig. S1).

The model simulations of the 1918 Marsh were run from 26 Oct 2014 to 11 Apr 2015. The best model fits (lowest RMSE) at South-, Mid-, and North Marsh, were for exclusion rates of 60% (RMSE = 47, bias = 4%), 89% (RMSE = 97, bias = −9%), and 99% (RMSE = 179, bias = −16%) (Fig. 3). When using ion exclusion rates greater than 60%, the resulting water concentrations were markedly higher than those using an ion exclusion rate of 0% (Fig. 3) and were similar in magnitude and patterns to measured chloride over the ice cover period. The numerical model slightly underestimated chloride concentrations at the Mid- and North Marsh, and overestimated chloride during the winter at the South Marsh site (Fig. 3). Model fits were compared to observational data by calculating the RMSE of residuals. Because the model only considers the observational chloride concentration at the first time-step, the predictions are not “reset” following a poor estimate. Specifically looking at the South Marsh site, when \( P_{\text{exc}} > 0.6 \), the model overestimates chloride on 7
Dec and all subsequent predictions are too high. However, the predictions match the pattern among dates. The model predictions were more precise for the Mid- and North Marsh sites, but at no time did the model predict chloride concentrations above 750 mg L$^{-1}$, less than the maximum recorded concentration of 1251 mg L$^{-1}$.

**Fig. 2.** (a) Chloride concentrations in South-(circles), Mid-(squares), and North Marsh (triangles) from Oct 2014 to May 2015. The gray timeseries represents the range in daily air temperature. (b) Symbols denote the measured ice thickness at the three sites. The lines and shaded area represent the seasonal ice thickness.

**Fig. 3.** (a) Chloride concentrations at South Bridge inlet. (b–d) Chloride concentrations at South-, Mid-, and North Marsh from late Oct 2014 to May 2015. Droplines are provided to show sampling dates. Black squares denote observed values while gray circles/line represent modeled chloride concentrations given 0% ion exclusion ($P_{exc} = 0\%$) during ice thickening. The yellow area represents the range in modeled chloride concentrations given rejection rates between 60% and 100%. Red circles/lines represent the best model fit (lowest RMSE). Dashed horizontal lines denote the WI DNR’s acute (757 mg L$^{-1}$) and chronic (395 mg L$^{-1}$) chloride water quality criterion, and the EPA’s chronic water criteria (230 mg L$^{-1}$). Ice thickness is represented by a gray polygon (not to scale).
The model was also run independently for each time step, by using observational data for \textit{Marsh}Cl\textsubscript{t-1} at each time step and allowing the exclusion rate to change. This method improved the overall model fits at Mid Marsh (RMSE = 76), and North Marsh (RMSE = 176), but provided a poorer fit at South Marsh (RMSE = 53) (Supporting Information Fig. S2).

**Discussion**

At all three sites in the Marsh, chloride concentrations rose above the chronic chloride water quality criterion of both the EPA (230 mg L\textsuperscript{-1}) and the WIDNR (395 mg L\textsuperscript{-1}) during the winter months. Following ice melt, concentrations dropped back below 395 mg L\textsuperscript{-1} (Fig. 3). The seasonal variability in chloride concentrations in the 1918 Marsh was as high as 1000 mg L\textsuperscript{-1} at North Marsh. Large seasonal fluctuations, comparable to those seen in the 1918 Marsh, are more expected in small, shallow water bodies, than deeper lakes, such as Lake Mendota, where extreme salt loading is buffered by the large volume of water. When considering the health of the aquatic ecosystem, these large pulses of salt are a concern (Herbert et al. 2015), even though the summertime concentrations may be below water quality thresholds.

The simple ice formation model is a reasonably good predictor of observed chloride concentrations in the 1918 Marsh. The model fit was enhanced by the dry winter conditions of 2014–2015, which increased water residence time in the marsh. Because the model does not account for lateral flow, any overestimates, such as those on 7 Dec 2014, are likely explained by flushing events. In this instance, there was 9 cm of new snow from Nov 25 to Nov 29, followed by air temperatures above 0°C. Dilute snow melt run-off into the Marsh would have diluted and flushed more concentrated water beneath the ice. Following 7th Dec, air temperatures remained below 0°C, and model fit improved. Thus, we speculate that lateral flow over the winter was minimal. We also speculate that the model predictions at Mid and North Marsh were less than observational data, including the 1250 mg L\textsuperscript{-1} concentration at North Marsh, owing to highly saline runoff from an adjacent snow storage site (Fig. 1). The snow pile, which is contaminated with road salt from snow removed from streets and parking lots on the University of Wisconsin campus, drains toward the north end of the marsh (Helmüller et al. pers. comm.).

