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Lakes protect downstream riverine habitats from chloride toxicity

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Abstract

Freshwater salinization from anthropogenic activities threatens water quality and habitat suitability for many lakes and rivers in North America. Recognizing that salinization is a stress on freshwater environments globally, research on watershed salt transport is necessary for informed management strategies. Prior to this research, there were few studies that examined salt export regimes along a river–lake continuum to investigate the drivers, temporal dynamics, and modulators of freshwater salinization. Here, we use high-frequency in situ monitoring to assess specific conductance–discharge (cQ) relationships, chloride concentrations and fluxes, and the role of lakes in downstream salt transport. The Upper Yahara River Watershed in southern Wisconsin, USA, is a mixed urban and agricultural watershed where the lakes' chloride concentrations have risen from < 5 mg L^{-1} in the 1940s to > 50–80 mg L^{-1} in 2021. Our results suggest cQ behavior depends on land use, with urban areas exhibiting more frequent mobilization events during stormflow and agricultural areas exhibiting predominantly dilution dynamics. In addition, chloride loading is driven by hydrology and watershed size whereas concentrations and yields are a function of anthropogenic drivers like urbanization. We demonstrate how an in-network lake attenuates downstream salinity, dampening the hydrologic, anthropogenic, and seasonal patterns observed in rivers upstream of the lake. Importantly, biogeochemical processes in lakes overlay a seasonal signal on salinity that must be considered when investigating temporal dynamics of anthropogenic salinization. This research contributes to understanding of temporal dynamics of salt export through watersheds and can be used to inform management strategies for habitat protection.

The movement and cycling of solutes and nutrients through watersheds are influenced by a variety of factors including source acquisition, flow routing, legacy storage, and biological and biogeochemical transformations (Basu et al. 2011; Lin et al. 2021). At a coarse scale, water and conservative solutes move together through the landscape, and hydrological flowpaths and connectivity are a large determinant of solute movement (Covino 2017). The degree of connectivity in a watershed results in solutes either moving quickly downstream (short residence time) or being retained in the watershed (long residence time). The presence of lakes in river networks slow water movement, and results in high rates of biogeochemical processing and sedimentation (Harvey and Schmadel 2021). Lentic environments thus act as moderators of solute transport and have been shown to buffer downstream nutrient delivery (Goodman et al. 2011; Kalinin et al. 2016; Schmadel et al. 2018; Stachelek and Soranno 2019).

Solute tracing in watersheds is a common method used to understand terrestrial impacts on water quality, source water contributions, climatic changes, and generally the hydrologic cycle and watershed transport and storage (Peters and Ratcliffe 1998; Gooseff et al. 2002; Kirchner and Neal 2013; Oni et al. 2013). For example, the mostly conservative nature of salt has led to salt injections into streams as a common method of measuring discharge and investigating hydrological flowpaths (Muehlbauer et al. 2012). Despite the great wealth of hydrological research on solute transport, there are few studies that investigate the transport of salt along a river–lake continuum explicitly within the context of anthropogenic freshwater salinization as an emerging anthropogenic stressor to freshwater environments (Reid et al. 2019). In the Midwest and Northeast United States, thousands of lakes and rivers are at risk of salinization from anthropogenic salt pollution, stemming mainly from road deicer runoff, but also agricultural sources and water softener effluent (Dugan et al. 2020). Salinization is a threat to water quality and habitat suitability as it can

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impact biotic functioning of organisms (Arnott et al. 2020; Hébert et al. 2022; Hintz et al. 2022), trigger trophic cascades (Hintz et al. 2017), lead to more frequent and intense harmful algal blooms (Lind et al. 2018), and cause prolonged or permanent anoxic conditions in lakes (Ladwig et al. 2021), which can significantly alter biogeochemical cycling (Novotny and Stefan 2012; Sibert et al. 2015; Dupuis et al. 2019).

Salinity refers to the mass of dissolved inorganic solids in water, and in most limnological settings, is considered the sum of the mass fraction of the major cations (Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}) and anions (Cl^{-}, SO_4^{2-}, HCO_3^{-}, CO_3^{2-}). Because of these charged ionic constituents, salinity can be approximated by specific conductance (SpC); a measure of water's ability to conduct electrical flow temperature corrected to 25°C, expressed in μS cm^{-1} (Dugan and Arnott 2022). Monitoring of salinization (increasing salinity) is also conducted via measurements of chloride concentrations (Cl^{-}) because it is a common anion found in most anthropogenic salts (e.g., road salt). Ultimately, both SpC and chloride are used to track salinization, keeping in mind the relationship between the two variables is site-specific due to the influence of other major ions. Given the relative ease of high-frequency monitoring of SpC, the relationship between chloride concentration and SpC can provide insights into chloride ecotoxicity and habitability of aquatic environments (Dugan and Arnott 2022).

In freshwater environments, toxicity guidelines are often set for acute exposure limits (the ability of organisms to withstand short duration exposures to high concentrations) and chronic toxicity limits (long-term exposure; US Environmental Protection Agency [EPA] 1988). Recognizing that salinity and ion concentrations in freshwater environments are impacted in part by stormflow and hydrologic connectivity (Liu and Bao 2020; Oberhelman and Peterson 2021), it is important to understand the drivers of spatiotemporal variability that may cause concentrations to exceed ecotoxicity thresholds. A useful method to examine variability in water chemistry is by examining concentration–discharge relationships, or export regimes (Diamond and Cohen 2018; Zimmer et al. 2019), which Botter et al. (2020) describe as a "fundamental descriptor of the spatiotemporal interaction between hydrological, geochemical, and biogeochemical processes in the catchment." Export regimes can differ over seasonal and hydrological scales (Minaudo et al. 2019; Knapp et al. 2020) in addition to being influenced by watershed characteristics, especially land use, which can establish and modify hydrological behavior and solute loading (Musolff et al. 2015; Minaudo et al. 2019). Concentration–discharge relationships can be described as either chemostatic or chemodynamic. In chemostasis, there is little to no change in concentration as streamflow changes, whereas chemodynamic behavior can either dilute (concentration decreases with increasing discharge), or mobilize (concentration increases with increasing discharge). Examining salt loading and export at the subwatershed scale may distinguish important dynamics caused by source complexity due to land use. Land use has demonstrated ability to alter solute loads and yields, that is, load per area (Li and Bush 2015). Understanding spatiotemporal variation of salt yield within a watershed can help determine high risk areas for toxicity and influences that individual, smaller areas have on overall watershed water quality (Mooney et al. 2020; Dugan et al. 2023; Oberhelman and Peterson 2021). In our study, we use concentration–discharge theory to examine SpC–discharge (cQ) relationships in streams across space and time to investigate seasonal patterns, land use drivers, and the influence of connectivity on the salinization of a freshwater watershed.

Here, we use high-frequency SpC sensors coupled with routine water sampling to investigate seasonal patterns in watershed chloride transport across headwater tributaries, and the role of lakes in dampening downstream chloride transport. Our study is focused on the Upper Yahara River Watershed in Dane County, Wisconsin, USA. In the Midwest United States, a link has been established between chloride concentrations and both road density and agriculture (Trowbridge et al. 2010; Corsi et al. 2015; Oberhelman and Peterson 2020), suggesting that the use of road salt during winter months and synthetic fertilizers are a ubiquitous and serious threat to our freshwaters (Kaushal et al. 2005; Laceby et al. 2019; Overbo et al. 2019). The agriculturally-intensive and highly urbanized Upper Yahara River Watershed is no exception. Over the last 80 years, two large lakes in the watershed, Lake Mendota and Lake Monona, have exhibited long-term increases in chloride (NTL-LTER 2019*a*) and in 2021, the chloride concentrations were ~ 50–80x higher than concentrations in the early 1900s (Birge and Juday 2013). Despite the known increase, chloride transport and dynamics within this watershed have not been studied. We had four research questions: (1) Is SpC an adequate proxy for tracking chloride concentrations in the Upper Yahara River Watershed? (2) Does land use influence SpC–discharge relationships across the subwatersheds draining to Lake Mendota? (3) Is there a relationship between land use and chloride loads and yields across subwatersheds draining to Lake Mendota? (4) Does the presence of lakes in the Upper Yahara River network modify downstream specific conductivity and chloride dynamics?

