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The Impacts of Road Salt on Water Quality and Phosphorus Dynamics in an Urban Lake

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The Impacts of Road Salt on Water Quality and Phosphorus Dynamics in an Urban Lake

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Abstract

Road salt runoff from de-icing applications has notably increased chloride concentrations in lakes throughout north temperate regions of the planet, with negative impacts on freshwater ecosystems. For the past 20 months, I have monitored the water quality of a chloride-impaired lake and associated tributary in Grand Rapids, Michigan. Chloride levels in the deepest part of the lake have reached up to 331 mg/L, above EPA chronic toxicity thresholds. The salt-induced density gradient has prevented the lake from completely mixing during my study period and created persistent hypoxia in the hypolimnion. Total phosphorus (TP) concentrations in the hypolimnion can exceed 7500 µg/L, in contrast to epilimnion TP concentrations of ≤40 µg/L, suggesting internal phosphorus loading may be significant in this lake. I conducted an experiment to examine the impacts of excess chloride on sediment phosphorus release. Sediment cores collected from the lake bottom were brought back to the lab and measured for phosphorus release under different oxygen (present/absent) and chloride (high/low) treatments over the course of 25 days in a controlled environment. Mean maximum TP release was greatest in cores exposed to the high chloride/anoxic treatment ($1.71 - 2.23$ mg m^{-2} d^{-1}) compared to low

chloride/anoxic treatment ($0.83 - 1.42$ mg m^{-2} d^{-1}), suggesting that elevated road salt concentrations may exacerbate internal phosphorus loading. However, the release of soluble reactive phosphorus was influenced by the sediment source, suggesting that phosphorus release from salinization is dependent on sediment composition. The results from my study have management implications. Excess phosphorus concentrations in the hypolimnion need to be reduced prior to addressing the elevated chloride, to avoid lake turnover and introduction of high phosphorus concentrations into the upper layers of water, where in combination with higher light

levels, algal blooms would form. Once phosphorus concentrations are reduced, perhaps via

chemical inactivation, the excess salt issue can be addressed. However, elevated hypolimnetic

phosphorus concentrations are a symptom of the larger issue of road salt runoff into the lake.

Without a reduction in saline deicer application and associated runoff into the ecosystem, lakes

will continue to experience negative impacts from elevated chloride concentrations.

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Chapter 1

Introduction

Anthropogenic inputs to freshwater aquatic environments threaten to alter the structure

and function of these ecosystems (Carpenter et al. 1998, Reid et al. 2019). Human exploitation

and contamination particularly endanger freshwater lakes, which are strongly influenced by

terrestrial processes and have generally long water residence times that allow for the

accumulation of external inputs and pollutants (Wetzel 2001). Although lakes cover only 3% of

the earth's surface, long-term variation in these systems can offer indications of significant local,

regional, and even global changes (Williamson et al. 2008).

Two of the largest threats to freshwater lake ecosystems are eutrophication and

salinization (Reid et al. 2019). Eutrophication is the response of water bodies to excess nutrients

and may cause a number of problems in freshwater ecosystems including algal blooms, water

quality degradation, and fish kills (Conley et al. 2009). Human activity has accelerated the input

of phosphorus (P) and nitrogen (N) into aquatic ecosystems in a process known as cultural

eutrophication, magnifying impacts on natural waters (Schindler et al. 2016). Salinization refers

to the rising accumulation of ions in water bodies. Though increases in salinity can naturally

arise from local geology or groundwater inputs, the dramatic increase in salt concentrations in

freshwater systems around the world can be attributed to anthropogenic sources (Schuler et al.

2019). Human activities such as mining, agriculture, hydrologic changes, urban construction, use

of water softeners, and road salt application can all contribute to higher salinity levels in fresh

waters (Kaushal et al. 2021). Of particular concern is the utilization of road deicing agents in

northern temperate regions, which have had a twenty-fold increase in application over the last

half-century and have had measurable impacts on freshwater lakes (Dugan et al. 2017, Hintz et al. 2022).

North temperate regions have the highest densities of lakes on earth (Dugan et al. 2017). The ubiquity of eutrophication and increasing urbanization and associated chloride (Cl^-) runoff in these regions are dual problems threatening lake water quality. Though humans continue to increase the input of nutrients and road salt into lentic environments, there is limited research on the interactive effects of excess salt and nutrients.

Phosphorus and Eutrophication

P is an essential nutrient that comprises DNA and facilitates photosynthesis (Conley et al. 2009). Typically a limiting agent for growth, excess P in aquatic environments is known to contribute to the proliferation of algal blooms (Schindler et al. 2016, Brownlie et al. 2022). P naturally occurs in the environment, but humans have greatly altered the global P cycle by mining phosphate rock and applying millions of metric tons of P-based fertilizer for agriculture that then wash off into surface waters via precipitation-induced runoff (Smith et al. 2003). Nonpoint source pollution from industrial and urban areas may also add large amounts of P to water bodies (Carpenter 1998, Brownlie et al. 2022). These external inputs of P can create blooms of algae that impair aquatic ecosystems by reducing water clarity, decreasing dissolved oxygen concentrations, disrupting food webs, and producing toxins (Conley et al. 2009, Dodds et al. 2009).

Eutrophication is a process that occurs naturally in the environment over time but is exacerbated by anthropogenic development. Eutrophication specifically caused by a flux of nutrients from human activity is known as cultural eutrophication (Schindler et al. 2012, Schindler et al 2016). The consequences of cultural eutrophication include blooms of blue-green

algae (cyanobacteria), tainted drinking water supplies, degradation of fisheries and recreational activities, and hypoxia (Conley et al. 2009, Brownlie et al. 2022). Harmful algal blooms (HABS) resulting from excess nutrient input to waterways produce noxious toxins that present health risks to wildlife and humans, creating adverse economic impacts. The estimated cost of damage from cultural eutrophication in the United States alone is estimated at nearly $2.2 billion annually (Dodds et al. 2009).

There have been many attempts to reduce anthropogenic nutrient input into aquatic ecosystems. Though laws exist for the control of point-source loading of nutrients into waterways, eutrophication is still prevalent around the world (Reid et al. 2019, Brownlie et al. 2022). Nonpoint source runoff from urban and agricultural land continues to fuel cyanobacteria blooms that degrade lake water quality (Conley et al. 2009, Dodds et al. 2009). Predicted climate change, land use alteration, and human population growth have the potential to further impair aquatic ecosystems (Schindler et al. 2016, Reid et al. 2019). Therefore, it is imperative for scientists to continue research looking into alternative ways for improving water quality in nutrient-rich waters and finding effective management strategies for controlling cultural eutrophication.

