



Limnology and Oceanography Letters 2021 © 2021 The Authors. Limnology and Oceanography Letters published by Wiley Periodicals LLC on behalf of Association for the Sciences of Limnology and Oceanography. doi: 10.1002/lol2.10191 doi: 10.1002/lol2.10191

LETTER

The slow and steady salinization of Sparkling Lake, Wisconsin

Hilary A. Dugan 🗅,* Linnea A. Rock 💿

Center for Limnology, University of Wisconsin-Madison, Madison, Wisconsin

Scientific Significance Statement

Even in rural areas, groundwater-fed lakes may be at high risk for slow, long-term salinization depending on groundwater flow paths. We use 40 years of monitoring data from Sparkling Lake, Wisconsin to show that the slow steady rise in chloride is the result of terrestrial retention of road salt. The enormity of chloride that resides on the landscape has slowed surface water impairment, but also will delay any recovery in the near term.

The concentrations of conservative solutes in seepage lakes are determined by the relative inputs of precipitation vs. groundwater. In areas of road salt application, seepage lakes may be at high risk of salinization depending on groundwater flow. Here, we revisit a 1992 analysis on the salinization of Sparkling Lake, a deep seepage lake in Northern Wisconsin. The original analysis predicted a rapid increase in chloride concentrations before reaching a steady steady of 8 mg L⁻¹ by 2020. Forty years of monitoring Sparkling Lake show that rather than reaching a dynamic equilibrium, chloride concentrations have steadily increased. We update the original box model approach by adding a soil reservoir component that shows the slow steady rise in chloride is the result of terrestrial retention. For freshwater rivers and lakes, chloride retention on the landscape will both delay chloride impairment and prolong recovery and must be considered when modeling future chloride contamination risk.

Salinization is a global threat to freshwater resources (Herbert et al. 2015; Cañedo-Argüelles et al. 2016; Kaushal et al. 2018; Schuler et al. 2019). Of concern, is the salinization of near-surface groundwater due to the abundant use of salt as a winter deicer. Reports of groundwater contamination began appearing in the published literature in the 1970s (Huling and Hollocher 1972) following a surge in road salt use in the 1960s (Jackson and Jobbágy 2005). During the intervening decades, there have been numerous reports of groundwater salinization associated with urban land use (Williams et al. 2000; Kelly et al. 2008; Cassanelli and Robbins 2013). Where salinized

groundwater feeds surface lakes, the input and accumulation of ions in lake hypolimnia can lead to delayed, diminished, or inhibited lake mixing. The changing density of lake water contributes to the transition of normally dimictic lakes to meromictic or monomictic lakes, which can have serious, cascading consequences on lake biogeochemistry and lake habitat (Koretsky et al. 2012; Dupuis et al. 2019), and decreases the availability of safe drinking water (Kaushal 2016).

The Northern Highlands Lake District in Northern Wisconsin is a region prized for the thousands of pristine lakes that dot the landscape. In this region, groundwater seepage lakes

^{*}Correspondence: hdugan@wisc.edu

Associate editor: Stephanie Melles

Author Contribution Statement: HD and LR co-conceived the intellectual backbone of this study. HD performed all modeling and statistical analyses, and LR performed all field and laboratory analyses. HD led the writing of the manuscript.

Additional Supporting Information may be found in the online version of this article.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

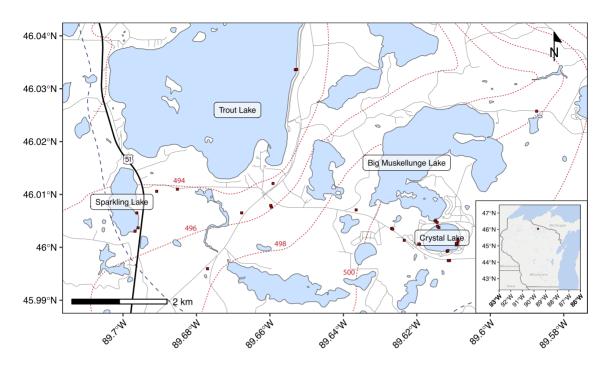


Fig 1. Location of Sparkling Lake and Big Muskellunge Lake in Northern Wisconsin (see inset map). Red squares locate groundwater wells with water chemistry observations. Water table contours (red dotted lines) and groundwater divide (dashed line) are redrawn from Pint et al. (2003). Highway 51 runs along the eastern shore of Sparkling Lake.

are common; accounting for 59% of lakes (Eilers et al. 1988). These lakes differ from drainage lakes in that solutes are predominantly provided by groundwater and direct atmospheric deposition, residence times are long, and groundwater inputs are driven by landscape position relative to the water table (Webster et al. 2006). Seepage lakes are a window into groundwater flow paths and may be susceptible to long-term changes in water chemistry if aquifers are retaining anthropogenic solutes (Robinson et al. 2017; Baraza and Hasenmueller 2021).