Our ability to numerically model changes in chloride beneath the ice of 1918 Marsh was limited by the bi-weekly sampling of ice thickness and water depth. Given that the air temperature exceeded 0°C throughout November and December, it is likely our sampling missed sporadic freeze and thaw events. This is evident in our 2-week simulations inability to consistently predict the change in chloride over a single time step (Supporting Information Fig. S2). At the South Marsh site, our model predicted chloride with a < 1% error at 4 of 10 time points. Conversely, the error was > 10% for three of the time steps. Model predictions would be improved by better knowledge of water depth, ice thickness, and flow; all of which could be measured at a higher frequency using field deployable sensor technology.

Our model suggests that chloride exclusion rates in 1918 Marsh are likely between 0.6 and 1.0 (complete rejection), but is unable to narrowly constrain these rates given the paucity of observational data. Other field and lab studies of ion rejection in freshwater ice during freezing are rare (Table 1). Furthermore, the rate of ion exclusion in freshwaters likely changes with the rate of freezing and the temperature profile of the ice cover, as it does in seawater (Notz and Worster 2009).

The numeric model demonstrates that chloride concentrations in the marsh are approximately double the theoretical concentration given no ion rejection (Fig. 3). In the 1918 Marsh, this raises chloride levels from ~ 250–400 mg L\textsuperscript{-1} to upward of 800 mg L\textsuperscript{-1}, even with ion exclusion as low as 60%. This doubling of chloride, pushes the 1918 Marsh concentrations to the WI DNR’s acute toxicity threshold of 757 mg L\textsuperscript{-1} (Wisconsin DNR 2008). Concentrations of this magnitude would be expected to harm freshwater biota in lakes (Corsi et al. 2010; Hintz et al. 2017; Jones et al. 2017), and there is an extensive literature on the toxicity of chlorides on individual taxa and life stages (EPA 1988; Environment Canada and Health Canada 2001; Evans and Frick 2001). We use “expected to” because published toxicity criteria are based almost exclusively on non-winter water temperatures. In very rare cases, when toxicity was tested at cooler temperatures, there was no consistent pattern to indicate whether toxicity levels at temperatures near 0°C would be higher or lower.

In freshwater systems, the process of ion rejection from ice formation routinely is overlooked as a driver of water quality. In deep lakes, ion accumulation is negligible as a percentage of lake volume; however, most lakes on earth are shallow. A recent evaluation of global lake volumes estimates that the 1.24 million lakes on Earth between 0.1 km\textsuperscript{2} to 1 km\textsuperscript{2} have a mean depth of 3.5 m (Messager et al. 2016). Combining this with the fact that the highest abundance of lakes are at mid to northern latitudes (Verpoorter et al. 2014), underscores that the process of ion rejection from ice formation and thickening is chemically and biologically relevant for millions of waterbodies. Whether a lake is at risk for under-ice chloride toxicity can be determined from the amount of ice as a percentage of lake depth and the pre-ice chloride concentrations (Fig. 4). This is particularly relevant in Midwest and Northeast North America, where road development and deicing practices have led to chloride concentrations orders of magnitude above background concentrations (Dugan et al. 2017).

The process of chloride rejection discussed here may have broader application in limnology, as nitrogen and...
phosphorus (Fang et al. 2016), dissolved gases (Wharton et al. 1987; Tyler et al. 1998), and compounds such as dissolved organic matter and dissolved organic carbon (Belzile et al. 2002) are all known to accumulate under ice in lakes. Given that phytoplankton are relatively abundant under lake ice (Hampton et al. 2017), the process of solute rejection from lake ice may be a significant driver of under ice productivity.

Conclusions

In environments where anthropogenic chloride loading is a recognized occurrence, such as in areas of road salt application, shallow water bodies are at a much higher risk of elevated chloride concentrations than are deeper water bodies during ice cover thickening. Future research should investigate the rates of ion and solute rejection in freshwater ice covers, the rate of wintertime flushing in shallow systems, and the thresholds of chloride toxicity at near-freezing temperatures. Most importantly, we encourage winter water samples of chloride to be obtained to compare with summer values where ion exclusion may be an issue.