Methods

Study area

The Upper Yahara River Watershed in Dane County, Wisconsin, spans 82,000 ha and contains two large drainage lakes: Lake Mendota, 3961 ha and 25.3 m deep, and Lake Monona, 1324 ha and 22.5 m deep (Fig. 1a,b). The land use of the watershed is 59% agricultural, with developed shorelines around the lakes and the City of Madison situated on the isthmus between the two lakes. Lake Mendota has four major tributaries: Yahara River (YR-I), Pheasant Branch Creek (PB), Sixmile Creek (SMC), and Dorn Creek (DC). YR-I has a sizeable marsh lake (23 ha, 3 m depth) upstream of the sampling location. Roughly 8.2% of Lake Mendota's drainage area is directly

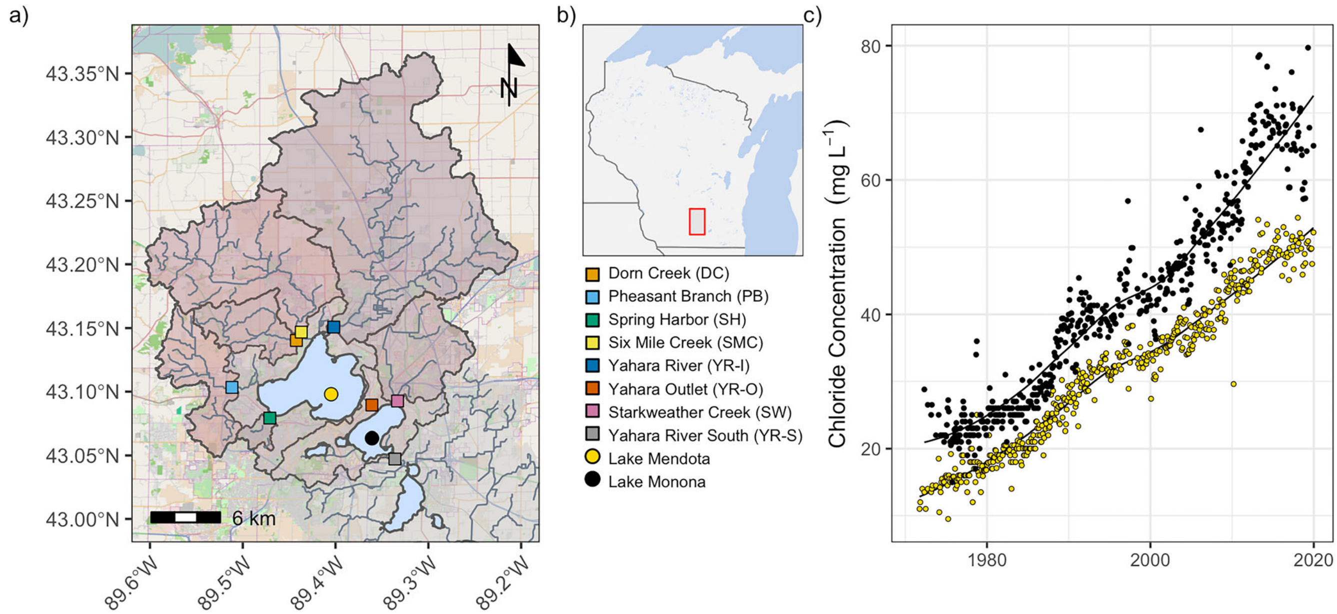

Fig. 1. (**a**) Upper Yahara River Watershed and tributary subwatersheds feeding into Lake Mendota and Lake Monona. (**b**) Location of the study area in southern Wisconsin, USA. (**c**) Chloride concentrations in the surface water of Lake Mendota (gold) and Lake Monona (black) since 1970 (data from Public Health Madison Dane County, 2020).

connected to the lake via storm sewers. This includes the Spring Harbor storm sewer (SH), which drains 18.4% of the sewershed area. Lake Mendota has one major outflow, the Yahara River (YR-O), where a lock and dam system controls lake level and downstream flow. Typically, Lake Mendota is lowered in the late-fall before the lake freezes, which results in high downstream flow. Lake Monona has two major tributaries: the Yahara River (YR-O), which connects the two lakes, and Starweather Creek (SW). The Yahara River south of Lake Monona (YR-S) is the sole outflow. These subwatersheds vary in size and land-use characteristics (Table 1). The Yahara River Outlet of Lake Monona (YR-S) is the outflow of the Upper Yahara River Watershed and all tributary subwatersheds are nested within (Fig. 1a). Subwatersheds were delineated using the USGS StreamStats R package (Hagemann 2021). Land use for each subwatershed was extracted from the 30-m resolution 2019 National Land Cover Database using FedData R package (Bocinsky 2022), and road density was extracted from the 2020 US Census Bureau data using the Tigris R package (Walker 2022; Table 1). Outfall basins were obtained from the City of Madison's GIS portal.

Field monitoring and data preparation

In-situ Onset HOBO U24 loggers were used to continuously monitor electrical conductivity (μS cm^{-1}) and water temperature (°C) every 30 min at the following tributaries from 19 December 2019 through 10 April 2021 (the study period): DC, PB, SMC, YR-I, YR-O, SW, and YR-S (Fig. 1; Table 1). Before initial deployment, all loggers were calibrated using a two-point calibration with 100 and 500 μS cm^{-1} KCl standards. Loggers were placed in protective PVC housing built according to the manufacturer's guidelines. Deployment locations were carefully chosen to ensure river water was well mixed and flowing, and the installation method was

Table 1. Watershed characteristics for the studied tributaries. Agriculture includes pasture and cultivated crops. Developed area includes low, medium, and high development.

Site	Drainage area (ha)	Agriculture %	Developed %	Road density (m ha^{-1})
Dorn Creek (DC)	3269.92	82.80	9.39	20.30
Pheasant Branch Creek (PB)	4750.24	53.34	41.03	56.64
Spring Harbor storm sewer (SH)	912.15	4.09	86.30	106.71
Sixmile Creek (SMC)	12,530.32	73.99	15.91	28.82
Yahara River (YR-I)	29,405.99	71.68	17.09	34.61
Yahara River Outlet (YR-O)	60,800.41	60.22	22.95	38.01
Starkweather Creek (SW)	5521.45	28.38	60.77	82.17
Yahara River South (YR-S)	72,207.73	53.00	29.20	46.17

dependent on site characteristics. In the Lake Mendota watershed, loggers were co-located with US Geological Survey (USGS) gauge stations, which measure river discharge at intervals ranging from 5 min to 6 h. The USGS gauge station at Spring Harbor (#05427965) storm sewer was equipped to measure both discharge and SpC (using a YSI-600), and therefore, a HOBO logger was not deployed at that location. The USGS also collected and analyzed water samples for chloride at Spring Harbor. We used the entire Spring Harbor record, which extends back to 2014 with 111 chloride observations. USGS data were downloaded from the National Water Information System via the dataRetrieval R package (De Cicco et al. 2018). In the Lake Monona watershed, neither Starkweather Creek nor the outflow (YR-S) had a gauging station, and therefore, no discharge data were available.