However, effects from excess nutrient loading can continue even after a reduction in external P inputs. A process known as internal phosphorus loading (IPL) can exacerbate eutrophication within a lake from legacy nutrients in benthic sediments (Søndergaard et al. 2003, Welch and Cooke 2005). Internal phosphorus loading is driven by a combination of physical and biogeochemical factors and is measurable only when the sediment P release exceeds sediment P retention (Steinman and Spears 2020). Common mechanisms for IPL include wind-mediated resuspension of sediment, bioturbation from burrowing invertebrates, and the mineralization of

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organic-bound P at the sediment surface (Nogaro et al. 2016, Steinman and Spears 2020). One of the best-known contributors to internal loading occurs during redox-sensitive desorption of P from iron complexes (Mortimer 1941). Under anoxic conditions, iron oxy-hydroxides (Fe^{3+}) bound to P are reduced to dissolved iron (Fe^{2+}), releasing phosphate (Mortimer 1941, Søndergaard et al. 2003). During lake mixing, the accumulated phosphate can enter the epilimnion, where algae have sufficient light to photosynthesize and grow. The massive source of nutrients released from internal loading and lake turnover has the possibility to create large algal blooms that impair water quality and can hamper lake recovery by decades (Jeppesen et al. 2005).

IPL will become a more prevalent problem moving forward. Warming lake temperatures from climate change are likely to prolong periods of stratification, intensifying seasonal hypoxia that reduces iron-hydroxides and releases P into the overlying water column (North et al. 2014, Woolway et al. 2021). Additionally, increases in P runoff from growing pressures of urbanization and agriculture can wash off into freshwater systems, resulting in P additions to the sediments and generating conditions favorable for future internal loading (Carpenter et al. 1998, Macintosh et al. 2018).

Chloride in Freshwater Lakes

Road deicing agents are a major source of salt to freshwater ecosystems in temperate regions around the world. In the United States, the amount of road salt applied annually has increased by 24 million metric tons over the last half-century (Lilek 2017). Road deicers are imperative for wintertime transportation and are estimated to reduce roadway accidents by 80% (Kaushal et al. 2021). However, urbanization and the expansion of roadways have warranted

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greater use of road deicers in the temperate regions of the country (Dugan et al. 2017). This rise in road salt use corresponds to the increased Cl^- levels observed in lakes throughout the Northern U.S. (Novotny et al. 2008, Wyman and Koretsky 2018, Wiltse et al. 2020). Cl^- concentrations in an inland lake in southern Michigan (USA) were 2.5 times higher in 2013 than measurements taken in 1980 (Wyman and Koretsky 2018). A similar trend was discovered in lakes in the Twin Cities Metropolitan Area in Minnesota USA, where the study showed an increase in salinity levels of urban lakes from 1984 to 2005, with Cl^- concentrations 25 times higher than other non-urban lakes in the region (Novotny et al. 2008).

The most common salt compound applied on roadways in the US is sodium chloride (NaCl) though magnesium chloride and calcium chloride formulations are also commonly used for deicing (Hintz et al. 2017). These salt mixtures have rapid dissolution into roadside environments, quickly raising salinity in nearby surface waters (Wyman and Koretsky 2018, Baraza and Hasenmueller 2021). High concentrations of road salts can drastically change the chemical signature of waters from calcium/magnesium/bicarbonate-dominated waters to Na- and Cl^--dominated waters (Moore et al. 2017). Due to ion-exchange mechanisms in soils, road deicer constituents may be retained for months, leading to a gradual release of salt and elevated background concentrations of Cl^- even after road salt application has ceased (Baraza and Hasenmueller 2021). Since Cl^- is a conservative ion that is not readily bio-transformed or easily removed, road salt can persist in the environment and expose freshwater communities to elevated salinity concentrations for extended periods (Hintz and Relyea 2019).

Freshwater salinization negatively impacts multiple facets of freshwater ecosystems, including aquatic species from all trophic levels (Hintz and Relyea 2019, Mausbach and Dzialowski 2020). Salt adversely affects organisms by altering the osmotic balance between the

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organism and the surrounding environment and varying saline threshold levels exist for different

organisms and/or life stages (Findlay and Kelly 2011). For example, road salt concentrations of

5,000 mg/L were observed to interfere with osmoregulation, oxidative stress, metabolism, and

development of Atlantic salmon embryos (Tollefsen et al. 2015, Hintz et al. 2019)**.** Other aquatic

groups, such as zooplankton, experienced decreased reproduction and increased mortality at Cl^-

concentrations between 5 and 40 mg/L (Arnott et al. 2020). On a broader scale, Mausbach and

Dzialowski (2020) observed a decline in the biodiversity of saline-dominated metacommunities

of freshwater organisms. If road salt application trends continue, many lakes are predicted to

exceed the USEPA-stipulated aquatic life threshold criterion for chronic Cl^- exposure set at 230

mg/L (Hintz et al. 2022). Moreover, ecological impacts have been observed even below the

USEPA chronic Cl^- exposure threshold, suggesting that current thresholds may not be sufficient

to protect freshwater organisms from salinization (Schuler et al. 2019, Arnott et al. 2020, Hintz

et al. 2022).

Road salt runoff also impacts the physics of lake systems by increasing density gradients

and altering water quality. High Cl^- concentrations are known to create persistent density

gradients in freshwater lakes that delay or prevent the seasonal turnover of lake bottom waters

(Judd et al. 1970, Sibert et al. 2015, Wiltse et al. 2020). Many temperate lakes are dimictic and

experience spring and fall turnover that oxygenates bottom waters and redistributes nutrients that

accumulate in the stratified layers (Judd et al. 2005). However, saline runoff from road deicing

applications can increase the density of the hypolimnion, inhibiting complete lake mixing (Sibert

et al. 2015, Szklarek et al. 2022).

The disruption in the physical mixing pattern of the lake from elevated Cl^-

concentrations can create various undesirable effects. A lack of mixing can expand anoxic layers,

increase the mobility of heavy metals, and accumulate reduced solutes within the lake (Judd et al. 2005, Sibert et al. 2015, Wyman and Koretsky 2018). Oxygen is not replenished in bottoms waters during this salinized-induced stratification, turning the hypolimnion hypoxic or anoxic and leading to the oxidation of labile organic matter from anaerobic respiration. A series of electron acceptors are used in order of energetic yield to carry out the anaerobic respiration leaving a sequential vertical accumulation of the dissolved solutes that degrade water quality (Wyman and Koretsky 2018, Dupuis et al. 2019). Additionally, the increase in the spatial and temporal extent of anoxic conditions in lakes reduces suitable habitat for fish while the enhanced heavy metal mobility from cation exchange promoted by increased salinity also threatens species viability (Sibert et al. 2015, Wiltse et al. 2020). Overall, the formation of a benthic saline layer from road salt input has adverse effects on the ecosystem that are detrimental to water quality and aquatic life in lakes.