Even in rural settings with few roads, seepage lakes may be at high risk of salinization from road deicers depending on groundwater flow fields. An inventory of chloride in private well water data in Northern Wisconsin reveals highly heterogeneous groundwater quality (UWSP 2021). While chloride concentrations in the majority of wells are below 10 mg L⁻¹, and in some cases undetectable, there are also wells where chloride concentrations were measured at 610 and 980 mg L⁻¹ (UWSP 2021).

Here, we revisit a 1992 analysis on the salinization of Sparkling Lake, a 63-ha, 20-m deep seepage lake in Northern Wisconsin (Bowser 1992). The chloride concentrations seen in Sparkling Lakes are relatively low compared to more urban areas, but these trends are likely representative of slow salinization that may be taking place in other seepage lakes throughout regions of North America, and on other continents, where anthropogenic salt use is prevalent. The original analysis predicted a rapid increase in chloride before reaching a steady-steady concentration of 8 mg L⁻¹ by 2020. We update the original box model approach by adding a soil reservoir

component that shows the slow steady rise in chloride in Sparkling Lake is the result of terrestrial retention of chloride.

Study site and methods

The Northern Highlands Lake District in Northern Wisconsin is a mosaic of lakes, many of which are seepage lakes nested within the groundwater table. Estimates are that 90% of stream flow are groundwater-derived baseflow, and lakes on the surface penetrate more than 80% of the unconfined aquifer that permeates the 40-60 m of fluvial sand and gravel and glacial till that overlay Precambrian igneous and metamorphic bedrock (Attig 1985; Pint et al. 2003). Low natural chloride concentrations North-Central in Wisconsin lakes (median = 1 mg L^{-1} , n = 424; Birge and Juday 2013), along with a study of the geochemical evolution of shallow groundwater in the region that found no increase in chloride concentrations along flow paths (Kenoyer and Bowser 1992), support the conclusion that mineral weathering contributes little chloride to surface and groundwaters.

In this study, we focus on two seepage lakes, Sparkling Lake and Big Muskellunge Lakes (Fig. 1). They are both groundwater flow-through lakes, which gain water through precipitation and groundwater discharge and lose water through evaporation and groundwater recharge. Sparkling Lake is smaller in area, but both lakes have similar depths and residence times (Table 1). Average groundwater inflow rates into Big Muskellunge were estimated at 0.14–0.15 and 0.24–

Table 1. Characteristics of Sparkling and Big Muskellunge Lake and their watersheds (WS), including residence time (RT), percent
groundwater (GW) contribution, and road density (RD) in the watershed and within a 100 m buffer surrounding the lake. Reported
water column conductivity (Cond) from Nov 2018. Road density includes many roads that do not receive winter deicers.

Lake	Lake area (ha)	WS area (ha)	Max/mean depth (m)	Volume (m ³)	Cond (µS cm ⁻¹)	RT* (yr)	GW* (%)	RD WS† (m ha ⁻¹)	RD 100 m† (m ha ⁻¹)
Sparkling	63.7	237.4	20.0/10.9	$6.94 imes 10^{6}$	115	10.4	25	26.7	47.5
Big Muskellunge	363.4	555.6	21.3/7.5	27.2 × 10 ⁶	56	8.0	16	21.9	28.9

*Webster et al. (1996).

[†]Soranno et al. (2017).

 0.29 m yr^{-1} into Sparkling Lake, making up 16% and 25% of their annual hydrologic inputs, respectively (Krabbenhoft et al. 1994; Webster et al. 1996). The lakes typically freeze over from early December to late April. In this study, we focus on the salinization of Sparkling Lake from nearby Highway 51 (Fig. 1), and consider Big Muskellunge Lake as a natural reference.

Since 1982, major ion chemistry has been measured quarterly, typically in February, April/May, August, and November, by the North Temperate Lakes Long Term Ecological Research program (NTL-LTER 2020*a*). Samples are collected with a peristaltic pump and in-line filtered through a 0.40-m polycarbonate filter from the epilimnion, metalimnion, and hypolimnion. The majority of samples were taken at 0, 10, and 19 m depths in Big Muskellunge, and 0, 10, and 18 m in Sparkling. Measured analytes include chloride, sulfate, calcium, magnesium, sodium, potassium, iron, manganese, and specific conductance. Any suspect concentrations, as flagged, were removed from the data set. Lake level is measured fortnightly during the ice-free season at the shoreline using a twice-annually calibrated staff gauge referenced to meters above sea level.

To analyze long-term trends and patterns, we first linearly interpolated vertical concentration profiles to 1 m increments. In the majority of observations, ion concentrations were well mixed and linear interpolation was valid. We manually checked all chloride profiles, and in only a few cases did linear interpolation likely overestimate or underestimate total mass in the lakes. Any error introduced by these data would be inconsequential in the later analyses. We then linearly interpolated concentration profiles to monthly timesteps using the akima package in R (Akima and Gebhardt 2020), and computed bathymetrically weighted concentrations for each timestep. This time series was decomposed into a trend component using a 12-month moving average convolution filter fitted to the integrated ion concentration time series. The seasonal component was obtained by averaging the difference between the observed and trend component for each month over 1982-2018.