Weekly or biweekly during the study period, a handheld Thermo Scientific field meter was used to measure SpC at each river site to validate the in situ sensor measurements. The handheld meter was calibrated prior to every use with KCl standards of 100 μS cm^{-1} at 25°C and 500 μS cm^{-1} at 25°C. At each of the site visits, 30–60 mL of water was collected via grab sampling. Samples were filtered through 25-mm, 0.45-μm pore sized filters and refrigerated. Chloride concentrations were analyzed via ion chromatography on a Dionex 2100 equipped with IonPac AG11 analytical column.

All raw electrical conductivity measurements were converted to SpC corrected to 25°C using:

$$\mathrm{SpC} = \frac{C_e}{1-((25-T)*(a/100))} \tag{1}$$

where SpC = specific conductance in μS cm^{-1}, C_e = electrical conductivity in μS cm^{-1}, a = 2.1% °C^{-1} (temperature coefficient), and T = water temperature in °C.

Any measurements collected while the loggers were outside the water or frozen in ice were removed prior to analyses. For each discharge and SpC timeseries, a 6-h moving average was applied using the zoo R package (Zeileis and Grothendieck 2005) to filter noise from the data. For discharge, all negative values were set to 0 m^3 s^{-1}. Negative values were most common in the Yahara River site YR-I, where high winds can cause back flow from Lake Mendota.

In addition to tributary observations, we obtained major ion data for Lake Mendota and Lake Monona through the North Temperate Lakes Long-Term Ecological Research program (NTL-LTER). Depth-discrete concentrations of calcium, potassium, magnesium, sodium, chloride, and sulfate were collected quarterly. Dissolved inorganic carbon and pH were collected monthly, and were used to calculate concentrations of bicarbonate and carbonate (NTL-LTER 2019*a*,*b*).

Chloride loads and yields

In environments impacted by road salt, chloride has been shown to be the major driver of SpC (Cooper et al. 2014; Kaushal et al. 2018; Haake and Knouft 2019). Linear regressions were used to model the relationships between SpC and chloride concentration in each of the tributaries. Regressions were conducted in log–log space to normalize distributions and balance model fit in cases with few high concentration data points. Linear regression assumptions (normality of residuals, normality of random effects, linear relationship, homogeneity of variance) were checked using the performance R package (Lüdecke et al. 2021). All models sufficiently passed these tests, although some suffered from poor fit at extreme values. We provide 95% confidence intervals in application of these models.

Linear models of Cl ~ SpC were used to calculate continuous timeseries of chloride concentration from the high-frequency SpC timeseries along with a 95% prediction interval. Chloride concentrations were multiplied by discharge to estimate chloride loads (mass). We calculated the *z*-score of chloride mass loading for each tributary to directly examine the similarities and differences between the timeseries on the same scale. Chloride yields were calculated by normalizing loads by watershed area. To estimate the chloride contribution from storm sewers connected directly to Lake Mendota, we extrapolated the Spring Harbor storm sewer load by multiplying these data by 5.42 (100/18.4); with the explicit assumption that loading from all other storm sewers is identical to that of Spring Harbor. We believe this assumption is credible as the entire sewershed encompasses urban land use (developed roads), and all roads are maintained by the municipal and county roads departments who use similar salting practices. None of the storm sewers receive sewage effluent or other major industrial inputs of chloride.

Individual site data were summarized to median chloride concentration, chloride load, and chloride yield (n = 6). Individual linear models were used to investigate the significance of drivers (percent development in the watershed, road density, watershed size, and average discharge) on chloride characteristics. We also used linear models with interaction terms to investigate how season moderates landscape drivers. Site data were summarized by season (n = 25), and modeled using the following models:

$$\text{Chloride Load} \sim \text{Total Discharge} + \text{Developed:Total Discharge} \tag{2}$$

$$\text{Chloride Yield} \sim \text{Developed:Season} \tag{3}$$

cQ relationships

SpC–discharge relationships were analyzed in log–log space to facilitate direct comparisons between sites and remain consistent with methods in previous studies of hydrologic controls on solute transport (Musolff et al. 2015; Heppell et al. 2017; Knapp et al. 2020; Gorski and Zimmer 2021). We use SpC instead of chloride to minimize any errors associated with the linear model estimations of chloride concentrations.

At each gauged site (excludes ungauged SW and YR-S), cQ relationships were established for the entire study period as well as stormflow events and baseflow events. The cQ relationships were analyzed by examining the slopes in each subwatershed for all flows, as well as seasonally (January–March, April–June, July–September, and October–December). The slopes of the relationships were examined to identify chemostatic or chemodynamic behavior. Chemostatic behavior was defined as a $|\text{cQ slope}| < 0.05$. Negative cQ slopes (< -0.05) implied chemodynamic dilution behavior, as concentration decreases with increasing discharge, and positive cQ slopes (> 0.05) implied chemodynamic mobilization behavior, as concentration increases with discharge (Knapp et al. 2020).

Baseflow separation was executed using the Eckhardt method (Eckhardt 2005; Zipper 2018). The Eckhardt method was chosen because discharge data at timesteps less than 1-d can be used (Eckhardt 2008). The code from Zipper (2018) allowed for customization of baseflow index (BFI) maximum and recession constant. BFI maximum was set to 0.80, appropriate for a perennial stream (< 10% waterless duration; Eckhardt 2008) with a porous aquifer. The recession constant, or the rate that baseflow recedes after a stormflow event, is a ratio of baseflow to the previous day's baseflow. It was calculated using methods from Brutsaert (2008). Stormflow events were chosen based on the following rules adapted from Knapp et al. (2020) and Gorski and Zimmer (2021) and were identified using modified R code from Gorski (2020):

- Stormflow events were generated by precipitation, that is, precipitation had to occur within 2 d prior to the event to ensure extraneous events caused by wind were not evaluated. Precipitation data from the Dane County airport station were available from the National Centers for Environmental Information National Oceanic and Atmospheric Administration (Menne et al. 2012*a*,*b*).
- The rising slope of the stormflow events were $> 1 \times 10^{-6}$ $m^3\ s^{-1}$ per second.
- The difference between the peak discharge and the Eckhardt baseflow was greater than the annual average discharge.
- The recessing slope of the storm flow event was $< 0\ m^3\ s^{-1}$ per second.
- The stormflow event ended when the slope became $\leq 0\ m^3\ s^{-1}$ per second, or when the discharge returned to pre-event levels.

Results

Observed patterns in SpC and chloride time series

Among the tributaries upstream of the lakes, seasonal patterns of SpC and chloride behaved similarly, with peaks during the winter and early spring and decreases during the summer (Fig. 2). SpC of Spring Harbor storm sewer ranged from 0 to 57,700 $\mu S\ cm^{-1}$ and is shown separately from the larger tributaries (Supporting Information Fig. S1). The distribution of recorded SpC at individual sites was compared using Tukey's range test, which found significant differences in the mean SpC at all sites ($p < 0.001$), with the exception of Dorn Creek and Sixmile Creek, and YR-O and YR-S (Supporting Information Fig. S2a). The most developed watersheds, Spring Harbor, Starkweather Creek, and Pheasant Branch Creek, had the highest mean SpC over the study period, at 1005, 1235, and 1132 $\mu S\ cm^{-1}$, respectively.