References

Belzile, C., J. A. E. Gibson, and W. F. Vincent. 2002. Colored dissolved organic matter and dissolved organic carbon exclusion from lake ice: Implications for irradiance transmission and carbon cycling. Limnol. Oceanogr. 47: 1283–1293. doi:10.4319/lo.2002.47.5.1283
Bluteau, C. E., R. Pieters, and G. A. Lawrence. 2017. The effects of salt exclusion during ice formation on circulation in lakes. Environ. Fluid Mech. 17: 579–590. doi: 10.1007/s10652-016-9508-6
Center for Limnology; NTL LTER. 2012. North Temperate Lakes LTER: Chemical Limnology of Primary Study Lakes: Major Ions 1981 - current. doi:10.6073/pasta/91fcc6ddf77793be79188c2b671486fa
Chapra, S. C., A. Dove, and D. C. Rockwell. 2009. Great Lakes chloride trends: Long-term mass balance and loading analysis. J. Great Lakes Res. 35: 272–284. doi:10.1016/j.jglr.2008.11.013
Corsi, S. R., D. J. Graczyk, S. W. Geis, N. L. Booth, and K. D. Richards. 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. doi:10.1021/es101333u
Dugan, H. A., and others. 2017. Salting our freshwater lakes. Proc. Natl. Acad. Sci. USA 114: 4453–4458. doi:10.1073/pnas.1620211114.
Environment Canada and Health Canada. 2001. Canadian Environmental Protection Act, 1999. Priority substances list assessment report. Road salts. 181 p.
EPA. 1988. Ambient water quality criteria for chloride. US Environmental Protection Agency, Washington DC. 39 p.

Fig. 4. Risk assessment for chloride toxicity in waterbodies. (a) The amount of lake ice as a percentage of total depth (% ice) is determined based on ice depth vs. lake depth. The solid, dashed, and dotted lines represent the graphical area with 20%, 40%, and 60% ice. (b) Comparing % ice with pre-ice (or summer time) chloride concentrations can determine the risk of under-ice chloride toxicity. Any depth and concentrations units may be used to interpret this figure. Exclusion rate was set at 90%. If concentrations are measured in mg L$^{-1}$, lakes that fall to the right of the solid 230 mg L$^{-1}$ line represent increasing risk from no effect with continuous exposure to noticeable effects of exposure. For example, if lake ice is more than 40% of the lake depth, under-ice chloride concentrations would reach toxic levels (> 230 mg L$^{-1}$) if pre-ice concentrations were greater than 140 mg L$^{-1}$.

As the percent of ice increases, the pre-ice chloride concentration that would develop toxic winter levels, decreases.
Evans, M., and C. Frick. 2001. The effects of road salts on aquatic ecosystems. Environment Canada Series. N.W.R.I. Contribution Series; 02-308.

Fang, Y., L. Changyou, M. Leppäranta, S. Xiaohongh, Z. Shengnan, and Z. Chengfu. 2016 Notable increases in nutrient concentrations in a shallow lake during seasonal ice growth. Water. Sci. Technol. 74: 2773–2783. doi: 10.2166/wst.2016.433

Findlay, S. E. G., and V. R. Kelly. 2011. Emerging indirect and long-term road salt effects on ecosystems. Ann. N. Y. Acad. Sci. 1223: 58–68. doi: 10.1111/j.1749-6632.2010.05942.x

Hampton E., and others. 2017. Ecology under lake ice. Ecology Letters 20: 98–111. doi: 10.1111/ele.12699

Herbert, E., and others. 2015. A global perspective on wetland salinization: Ecological consequences of a growing threat to freshwater wetlands. Ecosphere 6: 1–43. doi: 10.1890/ES14-00534.1

Hill, A. R., and E. K. Sadowski. 2016. Chloride concentrations in wetlands along a rural to urban land use gradient. Wetlands 36: 73–83. doi: 10.1007/s13157-015-0717-4

Hintz, W. D., B. M. Mattes, M. S. Schuler, D. K. Jones, A. B. Stoler, L. Lind, and R. A. Relyea. 2017. Salinization triggers a trophic cascade in experimental freshwater communities with varying food-chain length. Ecol. Appl. 27: 833–844. doi: 10.1002/eap.1487

Jones, D. K., B. M. Mattes, W. D. Hintz, M. S. Schuler, A. B. Stoler, L. A. Lind, R. O. Cooper, and R. A. Relyea. 2017. Investigation of road salts and biotic stressors on freshwater wetland communities. Environ. Pollut. 221: 159–167. doi: 10.1016/j.envpol.2016.11.060

Kaushal, S. S., P. M. Groffman, G. E. Likens, K. T. Belt, W. P. Stack, V. R. Kelly, L. E. Band, and G. T. Fisher. 2005. Increased salinization of fresh water in the northeastern United States. Proc. Natl. Acad. Sci. USA 102: 13517–13520. doi: 10.1073/pnas.0506414102

Lawrimore, J. H., M. J., Menne, B. E. Gleason, C. N. Williams, D. B. Wuertz, R. S. Vose, and J. Rennie. 2011. An overview of the Global Historical Climatology Network monthly mean temperature data set, version 3. J. Geophys. Res. 116: D19121. doi: 10.1029/2011JD016187

Marsalek, J. 2003. Road salts in urban stormwater: An emerging issue in stormwater management in cold climates. Water Sci. Technol. 48: 61–70.