The NTL-LTER monitors groundwater chemistry annually in nine wells to the south of Big Muskellunge Lake and two wells on the eastern shore of Trout Lake (NTL-LTER 2020*b*). For this study, four groundwater wells proximal to Highway 51 and located to the southeast of Sparkling lake were sampled for chloride (mg L⁻¹) and specific conductivity (μ S cm⁻¹) (Table 2). Groundwater was collected into acid-washed 60-mL Nalgene bottles using a peristaltic pump after purging three times the standing volume in the well. Conductivity (μ S cm⁻¹) and temperature (°C) were measured with a Thermo Scientific handheld conductivity meter, calibrated prior to use with KCl solutions of 100 and 500 (μ S cm⁻¹) at 25°C. Samples were filtered through 25 mm, 0.45-m filters prior to analysis on a Dionex 2100 ion chromatograph, calibrated with six NaCl solutions ranging from 1 to 500 (mg L⁻¹) and run with a 30 mM NaOH eluent solution.

Anthropogenic chloride inputs into Sparkling Lake stem from road salt (NaCl) used as a deicer along Highway 51, a two-lane highway that runs north–south along the eastern edge of Sparkling Lake. Highway 51 is maintained in the winter by the Vilas County Highway Department and receives road salt at the prescribed rate of 200–300 lb per lane mile during winter snow events. Vilas County has likely been salting Highway 51 since the 1950s, but no long-term records exist to quantify annual salt use over the last 70 years. Recent annual county salt use in tons per lane mile totaled 10.30 (2019–2020), 12.89 (2018–2019), 25.33 (2017–2018) and 19.83 (2016–2017). The chloride concentration of local precipitation is seasonally < 0.1 mg L⁻¹ (NADP site WI36, 46.0512–89.6541) (NADP 2018).

To address "How long will it take Sparkling Lake to reach a steady-state concentration" (Bowser 1992) used a simple box model approach of a well-mixed lake. Assuming no loss of chloride by evaporation and no in-lake removal, the concentration of chloride at time t can be expressed as the finite difference equation:

$$C_t = C_\infty + (C_{t-1} + C_\infty)e^{-\alpha t}, \tag{1}$$

where C_t = concentration in the lake at *t*-years since the start of road salting, C_{∞} = weighted concentration of chloride from groundwater and precipitation, α = annual flux of

Well	Chloride (mg L ⁻¹)	Conductivity (μ S cm ⁻¹)	Temp (°C)	Water depth (cm)	Well depth (cm)	Location
8	3.36	26.57	14.0	132	236	46.00651, -89.69623
7a	3.14	37.09	12.9	261	388	46.00369, -89.69589
7b	148.75	484.9	13.2	287	639	46.00369, -89.69589
5	16.11	58.86	13.4	45	130	46.00306, -89.69671
5	14.03	57.59	12.7	45	130	46.00306, -89.69671

Table 2. Groundwater chloride concentrations near Sparkling Lake measured on July 17, 2020.

groundwater out/volume of the lake at steady state, t = time since the start of road salting. See full derivation in Bowser (1992).

Groundwater inflow rates into Sparkling Lake were estimated by Krabbenhoft et al. (1990*a*,*b*) using a stable isotope (¹⁸O/¹⁶O) mass balance method and a three-dimensional groundwater flow/solute transport model. The two methods showed similar results. The average inflow rates from the transport model were 1.6×10^5 m³ yr⁻¹ compared to 2.3×10^5 m³ yr⁻¹ from the isotope method. Groundwater outflow rates estimated from the model were 4.1×10^5 m³ yr⁻¹ compared to 4.4×10^5 m³ yr⁻¹ from the isotope mass balance method. Groundwater inflow rates were more sensitive to seasonal variation than groundwater outflow rates (Krabbenhoft et al. 1990*a*,*b*).

The box model approach in Eq. 1 assumes that all chloride discharged into the environment via road salting will immediately enter the lake. The result is logarithmic growth of chloride concentrations in the lake. Initially, the concentration increases rapidly but the rate of increase exponentially decays over time until steady state is reached at C_{∞} .

Based on observed trends, we added a storage component to Eq. 1. Although chloride is often considered a conservative solute, studies have shown that soil can store a limited amount of chloride (Kincaid and Findlay 2009; Robinson et al. 2017; Shannon et al. 2020). We modeled the terrestrial storage component as a sigmoid curve (s-curve), where at t = 0 (1950s) the rate of storage is high, that is, the most road salt is retained in the terrestrial landscape. Over time, the reservoir capacity decreases and the chloride load into the lake increases exponentially. Eventually, the storage capacity of the soil is saturated, and the concentration of chloride in the inflowing groundwater equals the annual salt loading onto the landscape.