Downstream of the lakes, at YR-O and YR-S, SpC and chloride concentrations showed much less annual variability, with only a small decrease in SpC from July to October. The lowest chloride concentrations occurred during the months of May to July, while the highest concentrations occurred during the months of January and February. Median chloride concentrations ranged from the lowest in Dorn Creek (31 $mg\ L^{-1}$) to the highest in Spring Harbor (325 $mg\ L^{-1}$). Overall, Spring Harbor exhibited the highest concentrations and the greatest variation in concentration (mean = 368 $mg\ L^{-1}$, standard deviation = 424 $mg\ L^{-1}$). Excluding the Spring Harbor storm sewer, Starkweather Creek had the highest concentrations and variation (mean = 198 $mg\ L^{-1}$, standard deviation = 116 $mg\ L^{-1}$). In the nonurban watersheds and the lake outflows (Dorn Creek, Sixmile Creek, YR-I, YR-O, YR-S) and Pheasant Branch Creek (38% developed), our manual sampling appeared to capture the range of chloride concentrations, as the maximum manually sampled SpC was similar to the maximum SpC recorded on the in situ SpC sensors (Table 2). In Starkweather Creek, the most urban watershed, and Spring Harbor storm sewer, maximum recorded SpC was 2–3× greater than manually sampled SpC. Therefore, it is possible that chloride concentrations in Starkweather Creek were > 1000 and > 15,000 $mg\ L^{-1}$ in Spring Harbor.

Linear regressions of SpC and chloride had strong correlation in the highly urbanized watersheds (Spring Harbor: $r^2 = 0.95$, Starkweather Creek: $r^2 = 0.87$, Pheasant Branch Creek: $r^2 = 0.87$). Correlations were weaker, yet still significant, in the more agricultural watersheds (YR-I: $r^2 = 0.58$, Sixmile Creek: $r^2 = 0.54$, Dorn Creek: $r^2 = 0.36$; Fig. 3; Supporting Information Table S1). There was no correlation between SpC and chloride downstream of Lake Monona at YR-S. Across the gauged Lake Mendota tributaries, median chloride concentrations were strongly correlated to the percentage of development and road density in the subwatersheds ($p < 0.001$, $r^2 = 0.99$ and $p < 0.001$, $r^2 = 0.98$, respectively; Supporting Information Table S2).

To explore the weak to nonexistent relationship between SpC and chloride in the lake outflows (YR-O and YR-S), we examined seasonal changes in individual ion concentrations in the surface of Lake Mendota and Lake Monona. In both lakes there were no seasonal patterns in chloride concentrations (Fig. 4). However, there were annual decreases in bicarbonate from July to October, as well as August minima in calcium and maxima in pH that correspond to the SpC minima.

Hydrograph analysis and salinity regimes

Over the study period, the majority of flow events exhibited either chemostatic or dilution behavior with respect

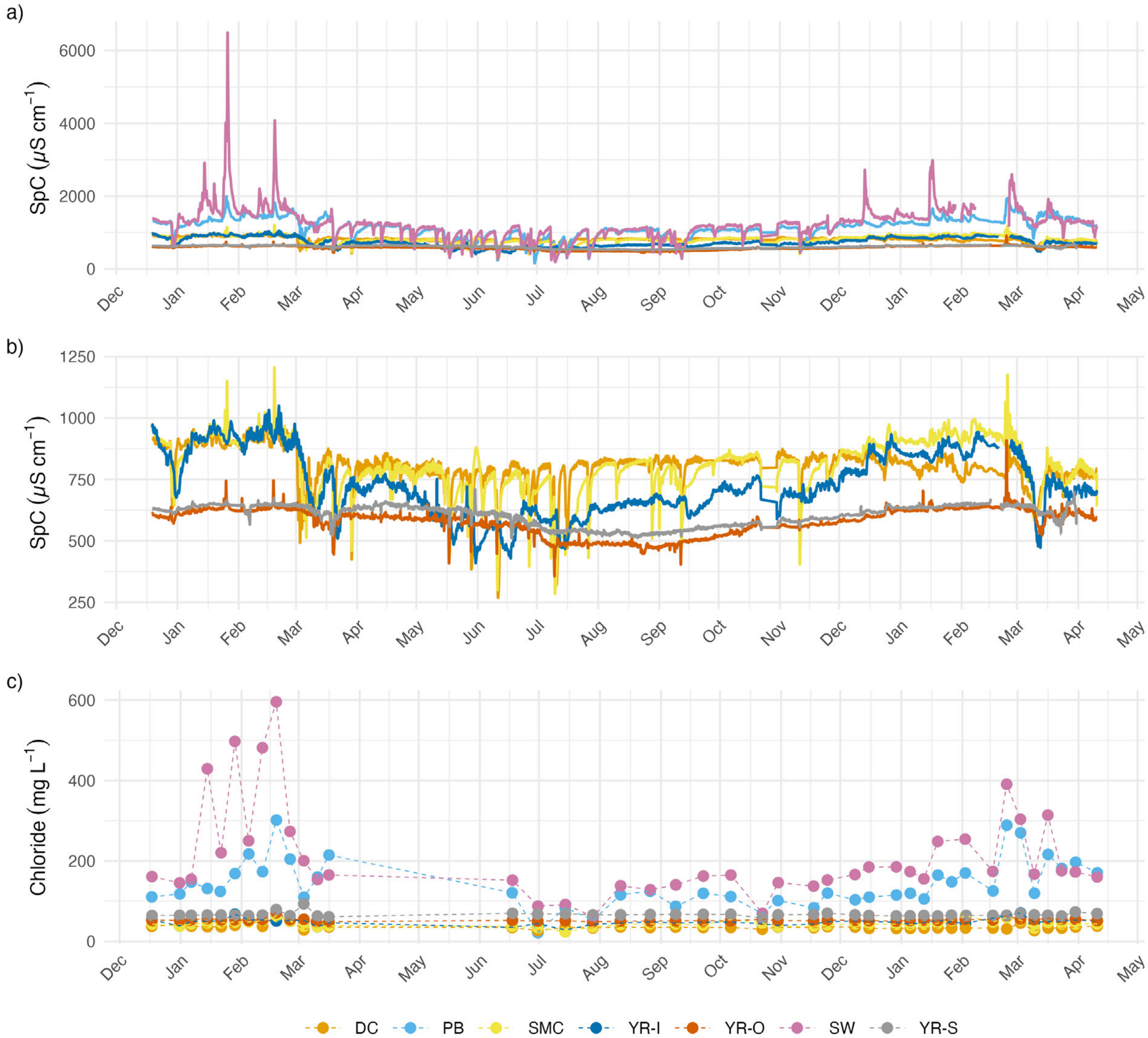

Fig. 2. Timeseries of (**a**) SpC in all river tributaries from December 2019 to April 2021. (**b**) SpC in the river tributaries excluding the highly developed subwatersheds (PB and SW). (**c**) Manually sampled chloride concentrations. Due to high concentrations, SH is shown in Supporting Information Fig. S1.

to SpC (Fig. 5; Supporting Information Fig. S3) with some notable mobilization events. Spring Harbor in particular had numerous storm events that mobilized salts, specifically in January–March and April–June. In the least developed watersheds Sixmile Creek and Dorn Creek, all stormflow events diluted SpC concentrations (Table 3). The Yahara River, the largest of the rivers, exhibited mainly chemostatic stormflow events. Though YR-I had 12 events that mobilized salt and 13 events that diluted salt. Note that YR-I is prone to backflushing from Lake Mendota, which likely contributes to the high number of stormflow events compared to the other Lake Mendota inflows and may have led to some discrepancy with the expected results for this tributary.