Combined Impacts of Excess Chloride and Phosphorus

Anthropogenic input from road salt deicers has large implications for the mixing dynamics and biogeochemical cycles in lakes, inducing the potential to exacerbate existing issues in eutrophic lakes (MacLeod et al. 2011, Lind et al. 2018, Wyman and Koretsky 2018). Low dissolved oxygen concentrations induced by the benthic layer of dense saline water can stimulate P diffusion in iron-rich sediments due to the release of the P from ferric oxy-hydroxides (Mortimer 1941, Novotny and Stefan 2012, Søndergaard et al. 2003). Prolonged anoxia near the lake bottom could intensify cultural eutrophication by IPL (Mortimer 1941, Novotny and Stefan 2012) potentially leading to large accumulations of P which, if able to reach the surface, could cause significant algal blooms and further impair the lake ecosystem. Model results of a lake in Minnesota demonstrated how dissolved oxygen would respond to the

presence of a benthic saline layer with predictions that these conditions would facilitate IPL (Novotny and Stefan 2012). An urban lake in Kalamazoo, Michigan attributed higher hypolimnetic levels of phosphate to IPL caused by the persistent Cl^--induced density stratification, one of the few field-based studies to link elevated road salt concentrations to IPL (Sibert et al. 2015).

Though excess nutrients and Cl^- are some of the most prominent threats to lakes, particularly in temperate regions, there is not a robust understanding of how road salts alter processes such as P nutrient cycling, and vice versa (Hintz et al. 2019). With an increase in cultural eutrophication and road salt use across the globe, there are few studies that have looked at the direct impacts of both excess P and Cl^- in freshwater lakes. Lind et al. (2018) were the first to study the combined effects of salt contamination and nutrient pollution on lake communities. They used outdoor mesocosms with controlled concentrations of P and a common road salt deicer to measure the direct, indirect, and interactive effects of salt, nutrients, and light. Their results indicated that individually, eutrophication and salinization have major effects on ecosystem function and that their combined effects are expected to promote large algal blooms and decrease the abundance of invertebrates and macrophytes. Several studies have measured both phosphate and Cl^- levels but did not analyze how excess Cl^- impacted the eutrophication of these systems, though increases in phosphate concentrations were observed in the hypolimnion where Cl^- concentrations were highest (MacLeod et al. 2011, Koretsky et al. 2012, Wyman & Koretsky 2018).

North temperate regions have the highest densities of lakes on Earth (Dugan et al. 2017). The ubiquity of eutrophication and increasing urbanization and associated Cl^- runoff in these regions are dual problems threatening lake water quality. Insufficient knowledge of the

combined impacts of nutrient and road salt input necessitates further research into the additive and synergistic effects of excess P and Cl$^-$ to help develop remediation plans for lakes with elevated concentrations of these contaminants.

Purpose

The purpose of this study was to examine the impacts of excess road salt on water quality and IPL in an urban eutrophic lake in Grand Rapids, Michigan. The findings from this study will be useful for helping inform a restoration strategy for Church Lake and ultimately contribute knowledge to make scientifically sound lake management decisions for other lakes impacted by concurrent stressors of eutrophication and salinization.

Scope

This thesis focuses on the abiotic responses of a lake and associated tributary receiving large amounts of Cl$^-$ from road salt runoff. Specifically, I investigated how water quality and lake mixing were affected by elevated Cl$^-$ concentrations. Additionally, I compared sediment P release among four treatments, using a 2×2 factorial design that manipulates two levels of Cl$^-$ (low; high) and redox state (oxic; anoxic) to see if higher concentrations of Cl$^-$ from road deicing runoff would impact IPL rates.

Research Questions

To examine the impacts of excess P and Cl$^-$ on a temperate freshwater lake, I will address the following research questions:

Q1) Does excess Cl$^-$ impact lake water quality?

Hypothesis H1: I hypothesize that elevated Cl⁻ will impact water quality by restricting lake turnover and increasing the extent of low dissolved oxygen concentrations (either hypoxia: < 2 mg/L or anoxia: <0.5 mg/L), as well as the concentration of solutes below the chemocline.

Rationale H1: The increased density gradient from high levels of Cl⁻ will prevent seasonal mixing and stop oxygenated epilimnetic waters from reaching the hypolimnion (Judd 1970, Novotny et al. 2008). Dissolved solutes such as manganese, ferrous iron (Fe^{2+}), ammonia, and sulfide can accumulate under anoxic conditions at the lake bottom (Koretsky et al. 2012, Wyman & Koretsky 2018). Consequently, these metals and compounds should dominate in the hypolimnion and sediment porewater.

Q2) Do high Cl⁻ concentrations influence IPL rates?

Hypothesis H2: Sediment core incubation experiments will show that sediment P release rates are greater in anoxic cores compared to oxic cores, but there will be no difference in P release between Cl⁻ levels.

Rationale H2: Since there is currently no research on Cl⁻ impacts on IPL rates, my null hypothesis is Cl⁻ will have no direct effect on IPL rates. However, several studies in stream and wetland environments have observed increases in sediment P release with increasing salinity concentrations due to ion exchange processes (McManus and Davis 2020). Additionally, it is well known that low dissolved oxygen concentrations stimulate P diffusion in iron-rich sediments due to the release of P from ferric oxy-hydroxides (Mortimer 1941, Søndergaard et al. 2003). Therefore, high levels of Cl⁻ may indirectly increase IPL rates via anoxic conditions created by the salinity gradient.