The proportion of used storage capacity of soil (S_t) from 0 to 1 is modeled as:

$$S_{t} = \frac{S_{t-1} \times e^{\beta}}{1 - S_{t-1} + (S_{t-1} \times e^{\beta})}$$
(2)

where β is the rate of chloride retention. Eq. 1 now takes the form:

$$C_t = (C_{\infty} \times S_t) + (C_{t-1} + (C_{\infty} \times S_t))e^{-\alpha t}$$
(3)

At time t = 0, the natural background concentration in the lake C_0 was set as 1 mg L⁻¹, based on historic sampling by Birge and Juday in the 1920s (Birge and Juday 2013). Repeated depth-discrete water column sampling in the summers of 1926–1929, measured chloride concentrations of 0.25–1.50 mg L⁻¹ in Sparkling Lake (n = 22) and 0.25–1.70 mg L⁻¹ in Big Muskellunge Lake (n = 23).

 C_{∞} is calculated using an annual groundwater inflow rate to Sparkling Lake of 29 cm yr⁻¹, and an average annual precipitation rate of 54 cm yr⁻¹ (Krabbenhoft et al. 1990*b*). The average concentration of chloride in the inflowing groundwater is calculated based on a 1-mile stretch of highway that is salted at 15 tons per year (13,600 kg) and a groundwater inflow rate of 2.3×10^5 m³ yr⁻¹. This equates to a groundwater concentration of 68 mg L⁻¹ and C_{∞} equal to 18.33 mg L⁻¹. Our groundwater concentration is 4× higher than the 19 mg L⁻¹ estimated by Bowser (1992), based on unpublished groundwater samples from 1982 to 1990. To estimate *a*, the annual flux of groundwater out is taken as 4.5×10^5 m³ yr⁻¹ divided by the volume of the lake, which results in a α value of 0.0605.

Results from Eq. 3 are sensitive to the initial value of S_0 and β . To set S_0 and β appropriately, we ran an optimization routine to minimize the root mean squared error between C_t and observed chloride concentrations in Sparkling Lake. Data from years 2004–2010 were withheld from the optimization routine, as they were likely influenced by drought conditions (Perales et al. 2020). Optimization was performed using the default *optim* function in R (R Core Team 2020). The model was run at an annual timestep and was not intended to explore interannual variation in chloride concentrations.

Results

In comparing the time series of lake levels and major ion concentrations in Sparkling and Big Muskellunge, it is clear that the lakes experience similar hydrology (Fig. 2). Comparing the concentrations of major cations Ca²⁺, Mg²⁺, and K⁺ in

Dugan and Rock

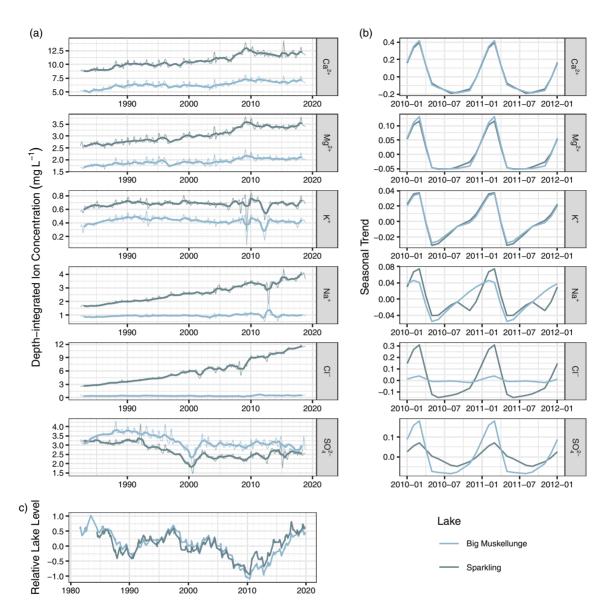


Fig 2. (a) Decomposed time series of long-term trends (thick line) and observed concentrations (thin line) in depth-integrated major ion concentrations in Big Muskellunge and Sparkling Lakes. (b) Two years of the decomposed seasonal component of time-series in (a). (c) Relative lake-level fluctuations in meters. Each time series was individually demeaned.

the two lakes, Sparkling Lake has higher absolute concentrations, but the long-term trends are nearly identical. The seasonal trend is also identical, with concentrations peaking in February/March. Where the lakes differ, is in Na⁺ and Cl⁻. In Big Muskellunge, sodium hovers around 1 mg L⁻¹, while in Sparkling, sodium has increased from 1.5 mg L⁻¹ in 1982 to over 4 mg L⁻¹ in 2018. Similarly, chloride in Big Muskellunge is typically in the range of 0.3–0.8 mg L⁻¹, while Sparkling Lake has increased from 2.5 mg L⁻¹ in 1981 to 12 mg L⁻¹ in 2018.

Mean groundwater concentrations of chloride in the wells located to the south of Big Muskellunge Lake ranged from 0.4 to 3.9 mg L^{-1} from 1984 to 2018. The highest concentrations

were found in the wells located to the SE of Crystal Lake. Groundwater samples analyzed in 2020 from the eastern edge of Sparkling Lake found highly variable chloride concentrations ranging from 3.14 to 148.75 mg L⁻¹ (Table 2). These concentrations are similar to those reported in Krabbenhoft et al. (1990*b*) of wells upgradient from Sparkling Lake that exceeded 200 mg L⁻¹.