The BFI in gauged tributaries ranged from 20% (Spring Harbor) to 83% (Sixmile Creek) for the individual tributaries (Table 3). The Lake Mendota outflow (YR-O) has a BFI of 76%. The average number of stormflow events across all rivers was 42, though it varied considerably between rivers. YR-I had the highest number of stormflow events ($n = 67$), and YR-O had the lowest number of stormflow events ($n = 8$; Table 3). Streamflow separation revealed that across the Lake Mendota watershed, tributaries had varying percentages of chloride exported during baseflow vs. stormflow (Supporting Information Table S3). Across the full record, 74% of Spring Harbor chloride was exported during stormflow, which would be expected for an urban storm sewer. The other tributaries had < 51% chloride export via stormflow. The Lake Mendota outflow (YR-O) had only 12% chloride export during stormflow overall and was the only tributary to consistently have greater baseflow contribution throughout the year.

Table 2. Date of maximum observed chloride concentration and SpC (manual sampling), as well as maximum recorded SpC (6-h moving average, sensor) at the monitored tributaries.

Site	Date	Max chloride (mg L^{-1}) (manual sampling)	SpC (μS cm^{-1}) (manual sampling)	Maximum SpC (μS cm^{-1}) (in situ sensor)
Dorn Creek	18 Feb 2020	65.3	1012	985
Pheasant Branch Creek	18 Feb 2020	302.0	1926	1996
Spring Harbor storm sewer	20 Feb 2014	6920.0	19,800	55,400
Six Mile Creek	02 Feb 2021	63.6	986	1206
Yahara River (YR-I)	02 Mar 2021	70.5	908	1050
Yahara River Outlet (YR-O)	18 Feb 2020	71.4	684	909
Starkweather Creek (SW)	18 Feb 2020	595.0	2863	6491
Yahara River South (YR-S)	03 Mar 2020	93.2	661	710

Chloride mass balance

Chloride load at the five tributaries was driven by total discharge, such that the watershed with the largest areas contributed the highest load (Fig. 6a). Across the Lake Mendota watershed, there was a significant, positive correlation between chloride load and the drainage area size (p-value < 0.001, $r^2 = 0.99$) and with average discharge in each tributary (p-value < 0.001, $r^2 = 0.98$). Yield of chloride, which accounts for varying subwatershed sizes, had significant, positive correlations with road density (p-value < 0.001, $r^2 = 0.98$) and percentage of development (p-value < 0.01, $r^2 = 0.99$; Supporting Information Table S2).

Chloride loading was further moderated seasonally by stormflow events and by the percent development within the watershed. Across the five inflowing tributaries, an ordinary least squares (OLS) linear model (Eq. 2) revealed that total discharge and the interaction term of development percentage : total discharge significantly influenced seasonal chloride load ($r^2 = 0.93$; Supporting Information Table S4). Stormflow contributions were important in this model in that they influenced total discharge. Chloride yields, where load was adjusted for watershed area, decreased along a gradient of high to low urban watershed development (Fig. 6b). An OLS linear model (Eq. 3) of chloride tield ~ Developed : Season had an adjusted r^2 of 0.84, with the interaction terms of Developed : January–March and Developed : April–June being significant (Supporting Information Table S4).

The mass of chloride flowing into Lake Mendota showed a pattern of high variability during the winter and early spring months. The long residence time of Lake Mendota dampened this signal in the outflow (YR-O, Fig. 7a). In 2020, the residence time of Lake Mendota was 2.6 years as calculated by lake volume (5×10^8 m^3) divided by annual outflow at YR-O. The anomalously large increase in chloride load in November and December at YR-O was a response to higher discharge due to human-controlled lake level lowering. The monthly mass

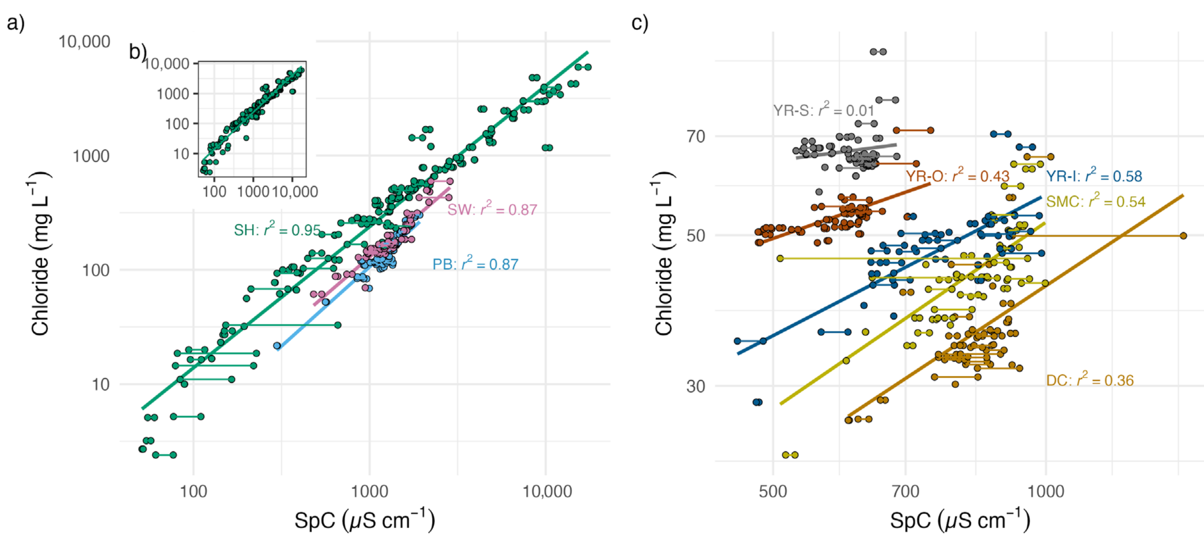

Fig. 3. Linear regressions of chloride concentrations vs. SpC for all tributaries and associated r^2 values from log–log models. Horizontal lines represent paired SpC measurements from the hand-held and in situ meters for all sites but SH. (**a**) Linear regressions for the tributaries with highly developed subwatersheds. (**b**) Inset showing the full linear regression for Spring Harbor (SH). (**c**) Linear regressions for the nonurban tributaries.