Chapter 2

Urban Lake Water Quality Responses to Elevated Road Salt Concentrations

ABSTRACT

Road salt runoff from de-icing applications is increasingly impacting water quality around the globe. Excess salt (especially chloride) concentrations can negatively impact the biological, chemical, and physical properties of freshwater ecosystems. Though road salt pollution is a prevalent issue affecting many northern temperate lakes, there are few studies on how freshwater salinization may interact with other ecological stressors such as eutrophication. My research investigates how excess chloride from road deicers may impact nutrient processes in lakes. Over the last 20 months, we have sampled a tributary and lake receiving large amounts of road salt runoff from a nearby highway in Grand Rapids, Michigan. Chloride concentrations in the deepest part of the lake consistently exceeded the EPA chloride chronic toxicity threshold of 230 mg/L, at times reaching up to 331 mg/L. These high chloride concentrations are believed to have altered the density gradient of the waterbody, preventing the lake from mixing, and causing permanent hypoxia in the deepest regions of the lake. The mobilization of benthic phosphorus into the overlying water column can occur in these low-oxygen conditions. This process, known as internal phosphorus loading, is significant in the studied lake, as phosphorus concentrations near the surface averaged 35 µg/L but have exceeded 7500 µg/L in the deepest part of the lake. If the salinity gradient breaks down and the lake mixes, the lake may mix and allow the high phosphorus concentrations to reach the surface where the excess nutrients and available light could stimulate algal blooms. Therefore, due to these ecological ramifications, it is important to address the elevated phosphorus concentrations in the hypolimnion prior to addressing the road salt inputs.

INTRODUCTION

The condition of lake ecosystems has been greatly impacted by anthropogenically-derived pollutants. High inputs of nutrients like phosphorus (P) and nitrogen (N) can cause cultural eutrophication of freshwater ecosystems, stimulating primary production and an excessive growth of algae (Conley et al. 2009, Schindler 2012). Algal blooms cause a suite of ecological problems, including bottom water hypoxia when oxygen is consumed during the decomposition of dying algae (Smith 2003). Under these low oxygen conditions, iron (Fe) hydroxides in the sediment are reduced to dissolved forms, promoting the release of P into the overlying water column (Mortimer 1941, Steinman and Spears 2020). This process, known as internal phosphorus loading (IPL), can exacerbate issues of eutrophication by continuing to supply nutrients to the water column even after external loads have been reduced (Søndergaard et al. 2003, Welch and Cooke 2005,).

In northern temperate areas, runoff from road deicers can increase the salinity of surrounding freshwaters, impacting the biological, chemical, and physical properties of these ecosystems. Elevated chloride (Cl^-) concentrations resulting from road salt application have been measured in urban lakes, as well as surrounding soils and groundwater, in the Northeast and Midwest regions of the United States (Novotny et al. 2008, Wyman and Koretksy 2018, Wiltse et al. 2020). High concentrations of salt can have negative impacts on freshwater organisms from all trophic levels, causing a reduction in growth, reproduction, and biodiversity (Findlay and Kelly 2011, Hintz and Relyea 2019). Additionally, inputs of road deicers can alter density gradients, inhibiting or stopping seasonal turnover in dimictic lakes (Judd 1970, Dupuis et al. 2019). The denser saline runoff may form a layer in the hypolimnion that can increase lake stability, raising the energy required to fully mix the lake beyond the threshold for wind action to sufficiently initiate fall and spring turnover. This persistent chemical stratification prevents oxygen from being

replenished to the bottom waters, leading to hypoxic or anoxic conditions in the hypolimnion (Wyman and Koretsky 2018). Prolonged periods of anoxia can reduce viable habitat for cold water fish species such as lake trout (Wiltse et al. 2020). Further, anerobic respiration can oxidize organic matter using a series of electron acceptors in order of energetic yield, leading to an accumulation of reduced solutes such as ammonium, manganous manganese, ferrous iron, and sulfide in the hypolimnetic water column (Koretsky et al. 2012). P bound to redox-sensitive Fe-oxides may also be released during the dissolution of particulate Fe, leading to IPL.

Though the salinization of freshwater lakes from road salt can create favorable conditions for sediment P release, there are few road salt contamination studies that concurrently assess P in these water bodies. Several papers described an increase in hypolimnetic anoxia as a result of Cl^- stratification (Novotny and Stefan 2012, Wilste et al. 2020) but only one study has reported a simultaneous increase in dissolved P in the bottom waters attributed to IPL (Sibert et al. 2015). Additionally, the combined impacts of excess P and Cl^- on ecosystems and food webs have received little attention, with the exception of Lind et al. (2018), who studied the additive and synergistic effects of salt contamination and nutrient pollution on experimental lake communities. Though salinization and eutrophication have been identified as two prominent threats to freshwater ecosystems (Reid et al. 2019), there is a concerning lack of research on how the co-occurrence of these stressors impacts lake environments.

Our study aims to address this knowledge gap by investigating the effects of excess road salt on lake water quality and nutrient processes in an urban lake in Grand Rapids, MI, USA. Preliminary monitoring of the lake showed high concentrations of Cl^- and P and low dissolved oxygen (DO) in the hypolimnion. We surveyed the lake over a period of 19 months to assess the extent to which the road salt contamination influenced the lake water quality. We also monitored

the water quality of the main tributary entering the study lake to assess whether it was the primary source of Cl^- delivery to the lake. We hypothesized that road salt runoff into the lake would prevent complete seasonal turnover, leading to permanently low DO conditions in the bottom waters, which in turn promote IPL and elevated P concentrations with depth.

METHODS

Study Area

Church Lake is the headwater lake for a series of three lakes located in eastern Grand Rapids in Kent County, Michigan USA (Fig. 2.1). The watershed is predominately developed apart from low-lying wetlands adjacent to the lake. The lake has a surface area of approximately 7.7 hectares and reaches a maximum depth of 16 m. A small tributary, originating from a 36-inch concrete culvert, flows into the east side of Church Lake. This tributary acts as a stormwater drain for runoff from Michigan State Highway 44/East Beltline Avenue, though likely also has inputs of groundwater due to steady baseflow year-round. East Beltline Avenue has a two-way annual average daily traffic count of 46,832 vehicles making it a busy thoroughfare with considerable salt application in the winter months (GVMC 2018). A small precipitation-dependent stream also flows out of the northwest end of Church Lake and moves through a wetland before reaching Middleboro Lake, located immediately downstream (Fig. 2.1).