Here, we modeled the evolution of chloride in Sparkling Lake as a function of time for a steady-state chloride concentration of 18.33 mg L⁻¹ using both the original (Bowser 1992) model (Eq. 1) and the soil-storage model (Eq. 3) (Fig. 3). The original model predicts a logarithmic increase in chloride concentrations starting at time t_0 , here taken as 1950. The

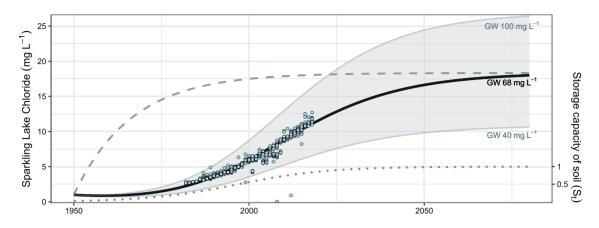


Fig 3. Modeled chloride trajectory in Sparkling Lake using a soil-reservoir box model (black line). Gray ribbon shows the sensitivity of the model to varying groundwater chloride concentrations with a rate of chloride retention of $\beta = 0.07882$. Blue circles are measured observations, the dashed line is the original box model from Bowser (1992), and the dotted line is the used proportion of soil storage capacity.

observed chloride concentrations do not fit this pattern. Instead, the rate of change in chloride appears to exponentially increase during the 1980s and 1990s and before linearly increasing in the 2000s (Fig. 3). The soil-storage model, which allows groundwater chloride to be stored until the reservoir is exhausted, was calibrated to observed concentrations and recreates the observed pattern. Optimization of the model resulted in an initial storage value $S_0 = 0.0242$ and the rate of chloride retention $\beta = 0.07882$. This model output predicts that in 2020, the soil reservoir was 86% full. Chloride concentrations will continue to increase in Sparkling Lake until the year 2075 where they will stabilize at the steady-state concentration of 18.33 mg L⁻¹.

Discussion

Chloride concentrations in Sparkling Lake area 12× the historical concentrations of 1 mg L⁻¹ recorded in the late 1920s, and 12× the present day concentrations of < 1 mg L⁻¹ in nearby Big Muskellunge Lake. Shallow groundwater chloride concentrations are similarly elevated. A U.S. Geological Survey study of groundwater wells across the glacial aquifer system of the Northern United States found a median chloride concentration of 4.1 mg L⁻¹ in forested land-use wells vs. 26 mg L⁻¹ in urban land-use wells (Mullaney et al. 2009). Groundwater concentrations bordering Sparkling Lake are more similar to urban groundwater wells (Kelly 2008), and one well is approaching the U.S. EPA secondary maximum contaminant level of 250 mg L⁻¹ for chloride in drinking water (Mullaney et al. 2009).

Given the similarities in major ion chemistry between Sparkling and Big Muskellunge Lakes, we conclude that the multidecadal increase in chloride and sodium in Sparkling Lake is solely a response to anthropogenic salt inputs stemming from Highway 51 and not a result of natural changes in ion weathering. In both lakes, the seasonal trend of higher ion concentrations in February/March aligns with observations of ion-rejection from ice covers leading to high in-lake concentrations. When lake ice begins to crystallize, ions are not incorporated into the lake ice lattice and are rejected into the surrounding water. Although the physical process of ion rejection has been more comprehensively studied in marine ice (Notz and Worster 2009), rejection of ions from freshwater ice has been recorded in a variety of lakes (Belzile et al. 2001; Pieters and Lawrence 2009; Zhang et al. 2012; She et al. 2016; Dugan et al. 2017b). Cryoconcentration accounts for the winter peak in ions, but does not account for amplified seasonality in chloride in Sparkling Lake. There is little evidence that the winter increases in Sparkling Lake are derived from direct winter runoff of road deicers; rather observations suggest that low to no precipitation in the winter likely leads to a buildup on groundwater-derived chloride due to a lack of flushing (Xu et al. 2021).

Long-term trends in ion chemistry in Northern Wisconsin are known to be influenced by landscape position and periods of below-average precipitation (Webster et al. 1996, 2006). When precipitation is low, the water table and lake levels are drawn down due to a shift in the balance between precipitation and evaporation, and solute concentrations increase due to evapoconcentration. However, the total mass of ions only increases in lakes that receive a significant portion of their inflow from groundwater (Webster et al. 1996). Over the period of record, the region has undergone two major droughts: 1987-1990 and 2005-2010 (Fig. 2). Looking specifically at 2005-2010 drought (Perales et al. 2020), cations increased in Sparkling and Big Muskellunge Lakes (Fig. 2) and in all NTL-LTER study lakes (Data S1). This is consistent with evapoconcentration and a hydrologic shift toward base-flow and groundwater. Uniquely, chloride did not increase from 2005 to 2009 (Figs 2, S5). In Sparkling Lake, this is one of the few documented periods when chloride decreased. In 2010, when lake levels rose 0.5 m, chloride concentrations immediately resumed their upward trajectory. During drought years, there is likely less road salt applied to roads, as total snowfall and snow events are below average. Compounded on this, there is less melt water and precipitation to flush accumulated salts through soils. The unique response of chloride to periods of drought in all NTL-LTER lakes leads us to believe that anthropogenic chloride inputs may be impacting all of the study lakes, at an almost imperceptible scale.