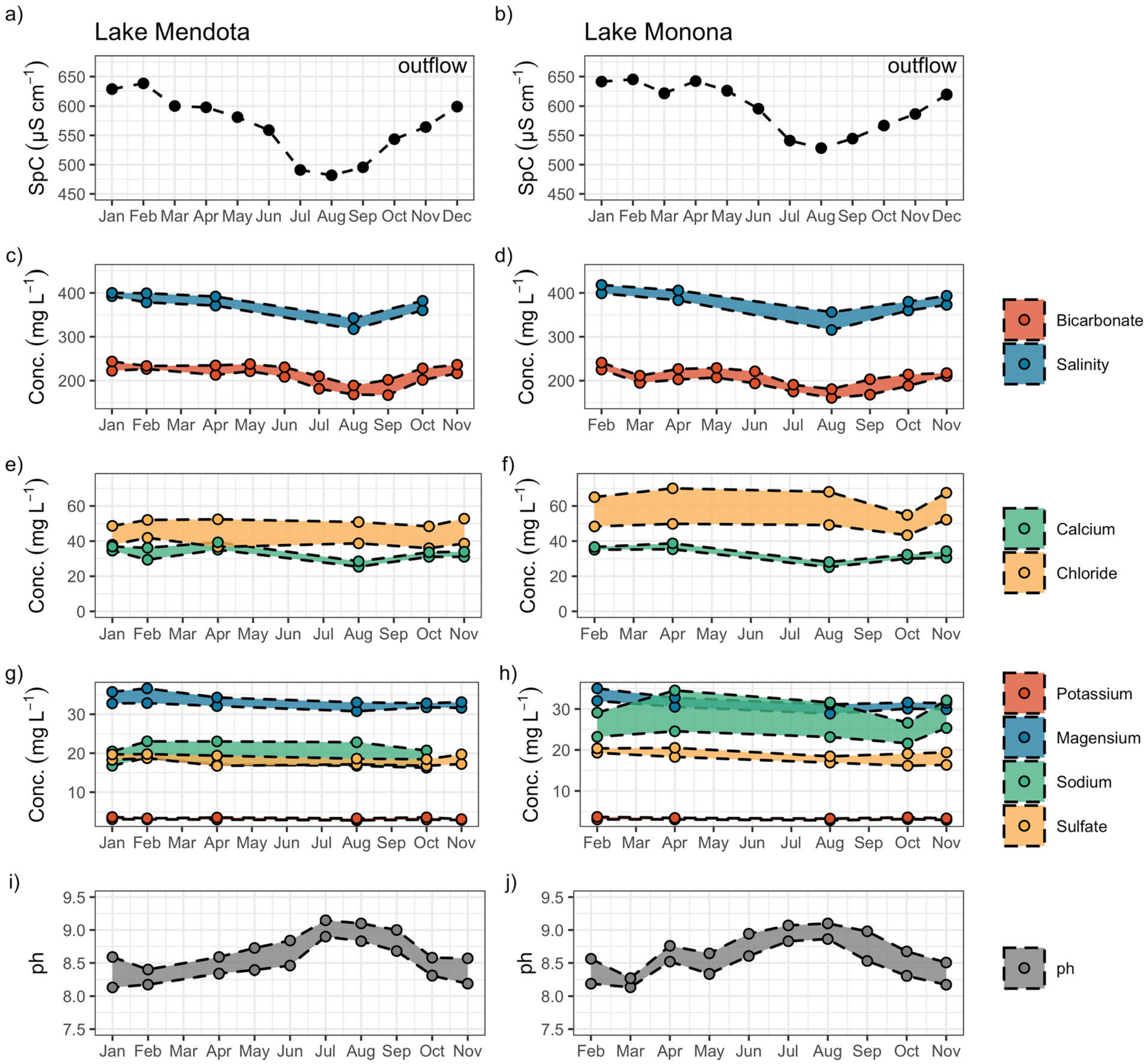

Fig. 4. (**a**,**b**) Monthly changes in SpC in the lake outflows over the study period. (**c**–**j**) Seasonal patterns in major ion concentrations and pH in the surface of Lake Mendonta and Monona. Ribbons illustrate the range between 25th and 75th percentile of the long-term concentrations. The ribbons for chloride and sodium are wider due to long-term increases (not seen in other parameters).

balance of chloride reveals that Lake Mendota was a sink of chloride in the winter, specifically March, and a source of chloride in the late summer and fall. Our calculated annual 2020 mass balance for the lake was −1213 Mg (95% prediction interval −2247 to 1086 Mg), with 8834 Mg flowing in and 10,047 Mg leaving the lake. Care should be exercised when using this value, as there is large uncertainty surrounding both storm sewer contributions and the SpC–chloride relationships in the lake outflow.

Discussion

Validity of using SpC as an indicator of chloride dynamics

Concern around anthropogenic chloride pollution has led to renewed interest in freshwater salinity regimes. Given the importance of chloride as a regulated water quality indicator, and difficulty in measuring chloride concentrations in situ, an important question is whether relative fluctuations in SpC (a proxy for salinity) are a reliable indicator of fluctuations in chloride concentrations. In many freshwater environments with high chloride pollution, the answer is yes, SpC is a reliable indicator (Cooper et al. 2014; Kaushal et al. 2018; Haake and Knouft 2019). In the Upper Yahara Watershed, we found that SpC is a reliable indicator of chloride dynamics in headwater tributaries, especially those draining urban landscapes. However, our results reveal that seasonal biogeochemical processes in lakes alter this relationship.

Downstream of Lake Mendota and Lake Monona, we found that SpC–chloride relationships become weak to nonexistent as a result of in-lake processes. Given the long residence times

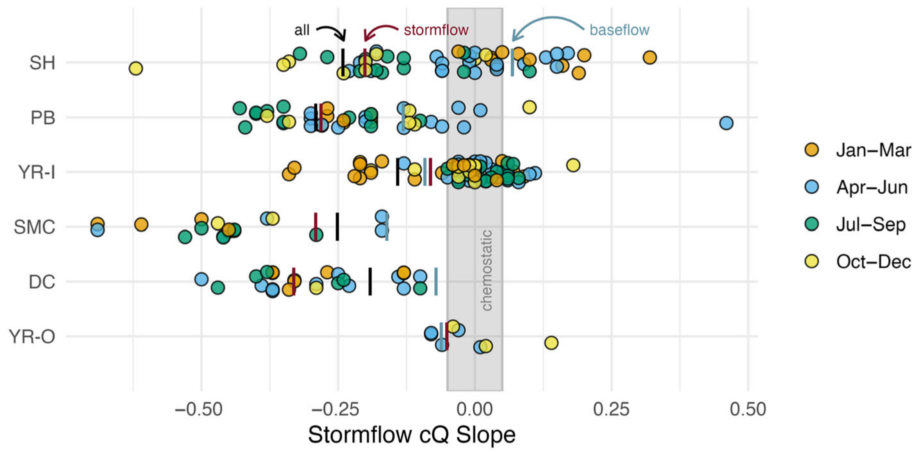

Fig. 5. Log of SpC – log of discharge (cQ) slopes of individual stormflow events at each monitoring station. Colors of circles indicate season in which stormflow event occurred. Vertical lines are the average cQ slopes of the full record (black), annual baseflow data (blue), annual stormflow data (red). Gray box indicates chemostatic behavior. Note that in YR-O, the average stormflow slope overlaps the full record.

of the lakes (Lake Mendota: ~ 4 years, Lake Monona: ~ 1 yr; Brock 1985), chloride concentrations show little seasonal variation in the surface water, and therefore are relatively constant in the outflows (YR-O, YR-S). However, outflow SpC decreases in the summer. We believe this is due to summertime bicarbonate uptake by phytoplankton, causing an increase in pH and a decrease in calcium solubility, leading to episodes of calcium precipitation (Walsh et al. 2019), which are reflected in the lower summer calcium concentrations (Fig. 4). Because Lake Monona receives the majority of its inflow from Lake Mendota, this phenomenon is compounded downstream of the second lake, leaving SpC an unreliable indicator of chloride dynamics in the outlets, as variations are being driven by changes in calcium and bicarbonate concentrations. This inference raises the reasonable question of whether biogeochemical processing alters salinity in rivers, and future investigations of watershed salinity dynamics are urged to collect seasonal samples for major ion analysis alongside chloride and SpC measurements.

Land use influence on cQ behavior in tributaries

Our analysis of export regime dynamics focuses on the tributaries of the Lake Mendota watershed. Given the positive correlation between SpC and chloride concentrations in these tributaries, we consider our discussion of hydrological and export regimes to reflect that of chloride or salinity.

Chloride is supplied to Lake Mendota watershed through anthropogenic activities, namely road salt application. Therefore, there is a finite amount available, and dilution export regimes would be expected based on the results of previous studies (Basu et al. 2011). Previous studies of salinity or chloride cQ relationships confirm long-term dilution regimes (Wulkowicz and Saleem 1974; Albek 1999; Uddin and Haque 2010; Knapp et al. 2020), though long-term dynamics are not always indicative of the entire story (Knapp et al. 2020). Stormflow events may at times mobilize solutes, during which rapid increases in chloride concentration might cause brief periods of acute toxicity to aquatic organisms.