Lake Water Quality

Water quality sampling occurred on a monthly basis at two sites in Church Lake. Site 1 was located at the deepest area of the lake with maximum depth of ~16 m and was monitored from April 2021 - April 2022, with prior supplemental data collected from August 2020 - March 2021 by the Steinman Lab as part of a separate study (Hassett et al. 2022). Site 2 was in a shallower location (~7 m) near the tributary inlet and was monitored from April 2021 – April 2022. Sites were not sampled during January 2021 or March 2021 due to safety concerns

regarding ice-cover thickness. At each monthly sampling event for both sites, in-situ measurements of temperature, dissolved oxygen (DO), total dissolved solids (TDS), specific conductivity, pH, and turbidity (NTU) were taken with a YSI 6600 multiprobe sonde (YSI Incorporated, Yellow Springs, OH) at 1 m intervals from the surface down to the lake bottom. Secchi disk depth was recorded at each site to measure the water transparency and turbidity of the lake. Water samples were collected at 3 m intervals using a Van Dorn water sampler for analysis of Cl^-, Total Phosphorus (TP), and Soluble Reactive Phosphorus (SRP). Cl^- is a common component of road deicing salts and is a conservative ion with minimal natural sources in the Church Lake watershed, making it a useful indicator of road salt in the system. Water samples were stored on ice during transportation back to the laboratory. Upon return, samples for TP were stored at 4°C, and 20 mL samples for SRP and Cl^- were filtered through a 0.45 µm acid-washed filter where SRP was stored at 4°C and Cl^- was frozen until analysis. TP and SRP were analyzed on a Seal AQ2 Discrete Analyzer (USEPA 1993) and Cl^- samples were analyzed by ion chromatography on a Dionex DX500 (APHA 1999). For TP and SRP, samples less than detection (7 µg/L and 5 µg/L, respectively) were designated as ½ the detection limit to assign a numerical value above zero for analysis (Hornung and Reed 1990).

Tributary Water Quality

Baseflow water quality monitoring of the Church Lake tributary occurred twice a month from April 2021- April 2022 with supplemental data collected from August 2020 - March 2021 by the Steinman Lab as part of a separate study (Hassett et al. 2022). The water quality of the Church Lake outlet was also monitored twice a month , though some dates samples could not be collected due to low flow or ice cover. Temperature, dissolved oxygen (DO), total dissolved solids (TDS), specific conductivity, pH, and turbidity (NTU) were measured with a YSI 6600

multiprobe sonde. Water samples were collected using acid-washed bottles and analyzed for TP, SRP, and Cl$^-$ in the tributary and TP and SRP in the outflow following the methods described above.

Four storm or snow melt events were sampled for water quality. The storm event sampling occurred during a rain event of greater than 0.1 inches following a minimum of 72 hours of dry weather conditions. Snow-melt events were determined on a discretionary basis when significant amounts of snow-induced runoff were entering the tributary. Additionally, a sample of the roadside snowbank near the stormwater drain feeding into the Church Lake tributary was taken to measure the Cl$^-$ concentration. The snow was allowed to melt at room temperature before the water was filtered and re-frozen for future analysis.

Manual stream flow measurements were taken in the tributary using a SonTek FlowTracker2 (SonTek/YSI Inc., San Diego, CA) at a permanently marked transect near the water quality sampling location (Fig. 2.1). Water depth and velocity were measured at 6-equally spaced points using the velocity-area method for discharge (Lamberti and Hauer 2017). Discharge was calculated and recorded by the FlowTracker2 and manually validated by the windows-based hydrologic software HYDROL_INF (Chu and Steinman 2009). In November 2020, a stream gage with Onset HOBO U20L-02 water level logger and barometric pressure logger (Onset Computer Corporation, Bourne, MA) were installed in the middle of the tributary below a couple of 2 ft tall weirs. Loggers recorded at 10-minute intervals to capture continuous stage measurements to create a stage-rating discharge curve. Due to equipment malfunction, continuous stream stage measurements were not recorded until February 2021. Field stage measurements were recorded at every sampling event to verify logger stage readings. Stream

gage stage measurements were all adjusted by 1.5 cm to account for the average difference between the actual field stage and measured stream gage.

Analysis

Measured discharge was regressed against stage values to calculate a stage-discharge rating curve. This relationship was then used to extrapolate continuous discharge based on the continuous stage measurements from the water level loggers. Linear regression was used to determine the relationship between Cl⁻ and specific conductance values within the Church Lake tributary site, as specific conductance can act as a proxy for Cl⁻ in streams that are heavily impacted by road salt (Novotny et al. 2008).

A coarse estimate of the Cl⁻ load entering Church Lake was calculated using discharge measurements and in-situ Cl⁻ concentrations. The load was calculated using the following equation adapted from the National Nonpoint Source Monitoring Program (Meals et al. 2013):

$$M = k \sum_{i=1}^{n} c_i * q_i * \Delta t$$

Where M = mass of load, k = a conversion factor, c_i = Cl⁻ concentration, q_i = the discharge of the corresponding concentration, Δt is the time interval of the measurement (typically 10 minutes). To get continuous Cl⁻ concentrations, the in-situ measurements of Cl⁻ for the winter (periods of salt application) and spring/summer/fall were plotted separately against measured discharge taken at the same time as the Cl⁻ sample. The resulting regression for each season was then used with the continuous discharge measurements to establish continuous Cl⁻ concentrations in the tributary.

Lake water quality parameters were plotted on a depth profile time series using Golden Software's Surfer 10 interpolation package (Golden Software 2011). All data were imported into

Surfer from a .csv file using the Nearest Neighbor interpolation engine. Months without

sampling data were not plotted.

RESULTS

Lake Water Quality

Site 1 at Church Lake was consistently stratified, with low DO and pH, and consistent

temperature in the hypolimnion. The lake had strong thermal stratification in the summer

months, with weak thermal stratification in the late fall and early spring, and reverse

stratification during periods of ice cover (Fig. 2.2). The thermocline extended to 6-7 m in depth

when the lake was thermally stratified. The lake was isothermal during December sampling

events and was isothermal in the spring between March and April sampling events; despite the

isothermal nature of the lake, mixing did not occur at this site, likely due to a salt density

gradient (see below). DO remained supersaturated in the epilimnion throughout all seasons

except during periods of ice cover (Fig. 2.3). The hypolimnion remained hypoxic (< 2 mg/L DO)

below 6-7 m during all seasons apart from when the lake was isothermal, where oxic conditions

persisted to a depth of 9 m. The pH in Church Lake decreased with depth in all seasons, though

during isothermal conditions in the fall and spring, pH varied less with depth (Fig. 2.4). The pH

in the epilimnion averaged ~ 8.5 whereas the pH in the hypolimnion ranged from 6.27 to 7.57.

Periods of ice cover had reduced pH in both the epilimnion and hypolimnion.