Sparkling Lake chloride concentrations are expected to keep rising until in-lake concentrations equilibrate with sources. Previous modeling using a steady-state box model predicted a logarithmic trend; a rapid increase followed by tapering off to steady state (Fig. 3). This model does not fit the observed data. Our steady-state box model that incorporates a storage component fits the observed data well as a sigmoid curve, and supports the hypothesis that the terrestrial landscape has a limited capacity to retain chloride (Fig. 3). The largest uncertainty in our model is the long-term average concentration of chloride in the groundwater. Keeping in mind the low sample size, our data do not show any increase in groundwater concentrations over the last three decades (Bowser 1992), which supports the use of a steady-state model. Because of the large range in well-water chemistry, we calculated annual chloride loading based on known road salt use at the county level. Going forward, as the Wisconsin Department of Transportation begins to employ vehicle location GPS equipment, more accurate estimates of salt loading within individual watersheds will become possible. In addition, a statewide switch toward liquid brine application promises to reduce total salt use. Continued monitoring of groundwater and lake chloride concentrations will be critical in evaluating new road salt application measures aimed at lessening the negative impacts of winter road maintenance on freshwater resources.

Chloride retention in soils bucks the widely held view that chloride is a conservative ion that "goes where the water goes." Although, by now this paradigm should be shifting as the phenomenon of delayed leaching of chloride to groundwater and surface water has been noted by numerous studies (Kelly et al. 2008; Kincaid and Findlay 2009; Robinson et al. 2017; Oswald et al. 2019; Shannon et al. 2020). At the same time, the salinization of soils in the watershed may promote nitrate leaching (Haq et al. 2018) and mobilize toxic heavy metals including lead, cadmium, and mercury; all of which may be more abundant due to vehicular traffic (Schuler and Relyea 2018). In the short term, the retention capacity of soils may be beneficial to surface waters in that it will dampen heavy ion loads that would be associated with spring melt or winter run-off events. However, it also masks the magnitude of environmental damage by delaying the discharge of historic pollutants (Kelly et al. 2019). Models of watershed chloride loading that do not incorporate terrestrial retention estimates will likely result in inaccurate predictions of surface water chloride concentrations.

Sparkling Lake should be considered a representative case study for seepage lakes that are located near heavily salted roads. However, the conclusions drawn from this study could also apply to drainage lakes, where soil retention may lessen solute concentrations in river baseflow. Hundreds of lakes across the United States and Canada are known to be increasing in chloride, and predictive modeling of chloride concentrations could inform managers of the potential timeline and extent of chloride contamination (Kelly et al. 2008; Dugan et al. 2017a, 2020). This model is limited in its ability to recreate interannual dynamics, but could be expanded for more sophisticated predictive modeling by allowing groundwater concentrations and discharge to vary with time. As we start to see widespread efforts to reduce anthropogenic salt loading to the environment, knowing the degree to which landscape storage my delay and prolong surface water improvements will set a realistic timeline for evaluating the success of best management practices.

Data Availability Statement

The code and data required to perform the analysis described in this article are located at https://zenodo.org/record/4618111. All NTL-LTER data are cited in the references and available via the Environmental Data Initiative.

References

- Akima, H., and A. Gebhardt. 2020. Akima: Interpolation of irregularly and regularly spaced data. R package version 0.6-2.1. Available from https://CRAN.R-project.org/ package=akima
- Attig, J. W. 1985. Pleistocene Geology of Vilas County, Wisconsin; Wisconsin Geological and Natural History Survey: Madison, WI.
- Baraza, T., and E. A. Hasenmueller. 2021. Road salt retention and transport through vadose zone soils to shallow groundwater. Sci. Total Environ. **755**: 142240. doi:10.1016/j. scitotenv.2020.142240
- Belzile, C., W. F. Vincent, J. A. Gibson, and P. V. Hove. 2001. Bio-optical characteristics of the snow, ice, and water column of a perennially ice-covered lake in the High Arctic. Can. J. Fish. Aquat. Sci. **58**: 2405–2418.
- Birge, E., and C. Juday. 2013. North temperate lakes LTER: Historical Birge—Juday Lake survey 1900–1943. Environmental Data Initiative. doi:10.6073/pasta/dc7eed17e618e a6877f3a79175ba85f5
- Bowser, C. J. 1992. Groundwater pathways for chloride pollution of lakes, p. 283–301. *In* F.M. D'Itri [ed.], Chemical deicers and the environment. Lewis Publishers Inc.
- Cañedo-Argüelles, M., and others. 2016. Saving freshwater from salts. Science **351**: 914–916. doi:10.1126/science. aad3488
- Cassanelli, J. P., and G. A. Robbins. 2013. Effects of road salt on Connecticut's groundwater: A statewide centennial