Table 3. BFI calculated as the Eckhardt baseflow, and total number of stormflow events for each tributary. SpC vs. discharge slopes (log–log) were used to define events as mobilization (> 0.05), chemostatic (< 0.05 and > −0.05), dilution (< −0.05), or undefined if *p* values were > 0.05.

Site	Eckhardt BFI (%)	No. of events	Mobilization events	Chemostatic events	Dilution events	Undefined events
Dorn Creek (DC)	77	26	0	0	25	1
Pheasant Branch Creek (PB)	49	41	2	1	36	2
Spring Harbor (SH)	20	51	12	8	23	8
Sixmile Creek (SMC)	83	18	0	0	18	0
Yahara River (YR-I)	42	67	12	27	13	15
Yahara River Outlet (YR-O)	76	8	1	3	3	1

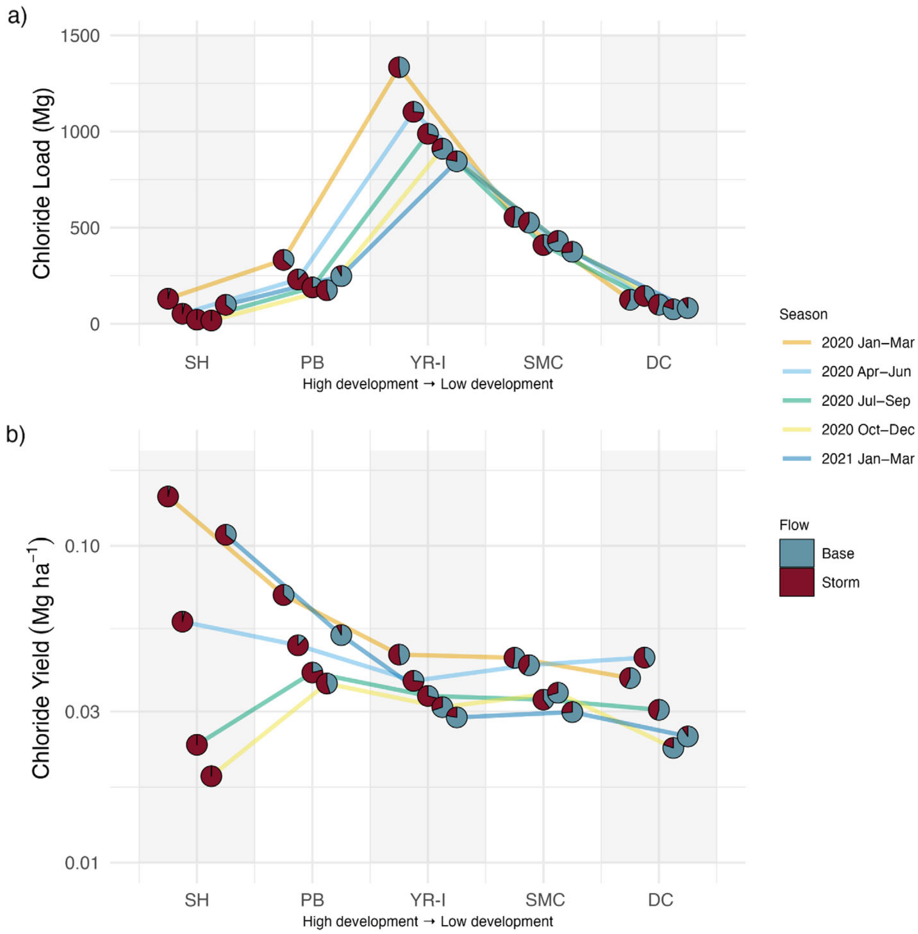

Fig. 6. (**a**) Total chloride load and (**b**) total chloride yield per season across the tributaries flowing into Lake Mendota. The proportion of stormflow vs. baseflow discharge is shown in individual pie charts.

In the Lake Mendota watershed, we saw mainly dilution regimes in the tributaries upstream of the lake, though deviations show how land use impacts salt transport. We observed considerable variation between rivers in the number of stormflow events; likely due to the differences between the rivers' hydraulic configurations, which can influence water residence time, biogeochemical cycling, hydrologic response, and streamflow generation (Covino 2017; Marcé et al. 2018). We believe that rural SMC and DC watersheds had fewer stormflow events because the rivers respond less quickly to rainfall events than the urban PB and SH watersheds. In effect, a single stormflow event in SMC and DC may be recorded as multiple events in SH. YR-I, was an outlier in this pattern, but we believe backflow and mixing from Lake Mendota at this site may have contributed to our high event enumeration.

All stormflow events in the agricultural Dorn Creek and Sixmile Creek tributaries showed dilution behavior (Fig. 5). Dorn Creek, with the highest overall percentage of agriculture (83%) and the lowest percentage of development (9%), demonstrated mainly chemostatic baseflow regimes in all seasons, which may indicate of legacy salt storage from agricultural practices in the soils and a small upstream wetland that dampens chloride pulses (Supporting Information Fig. S3). Previous studies in urban and rural streams have demonstrated high chloride concentrations year-round due to legacy salt storage in the terrestrial landscape. In watersheds where this is occurring, shallow groundwater contamination may become a problem (Kelly et al. 2008; Gardner and Royer 2010; Cooper et al. 2014; Robinson and Hasenmueller 2017; Kelly et al. 2019; Oberhelman and Peterson 2020). In addition, in all tributaries except Spring Harbor, chloride transport occurred mainly via baseflow, further indicating chloride storage and constant release (Supporting Information Table S3). Only during times of heavy rainfall (April–September) did chloride loading via stormflow increase throughout the watershed (Supporting Information Fig. S4). Year-round high concentrations raise the potential for toxicity at various stages of organism growth; and some stages may be more sensitive than others (Lawsona and Jackson 2021). Landscape storage can also lead to slow salinization that can result in decades of water quality problems as concentration continues to increase even if salt application on the landscape was to cease (Bester et al. 2006; Ludwikowski and Peterson 2018; Dugan and Rock 2023).