Throughout the entire sampling period, concentrations of Cl^- and P increased with depth

at Site 1. Cl^- consistently exceeded 200 mg/L at and below 10 m depth and the maximum

concentrations in the hypolimnion reached 331 mg/L in November 2021 (Fig. 2.5). The Cl^-

concentrations in the epilimnion were consistently lower than in the hypolimnion, ranging from

85 mg/L to 189 mg/L. The maximum epilimnion Cl^- concentrations at Site 1 were measured at

the surface in May 2021, with concentrations exceeding 200 mg/L. The concentrations of P also

increased significantly with depth, with SRP and TP concentrations typically exceeding 1000 µg/L below 9 m (Fig. 2.6 and Fig. 2.7). At 15 m depth, SRP and TP concentrations reached a maximum of 6597 µg/L and 7647 µg/L, respectively, in March 2022. Concentrations of SRP in the epilimnion were often below detection limits, and TP averaged 41µg/L during the sampling period, with the highest values measured under ice cover in March 2022. Concentrations in the hypolimnion decreased in the early fall and winter months, but there was a general increase in P concentrations over the duration of the study. In several instances, concentrations of SRP exceeded the TP values, though particulate iron was observed in digested samples. Elevated concentrations of Fe likely precipitated with P and interfered with the TP analysis, since the TP samples are not filtered prior to analysis.

The concentration of major ions and redox-sensitive solutes were measured per season (4 times total) in Church Lake at both sites. Calcium (Ca), dissolved iron (Fe^{2+}), dissolved manganese (Mn^{2+}), and ammonium all increased with depth at Site 1 coinciding with the depletion of DO (Fig 2.8). Ca in the epilimnion ranged from 30 mg/L to 50 mg/L and increased in concentration at 12 m depth ranging from 73 mg/L to 82 mg/L in the hypolimnion. Fe^{2+} concentrations were measured below detection limits in the surface waters but had concentrations ranging from 2.1 mg/L to 4.7 mg/L below 12 m depth. Concentrations of Mn^{2+} started to increase between 9 and 12 m in depth, with hypolimnetic Mn^{2+} measured between 5.2 mg/L and 6.4 mg/L. In October 2021, maximum Mn^{2+} concentrations were measured at 12 m depth, whereas the other sampling events typically saw maximum values at 15 m depth. Epilimnetic ammonium concentrations were typically below detection limits and increased to over 18 mg/L below 12 m depth, though small levels (0.31 mg /L – 0.46 mg/L) were detected in February 2021 during ice cover.

Site 2 had an average depth of 7.5m and had distinct water chemistry patterns compared to Site 1. This shallower Site 2 experienced complete turnover during periods of isothermality that lasted from late fall through early spring (Fig. 2.9). DO was present throughout the entire water column from late fall 2021 to January 2022, and elevated DO concentrations were measured at all sites again in April 2021 (Fig. 2.10). The onset of stratification at Site 2 began in May 2021 and by June 2021, hypoxic conditions were observed at 6m depth. Low dissolved oxygen conditions were measured below 5 m until the lake became isothermal in November 2021 and oxygen was redistributed throughout the water column. Inverse stratification was measured under ice cover in February 2022, where hypoxic conditions resumed at 6m depth. The pH decreased from the surface (~8.5) to the bottom (~7.35) during stratification but was relatively uniform in the water column during periods of turnover (Fig. 2.11).

There was no observed chemocline at Site 2 and measured Cl^- concentrations were generally similar between the surface and deeper depths, ranging from 101 mg/L to 192 mg/L (Fig. 2.12). On several dates, Cl^- concentrations were higher at the surface compared to the deeper depths. Additionally, the lowest Cl^- concentrations were often observed in the middle of the water column, with elevated concentrations at the surface and near-bottom. P concentrations at the surface of Site 2 were similar to the epilimnion of Site 1. In most samples, SRP was below the detection limit (Fig. 2.13). The highest levels of TP and SRP at Site 2 were measured at near-bottom depth in February 2022, when concentrations reached 146 µg/L and 82 µg/L, respectively (Fig. 2.14). Overall, P concentration increased with depth, except during January 2021 when the surface had slightly greater TP and SRP concentrations than the bottom water.

The concentration of metals at Site 2 had no discernable patterns between seasons (Fig. 2.15). Fe^{2+} was at or below detection limits at all depths. Mn^{2+} and NH_4^+ increased slightly

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between the surface and near-bottom depths, though no measurable amounts were detected in April 2022. Ca was relatively uniform between depths ranging in concentrations from 32 mg/L to 50 mg/L.

Tributary Water Quality

The tributary had elevated concentrations of Cl⁻ at baseflow year-round, though concentrations typically increased during the late winter after road salt application. The mean Cl⁻ concentration in the tributary was 315 mg/L but ranged from 163 mg/L to 714 mg/L during baseflow, with a maximum concentration of 954 mg/L measured during a snowmelt event in February 2021. In the non-winter months, the Cl⁻ concentrations with discharge were best explained by a linear regression (R^2 = 0.35, p = 0.004, n = 28), with the highest concentrations occurring during baseflow. Wintertime Cl⁻ concentrations were determined using a quadratic equation (R^2 = 0.52, p = 0.008, n = 11), where intermediate flows had the highest concentrations due to snowmelt. The total Cl⁻ load entering Church Lake between 24 February 2021 and April 2021 in the tributary was estimated to be 8,387 kg, though this is an extremely coarse estimate due to the extended intervals between in-situ Cl⁻ measurement. This is likely an underestimate of the Cl⁻ load to Church Lake, as other sources like groundwater or runoff from other surrounding paved surfaces were not included in this calculation.

There was a significant linear relationship between specific conductance and Cl⁻ in the tributary water (p < 0.001, R^2 = 0.915, Fig. 2.16, n = 48). Therefore, future data collection on the Church Lake tributary can use specific conductivity as an in-situ proxy to monitor Cl⁻ concentrations.

The tributary had measurable concentrations of P in nearly all samples, suggesting this waterway is one source of nutrient loading to Church Lake. The average TP concentration in the

tributary was 44 µg/L but ranged from levels below detection to 367 µg/L. Maximum TP and SRP values were measured during a classified snowmelt event in February 2022. SRP reached a high of 58 µg/L but had an average concentration of 19 µg/L throughout the year. There were no apparent seasonal trends in P concentrations.

The lake outlet had ephemeral flow that was dependent on precipitation, wind direction, and lake level. Samples from the outlet had similar water quality parameters to the surface water of the lake, though TP concentrations were higher and ranged from concentrations below detection limit to 228 µg/L, averaging 72 µg/L over the sampling year. A majority of the samples for SRP were below detection limits, but a maximum concentration of 179 µg/L was measured in late September 2021. Cl^- concentrations were measured only once in the outlet and were determined to be similar to surface Cl^- levels. Given the strong relationship between Cl^- and specific conductivity in this system, in-situ measurements of specific conductivity were used to infer salt concentrations in the outlet.