perspective. J. Environ. Qual. **42**: 737–748. doi:10.2134/ jeq2012.0319

- Dugan, H. A., S. L. Bartlett, S. M. Burke, J. P. Doubek, F. E. Krivak-Tetley, N. K. Skaff, J. C. Summers, K. J. Farrell, I. M. McCullough, A. M. Morales-Williams, D. C. Roberts, Z. Ouyang, F. Scordo, P. C. Hanson, and K. C. Weathers. 2017a. Salting our freshwater lakes. Proc. Natl. Acad. Sci. 114: 4453–4458. doi:10.1073/pnas.1620211114
- Dugan, H. A., G. Helmueller, and J. J. Magnuson. 2017b. Ice formation and the risk of chloride toxicity in shallow wetlands and lakes. Limnol. Oceanogr. Lett. 2: 150–158. doi: 10.1002/lol2.10045
- Dugan, H., and others. 2020. Lakes at risk of chloride contamination. Environ. Sci. Technol. **54**: 6639–6650.
- Dupuis, D., E. Sprague, K. M. Docherty, and C. M. Koretsky. 2019. The influence of road salt on seasonal mixing, redox stratification and methane concentrations in urban kettle lakes. Sci. Total Environ. **661**: 514–521. doi:10.1016/j. scitotenv.2019.01.191
- Eilers, J. M., D. F. Brakke, and D. H. Landers. 1988. Chemical and physical characteristics of lakes in the Upper Midwest, United States. Environ. Sci. Technol. 22: 164–172.
- Haq, S., S. S. Kaushal, and S. Duan. 2018. Episodic salinization and freshwater salinization syndrome mobilize base cations, carbon, and nutrients to streams across urban regions. Biogeochemistry 141: 463–486. doi:10.1007/s10533-018-0514-2
- Herbert, E. R., and others. 2015. A global perspective on wetland salinization: Ecological consequences of a growing threat to freshwater wetlands. Ecosphere **6**: art206. doi:10. 1890/ES14-00534.1
- Huling, E. E., and T. C. Hollocher. 1972. Groundwater contamination by road salt: Steady-state concentrations in East Central Massachusetts. Science **176**: 288–290. doi:10.1126/ science.176.4032.288
- Jackson, R. B., and E. G. Jobbágy. 2005. From icy roads to salt streams. Proc. Natl. Acad. Sci. USA **102**: 14487–14488. doi: 10.1073/pnas.0507389102
- Kaushal, S. S. 2016. Increased salinization decreases safe drinking water. Environ. Sci. Technol. 50: 2765–2766. doi:10. 1021/acs.est.6b00679
- Kaushal, S. S., G. E. Likens, M. L. Pace, R. M. Utz, S. Haq, J. Gorman, and M. Grese. 2018. Freshwater salinization syndrome on a continental scale. Proc. Natl. Acad. Sci. 115: E574–E583. doi:10.1073/pnas.1711234115
- Kelly, V. R., G. M. Lovett, K. C. Weathers, S. E. G. Findlay, D. L. Strayer, D. J. Burns, and G. E. Likens. 2008. Long-term sodium chloride retention in a rural watershed: Legacy effects of road salt on streamwater concentration. Environ. Sci. Tech. 42: 410–415.
- Kelly, V. R., S. E. Findlay, S. K. Hamilton, G. M. Lovett, and K. C. Weathers. 2019. Seasonal and long-term dynamics in stream water sodium chloride concentrations and the effectiveness of road salt best management practices. Water AirSoil Pollut. 230: 13. doi:10.1007/s11270-018-4060-2