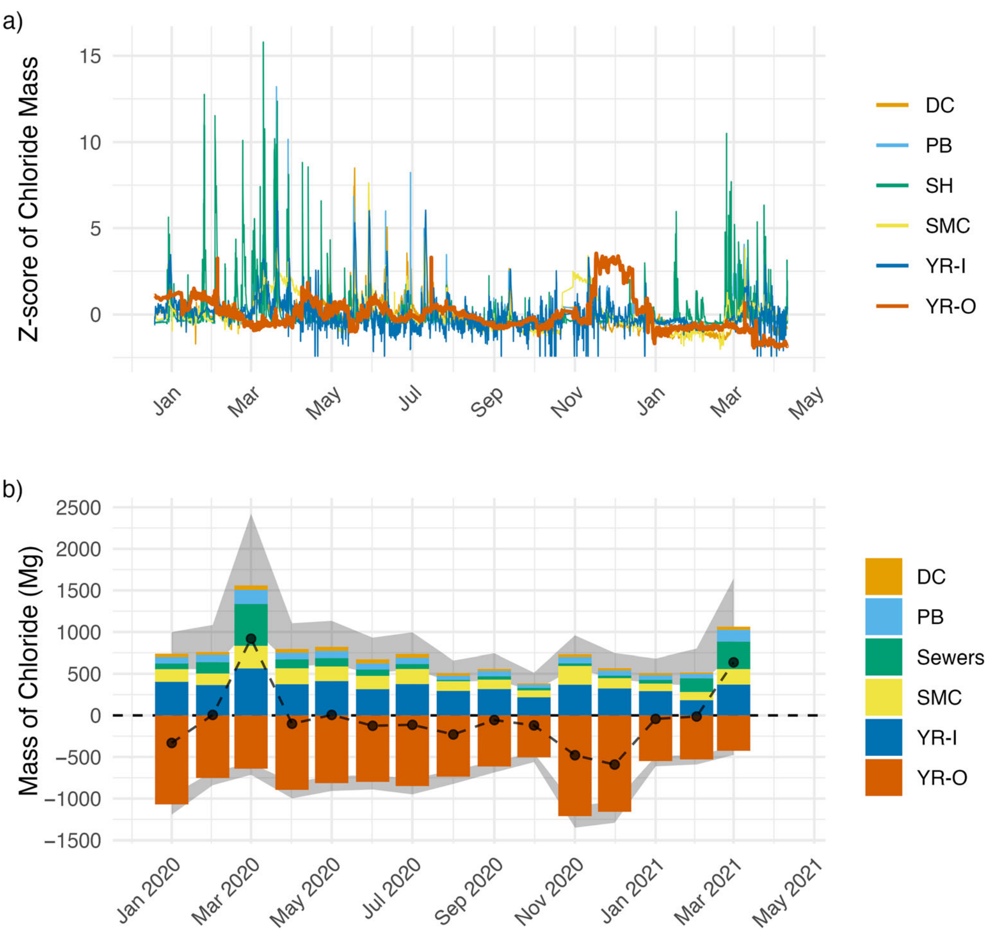

Fig. 7. (**a**) Timeseries of *z*-scores for each subwatershed's daily chloride load from December 2019 to April 2021. The thicker orange line is the Yahara River Outlet (YR-O) of Lake Mendota. (**b**) Monthly mass balance of chloride in metric tonnes (Mg) flowing into (positive bars) and out of (negative bars, YR-O) Lake Mendota. The colors of the bars indicate the river exporting that proportion of chloride load, including the total storm sewer load estimated by extrapolating SH. The gray ribbon represents the 95% prediction interval, and the black dotted line represents the monthly mass balance.

In the most urban watershed, Spring Harbor, stormwater mobilization events indicate an ample supply of salt in the winter and spring, which causes chloride concentrations to increase with flow (Fig. 5). Spring Harbor had multiple mobilization events that led to chloride concentrations exceeding EPA aquatic chronic toxicity threshold of 230 mg L^{-1} in the winter (Fig. 2; Supporting Information Fig. S1). Surprisingly, Pheasant Branch Creek a watershed with 38% urban development had only two stormwater mobilization events. While there were many large spikes in SpC and chloride concentration during the winter months in Pheasant Branch Creek, they occurred simultaneously with large increases in discharge. The difference in chemodynamic behavior between the Spring Harbor watershed and the Pheasant Branch Creek watershed suggests that only in the most urban watersheds is there enough salt on the landscape to increase chloride concentration during mobilization events. That said, Pheasant Branch Creek had many instances when winter chloride concentrations were >230 mg L^{-1} at low flows. Based on SpC dynamics, these episodes can last for days, suggesting a major threat to riverine habitat during baseflow conditions.

Land use drivers of chloride load vs. yield

In the Lake Mendota watershed, we found that tributaries with the largest watersheds contribute the greatest chloride load to the lake, demonstrating the importance of watershed size and total discharge. However, the relationship between total discharge and chloride load was moderated by the amount of developed land in the watershed. Urban watersheds play an outsized role in chloride loading. Area-normalized chloride yields reveal a similar conclusion that the highest yields are in developed watersheds in the winter and spring (Supporting Information Table S4). Similar to other Midwestern cities, this conclusion points to winter road deicing as the main source of salt driving chloride loading into Lake Mendota.

Upstream of Lake Mendota, the threat of chloride toxicity in riverine habitats is driven by land use, but once water enters Lake Mendota, the threat of chloride toxicity is dampened due to mixing and long residence times, and reiterates the need for different management approaches for protecting riverine habitat vs. lake habitat; a similar result to a study of chloride loading from Lake Michigan tributaries (Dugan et al. 2023). Assessing yields rather than loads may be more useful at the local level in discerning the areas most vulnerable to chloride toxicity, as even seemingly small contributions can play a large role in overall lake water quality (Mooney et al. 2020).

Lakes act as chloride and hydrologic reservoirs

Lakes play a key role in transporting and processing water and solutes downstream. How lakes impact the storage and export of salt in a watershed is largely governed by lake hydrology. Lakes can act as sources or sinks of solutes and nutrients depending on in-lake biogeochemical processes (Kalinin et al. 2016). For instance, lakes in a river network have been shown to be sinks of nitrate and phosphate, which decrease nutrient concentrations in downstream river reaches (Kalinin et al. 2016). Given that chloride is a relatively conservative solute, there are few biogeochemical transformations that remove chloride from the water. Processes like deposition and evapoconcentration can impact chloride concentrations, but are unlikely to be of any consequence in the Yahara lakes (Kirchner et al. 2010; Svensson et al. 2012). However, since lakes slow down the movement of water, it was expected that the presence of a lake in a river network should fundamentally change the salinity regime in downstream river reaches (Harvey and Schmadel 2021). In the case of Lake Mendota, with an average water residence time of 4 yr (Brock 1985), the long-term increase in chloride concentrations in the lake demonstrates that the lake is acting as a chloride reservoir (Fig. 1c), effectively delaying the transport of this salt downstream. Comparing the upstream tributaries to the lake outflow (YR-O), it is clear that the lake is inhibiting chloride pulses in the downstream river, which protects the downstream riverine habitat from salinity shocks. Overall, chloride concentrations in YR-O are similar to that of the lake, and show the smallest range of all the monitored rivers (Figs. 2, 7). In addition, the monthly chloride flux (Fig. 7) shows how the lake holds much of the loaded chloride. There is only a significant release of chloride load during the fall when water levels are lowered via a dam. Thus, the presence of Lake Mendota in this watershed both serves as a constant source of chloride to YR-O, while lessening the impact of both the hydrologic and anthropogenic controls on chloride observed in the upstream tributaries.

Conclusion

Using high-frequency in situ monitoring in a watershed that is undergoing anthropogenic salinization, we examined SpC–discharge relationships, chloride concentrations, and chloride flux to investigate seasonal patterns, local drivers, and the influence of in-network lakes on salinization. Lakes within river networks have the ability to significantly alter river export (Powers et al. 2014), though prior to this study, none have examined this in the context of the salinization, a serious threat to our freshwater lakes and rivers. Here, we demonstrated how in-network lakes in a mixed land use watershed attenuate downstream salinity, dampening the hydrologic, anthropogenic, and seasonal patterns observed in rivers upstream of the lakes. Given that the national trends of increasing urbanization and industrialization of agriculture are expected to continue (Urban 1991; Elmqvist et al. 2013), water quality impairments from freshwater salinization are likely to remain a threat in the future. Understanding the differences in controls on salinization between rivers and lakes and the utility and applicability of high-frequency monitoring provides important knowledge to assist in developing reduction strategies.

Data availability statement

Collected data are published and available through the Environmental Data Initiative at 10.6073/pasta/7134f06cd0af9b289030a9886f7ad83d (Rock and Dugan 2021). Scripts to create figures are accessible at 10.5281/zenodo.7709553 and can be reproduced using R (R Core Team 2020).

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Conflict of interest

None declared.

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