Messager, M. L., B. Lehner, G. Grill, I. Nedeva, and O. Schmitt. 2016. Estimating the volume and age of water stored in global lakes using a geo-statistical approach. Nat. Commun. 7: 13603. doi: 10.1038/ncomms13603

Notz, D., and M. G. Worster. 2009. Desalination processes of sea ice revisited. J. Geophys. Res. 114: C05006. doi: 10.1029/2008JC004885

Novotny, E. V., D. Murphy, and H. G. Stefan. 2008. Increase of urban lake salinity by road deicing salt. Sci. Total Environ. 406: 131–144. doi: 10.1016/j.scitotenv.2008.07.037

Panno, S. V., V. A. Nuzzo, K. Cartwright, B. R. Hensel, and I. G. Krapac. 1999. Impact of urban development on the chemical composition of ground water in a fen-wetland complex. Wetlands 19: 236–245. doi: 10.1007/BF03161753

Panno, S. V., K. C. Hackley, H. H. Hwang, S. E. Greenberg, I. G. Krapac, S. Landsberger, and D. J. O’Kelly. 2006. Characterization and identification of Na-Cl sources in ground water. Ground Water 44: 176–187. doi: 10.1111/j.1745-6584.2005.00127.x

Pieters, R., and G. A. Lawrence. 2009. Effect of salt exclusion from lake ice on seasonal circulation. Limnol. Oceanogr. 54: 401–412. doi: 10.4319/lo.2009.54.2.0401

Rush, V. H., and others. 1988. The role of disturbance in stream ecology. J. North Am. Benthol. Soc. 7: 433–455. doi: 10.2307/1467300

Richburg, J. A., W. A. Patterson, and F. Lowenstien. 2001. Effects of road salt and Phragmites australis invasion on the vegetation of a Western Massachusetts calcareous lake-basin fen. Wetlands 21: 247–255. doi: 10.1672/0277–5212(2001)021[0247:EORSAP]2.0.CO;2

She, Y., J. Kemp, L. Richards, and M. Loewen. 2016. Investigation into freezing point depression in stormwater ponds caused by road salt. Cold Reg. Sci. Technol. 131: 53–64. doi: 10.1016/j.coldregions.2016.09.003

Thunqvist, E-L. 2004. Regional increase of mean chloride concentration in water due to the application of deicing salt. Sci. Total Environ. 325: 29–37. doi: 10.1016/j.scitotenv.2003.11.020

Tyler, S., P. Cook, A. Butt, J. Thomas, P. Doran, and W. Lyons. 1998. Evidence of deep circulation in two perennially ice-covered Antarctic lakes. Limnol. Oceanogr. 43: 625–635. doi: 10.4319/lo.1998.43.4.0625

Van Meter, R. J., and C. M. Swan. 2014. Road salts as environmental constraints in urban pond food webs. PloS one 9: e90168. doi: 10.1371/journal.pone.0090168

Vervoort, C., T. Kutser, D. A. Seekell, and L. J. Tranvik. 2014. A global inventory of lakes based on high-resolution satellite imagery. Geophys. Res. Lett. 41: 6396–6402. doi: 10.1002/2014GL060641

Wharton, Jr, R. A., C. P. McKay, R. L. Mancinelli, and G. M. Simmons. 1987. Perennial N2 supersaturation in an Antarctic lake. Nature 325: 343–345. doi: 10.1038/325343a0

Williams, D. D. D., N. E. Williams, and Y. Cao. 2000. Road salt contamination of groundwater in a major metropolis. Water Res. 34: 127–138. doi: 10.1016/S0043-1354(99)00129-3

Wisconsin Administrative Code: Department of Natural Resources.

Zhang, Y., C. Li, X. Shi, and C. Li. 2012. The migration of total dissolved solids during natural freezing process in Ulansuhai Lake. J Arid Land 4: 85–94. doi: 10.3724/SP.J.1227.2012.00085
Acknowledgments

We thank the Lakeshore Nature Preserve for student funding, Emily Stanley and Elizabeth Runde for chemical analysis of the samples, and Corinna Gries for data management. We thank many other students and staff at the Center for Limnology and the Lakeshore Nature Preserve for assistance in the field. Thank you to the three anonymous reviewers who provided feedback that significantly improved this manuscript. This material is based upon work supported by the National Science Foundation under Cooperative Agreement DEB-1440297.

Submitted 25 January 2017
Revised 18 May 2017
Accepted 27 March 2017