- Kelly, W. R. 2008. Long-term trends in chloride concentrations in shallow aquifers near Chicago. Groundwater 46: 772–781. doi:10.1111/j.1745-6584.2008.00466.x
- Kenoyer, G. J., and C. J. Bowser. 1992. Groundwater chemical evolution in a sandy silicate aquifer in Northern Wisconsin: 1. Patterns and rates of change. Water Resour. Res. 28: 579–589. doi:10.1029/91WR02302
- Kincaid, D. W., and S. E. G. Findlay. 2009. Sources of elevated chloride in local streams: Groundwater and soils as potential reservoirs. Water Air Soil Pollut. **203**: 335–342. doi:10. 1007/s11270-009-0016-x
- Koretsky, C. M., A. MacLeod, R. J. Sibert, and C. Snyder. 2012. Redox stratification and salinization of three Kettle Lakes in Southwest Michigan, USA. Water Air Soil Pollut. **223**: 1415–1427. doi:10.1007/s11270-011-0954-y
- Krabbenhoft, D. P., M. P. Anderson, and C. J. Bowser. 1990a. Estimating groundwater exchange with lakes: 2. Calibration of a three-dimensional, solute transport model to a stable isotope plume. Water Resour. Res. 26: 2455–2462.
- Krabbenhoft, D. P., C. J. Bowser, M. P. Anderson, and J. W. Valley. 1990b. Estimating groundwater exchange with lakes: 1. The stable isotope mass balance method. Water Resour. Res. 26: 2445–2453.
- Krabbenhoft, D. P., C. J. Bowser, C. Kendall, and J. R. Gat. 1994. Use of oxygen-18 and deuterium to assess the hydrology of groundwater-lake systems, p. 67–90. *In*, Environmental chemistry of lakes and reservoirs. American Chemical Society.
- Mullaney, J. R., D. Lorenz, and A. D. Arntson. 2009. Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, Northern United States. Scientific Investigations Report 2009-5086, U.S. Geological Survey. doi:10.3133/sir20095086
- NADP. 2018. *National Atmospheric Deposition Program,* Madison, WI: NADP Program Office.
- Notz, D., and M. G. Worster. 2009. Desalination processes of sea ice revisited. J. Geophys. Res. **114**: C05006. doi:10. 1029/2008JC004885
- NTL-LTER. 2020a. North temperate lakes LTER: chemical limnology of primary study lakes 1981—Current. Environ. Data Initiat. doi:10.6073/pasta/a457e305538a0d8e669b58 bb6f35721f
- NTL-LTER. 2020b. North temperate lakes LTER: Groundwater chemistry 1984—Current. Environ. Data Initiat. doi:10. 6073/pasta/4948e8f43d5cd5a8ecde15bae05ae3ef
- Oswald, C. J., G. Giberson, E. Nicholls, C. Wellen, and S. Oni. 2019. Spatial distribution and extent of urban land cover control watershed-scale chloride retention. Sci. Total Environ. 652: 278–288. doi:10.1016/J.SCITOTENV.2018.10.242
- Perales, K. M., C. L. Hein, N. R. Lottig, and M. J. Vander Zanden. 2020. Lake water level response to drought in a lake-rich region explained by lake and landscape characteristics. Can. J. Fish. Aquat. Sci. **77**: 1836–1845. doi:10.1139/ cjfas-2019-0270

- 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
- Pint, C. D., R. J. Hunt, and M. P. Anderson. 2003. Flowpath delineation and ground water age, Allequash Basin, Wisconsin. Groundwater **41**: 895–902. doi:10.1111/j.1745-6584.2003.tb02432.x
- R Core Team. 2020. R: A language and environment for statistical computing. R Foundation for Statistical Computing.
- Robinson, H. K., E. A. Hasenmueller, and L. G. Chambers. 2017. Soil as a reservoir for road salt retention leading to its gradual release to groundwater. Appl. Geochem. 83: 72–85. doi:10.1016/J.APGEOCHEM.2017.01.018
- Schuler, M. S., and R. A. Relyea. 2018. A review of the combined threats of road salts and heavy metals to freshwater systems. Bioscience 68: 327–335. doi:10.1093/biosci/ biy018
- Schuler, M. S., M. Cañedo-Argüelles, W. D. Hintz, B. Dyack, S. Birk, and R. A. Relyea. 2019. Regulations are needed to protect freshwater ecosystems from salinization. Philos. Trans. Roy. Soc. B Biol. Sci. 374: 20180019. doi:10.1098/rstb. 2018.0019
- Shannon, T. P., S. J. Ahler, A. Mathers, C. D. Ziter, and H. A. Dugan. 2020. Road salt impact on soil electrical conductivity across an urban landscape. J. Urban Ecol. 6: 1–8. doi:10. 1093/jue/juaa006
- 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
- Soranno, P. A., and others. 2017. LAGOS-NE: A multi-scaled geospatial and temporal database of lake ecological context and water quality for thousands of US lakes. GigaScience **6**: 1–22. doi:10.1093/gigascience/gix101
- UWSP. 2021, *Well water quality viewer: Private well data for Wisconsin.* Univ. of Wisconsin-Steven's Point, Center for Watershed Science and Education.

- Webster, K., C. Bowser, M. Anderson, and J. Lenters. 2006. Understanding the lake-groundwater system: Just follow the water, p. 19–48. *In*, Long-term dynamics of lakes in the landscape (Long-Term Ecological Research Network Series). Oxford University Press.
- Webster, K. E., T. K. Kratz, C. J. Bowser, J. J. Magnuson, and W. J. Rose. 1996. The influence of landscape position on lake chemical responses to drought in Northern Wisconsin. Limnol. Oceanogr. **41**: 977–984. doi:10.4319/lo.1996.41.5. 0977
- Williams, D., N. E. Williams, and Y. Cao. 2000. Road salt contamination of groundwater in a major metropolitan area and development of a biological index to monitor its impact. Water Res. **34**: 127–138. doi:10.1016/S0043-1354 (99)00129-3
- Xu, S., and others. 2021. Investigating groundwater-lake interactions in the Laurentian Great Lakes with a fullyintegrated surface water-groundwater model. J. Hydrol. **594**: 125911. doi:10.1016/j.jhydrol.2020.125911
- 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.

Acknowledgments

Two reviewers provided thoughtful and constructive feedback on an earlier version of this manuscript. Thanks to Carl Watras and Paul Schramm for helping to locate and sample Sparkling Lake wells, and to the NTL-LTER base crew over the years. Happy retirement Pam Montz! This research was supported by National Science Foundation DEB-1440297 and DEB-2025982.

Submitted 25 November 2020 Revised 18 March 2021 Accepted 20 March 2021