DISCUSSION

The application of road deicing salts has implications for the biological, chemical, and physical properties of temperate freshwater ecosystems. Rising concentrations of Cl^-, a common component of road salts, have been seen in lakes throughout the northern regions of the United States, especially in urban areas (Novotny et al. 2008, Dugan et al. 2017, Dupuis et al. 2019). Our monitoring efforts of a Cl^- impaired lake in Grand Rapids, Michigan have shown how elevated concentrations of road salt can impact lake water quality by prolonging stratification, increasing bottom-water hypoxia, and increasing P and reduced solutes in the hypolimnion.

Typically, non-shallow lakes in temperate areas are dimictic and undergo complete vertical mixing during isothermal conditions in the spring and fall (Wetzel 2001). However, Church Lake does not appear to have completely turned over during every period of

isothermality in our study. At the deepest site of the lake, there was a uniform temperature in the hypolimnion during all seasons. Measurements of hypolimnetic temperature, DO, and pH could not be taken in-situ with the YSI during July 2021 and had to be measured using Van Dorn grabs brought to the surface. The exposure of the hypolimnetic grab samples to the air and warmer temperatures prior to measurement could explain the slightly higher values observed during July. During periods of isothermality when turnover is expected, the hypolimnion remained hypoxic. In December 2020, YSI data was measured only at near-surface, middle, and near-bottom depths when compared to data collected in 2021- 2022, when water quality parameters were measured every meter from the surface to the bottom. Though the lower spatial resolution data from December 2020 appears to show the DO distributed through more of the water column, the 15 m reading indicated that hypoxic conditions were present near the sediment-water interface. In the spring of 2021 and 2022, hypoxic conditions persisted below 6 m depth even when temperatures were uniform throughout the water column. Complete fall turnover did not occur in 2021, though DO concentrations increased between 6-9 m, suggesting mixing occurred to that depth. Additionally, the persistence of DO in the entire water column at Site 2 (~ 7.5m) during the spring and fall shows that the lake does thoroughly mix at shallower depths. However, the lack of complete turnover at Site 1 indicates that Church Lake, at least in part, has already transitioned from a dimictic to a monomictic or even a meromictic lake.

The elevated salt levels in the hypolimnion are the likely cause of this reduced mixing. Cl^- concentrations below 9 m depth typically exceeded 200 mg/L and at times reached over 330 mg/L. Epilimnion concentrations of Cl^- were less than hypolimnetic concentrations, and this difference was especially prominent during periods of anticipated spring turnover. Though the lake was isothermal, there was a distinct salinity-driven density difference between the surface

and bottom waters. In freshwater lakes, mixing dynamics are typically governed by temperature due to the thermophysical properties of water, where water is most dense at 4ºC (Wetzel 2001). However, the salinity of the hypolimnion increased the density of the bottom water, maintaining enough stability in the water column to prevent complete turnover during isothermal conditions. The salinity-driven density gradient was less prominent in the fall months, which could have allowed for the deeper mixing and distribution of DO observed in the Church Lake water column. Other studies of road salt-impaired Midwest lakes have seen similar events, with a lack of spring turnover but mixing events in the fall due to reduced Cl^- inputs during the summer months (Novotny et al. 2008, Wyman and Koretsky 2018).

In addition to the distribution of DO throughout the water column, other isochemical conditions should be observed during complete turnover events. However, the water column in Church Lake had a distinct chemical stratification, with reduced pH and elevated concentrations of P and chemically reduced solutes in the hypolimnion. . The pH decreased with depth in the lake, with some measurements below the 6.5 to 9 range stated in Rule 53 of the Michigan Water Quality Standards for surface water (Part 4 of the Natural Resources and Environmental Protection Act, 1994 Public Act 451).This decrease in pH with depth was seen in other road-salt stratified lakes, likely due to decompositional processes that result in increases in hypolimnetic CO_2 (Wetzel 2001, Sibert et al. 2015, Wyman and Koretsky 2018).

Extremely high amounts of TP and SRP were measured below 9 m depth throughout the duration of the study. The eutrophic classification for inland lakes in Michigan ranges from 25 to 50 µg/L of TP (Michigan EGLE 2012) and the values measured in the Church Lake hypolimnion were nearly 100 to 200 times greater than that threshold. Though there is some external P loading from the tributary, the differences in epilimnetic P concentrations, (averaging 41 µg/L

for TP), and hypolimnetic concentrations of TP (over 7,500 µg/L) suggest that IPL is also contributing to the increased P concentrations with depth. Under low oxygen concentrations, iron oxy-hydroxides (Fe^{3+}) loosely bound to P are reduced to dissolved iron (Fe^{2+}), releasing soluble P into the overlying water column (Mortimer 1941, Søndergaard et al. 2003). The elevated concentrations indicate that the internal P loading has likely been an ongoing, long-term issue in Church Lake, a consequence of the salinity–induced stratification and subsequent anoxia. Additionally, the low DO has created prolonged reducing conditions that have led to a buildup of Fe^{2+}, Mn^{2+}, and ammonium in the hypolimnion. These solutes were measured only in the anoxic regions of the lake, though they had detectable concentrations in all seasons, signifying permanently low DO conditions in the hypolimnion. Similar trends have also been measured in southwest Michigan lakes impacted by road salt stratification, demonstrating that elevated Cl^- concentrations can have implications for the broader lake biogeochemistry (Wyman and Koretksy 2018, Dupuis et al. 2019).

The tributary was identified as the major source of salt to the lake, contributing approximately 8,387 kg of Cl^- to Church Lake over a portion of our study period. The tributary is mainly fed by a stormwater drain that collects runoff from a section of East Beltline Avenue, a heavily trafficked Michigan state highway. In addition to the elevated Cl^- concentrations measured in the tributary, a sample of the snowbank piled on the side of the East Beltline had Cl^- concentrations of 1034 mg/L. A study of highway snowbanks in Ontario, Canada saw similar concentrations, with all samples having NaCl concentrations greater than 1000 mg/L and one sample even reaching a maximum of 9400 mg/L (Labadia and Buttle 1996). The melting snow and saline runoff from the roadside snowbank likely contributed to increased salt concentrations in the Church Lake tributary, as seen in February 2021 when Cl^- levels reached 954 mg/L during

a snowmelt event. Over 75% of our water samples from the tributary exceeded the USEPA Cl⁻ chronic toxicity threshold for freshwater organisms set at 230 mg/L with the snowmelt sample exceeding the value for the acute criterion of 860 mg/L (USEPA 1988). Our tributary measurements of Cl⁻ were grab samples, and it is possible that there were even higher concentrations of salt in the tributary that we were not able to capture. However, the strong linear relationship between Cl⁻ and conductivity could allow for continuous monitoring of salt concentrations if sensors monitoring specific conductivity were installed in the tributary. This may help provide an understanding of the timing of large Cl⁻ flushing events and a more accurate picture of the salt loading into Church Lake.

Outside of the winter months with higher road salt application, Cl⁻ concentrations in the tributary remained high through the summertime, frequently above the 230 mg/L chronic toxicity threshold, suggesting that Cl⁻ may be retained in the sediments or conveyed via groundwater. Though our study did not investigate salt inputs from groundwater, several studies have attributed higher summer Cl⁻ concentrations in lotic systems to Cl⁻ retention in the environment (Kelly et al. 2008, Corsi et al. 2015). The release of Cl⁻ during baseflow conditions can have year-round and long-term impacts on freshwater organisms and contribute to sustained salt loading to the lake (Findlay and Kelly 2011). Many aquatic taxa reproduce in the spring and summertime, and egg and juvenile stages have shown greater sensitivity to Cl⁻ concentrations than adults (Hintz and Relyea 2019). Therefore, sustained high concentrations of salt throughout the summer may disproportionally impact vulnerable organisms, leading to changes in species growth, reproduction, and community composition (Lawson and Jackson 2021). Though the reduction in road salt inputs will help improve freshwater ecosystems, recovery may be delayed due to the retention and slow release (i.e., legacy pollution) of Cl⁻ in the system.

Data from this study can be used to help inform a management strategy for Church Lake. Though reducing the amount of salt entering the system is necessary for the ultimate recovery of the lake, the elevated hypolimnetic P concentrations should be addressed prior to mitigating the Cl^- issues. The dense saline layer of water at the bottom of the lake has prolonged stratification and created anoxic conditions that have led to a buildup of P in the hypolimnion. Simultaneously, the lack of turnover has prevented most of this P from reaching the upper layers of the lake where there is enough light for photosynthesis. If the salinity gradient were to break down, the lake could fully turn over allowing the extremely high bioavailable P concentrations to reach the epilimnion and stimulate algal blooms. Therefore, it is important to treat elevated P concentrations before reducing the Cl^- concentrations. Methods to reduce IPL may include treatment with chemical inactivants such as Phoslock, or Al, Fe, or Ca salts, which precipitate P in the water column and trap it in the sediments (Steinman and Spears 2020). Sediment dredging has seen significant reductions in sediment P concentrations and release (Oldenborg and Steinman 2019, Lürling et al. 2020), though it has a more expensive upfront cost (Welch and Cooke 2005) and requires a location for deposition. Another method may be hypolimnetic water withdrawal which would remove both the elevated P and Cl^- concentrations in the bottom waters.

However, treating the P is only a symptom of the larger issues caused by excess road salt in the system. Current alternatives to traditional NaCl deicers, such as calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) also contain Cl^- and have other measured detriments to the environment. The LD_{50} of the alternative road deicers was roughly half that of the traditional NaCl deicers for the species *Chironomus dilutus* (Szklarek et al. 2022). Additionally, these road salt alternatives are traditionally more expensive by weight, though they exert high exothermic properties and are more efficient at increasing ice and snowmelt (Schuler et al. 2017, Szklarek et

al. 2022). Rerouting the tributary through a retention pond or wetland may slow down the larger

flushes of salt into the system, though a plume of Cl^- can still enter the groundwater from

retention systems, and lead to a slow and steady salinization of the lake (Snodgrass et al. 2017).

Therefore, reducing the application of road salt is the most permanent and environmentally

friendly resolution for improving the Church Lake ecosystem, and other lakes experiencing

similar ecological impairments.

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FIGURE CAPTIONS

Fig. 2.1 The sites of sampling locations in Church Lake located in Grand Rapids, MI USA. *Upper left inset*: shows the study location (black circle) within Kent County, MI. *Upper Panel:* a view of the hydrologically connected Tri-Lakes next to M44/East Beltline Ave in Grand Rapids, MI. *Bottom Panel*: zoomed in view of the sampling locations within Church Lake, the tributary, and outlet. Stars represent monthly sampling locations while orange circles show bi-monthly sampling locations.

Fig. 2.2 Depth-time isoplots of the temperature (°C) at sampling Site 1 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions.

Fig. 2.3 Depth-time isoplots of the dissolved oxygen (mg/L) at sampling Site 1 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions.

Fig. 2.4 Depth-time isoplots of the pH at sampling Site 1 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.5 Depth-time isoplots of the chloride (mg/L) at sampling Site 1 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.6 Depth-time isoplots of the soluble reactive phospohrus (mg/L) at sampling Site 1 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.7 Depth-time isoplots of the total phosphorus (mg/L) at sampling Site 1 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.8 Concentrations of (a) calcium (b) iron (c) manganese and (d) ammonium in July 2021, October 2021, February 2021, and April 2021 at Site 1 in Church Lake. Concentrations were measured every 3 m from the surface down to the lake bottom.

Fig. 2.9 Depth-time isoplots of the temperature (°C) at sampling Site 2 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions.

Fig. 2.10 Depth-time isoplots of the dissolved oxygen (mg/L) at sampling Site 2 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions.

Fig. 2.11 Depth-time isoplots of the pH at sampling Site 2 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.12 Depth-time isoplots of the chloride (mg/L) at sampling Site 2 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.13 Depth-time isoplots of the soluble reactive phospohrus (mg/L) at sampling Site 2 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.14 Depth-time isoplots of the total phosphorus (mg/L) at sampling Site 2 in Church Lake. Blank months show periods where data was not collected due to unsafe ice-cover conditions

Fig. 2.15 Concentrations of (a) calcium (b) iron (c) manganese and (d) ammonium in July 2021, October 2021, February 2021, and April 2021 at Site2 in Church Lake. Concentrations were measured every 3 m from the surface down to the lake bottom.

Fig. 2.16 The linear regression and equation between specific conductivity and chloride concentrations measured in the Church Lake tributary ($p < 0.001$, $R^2 = 0.915$, n = 48).

Fig. 2.1

Fig. 2.2

Fig. 2.3

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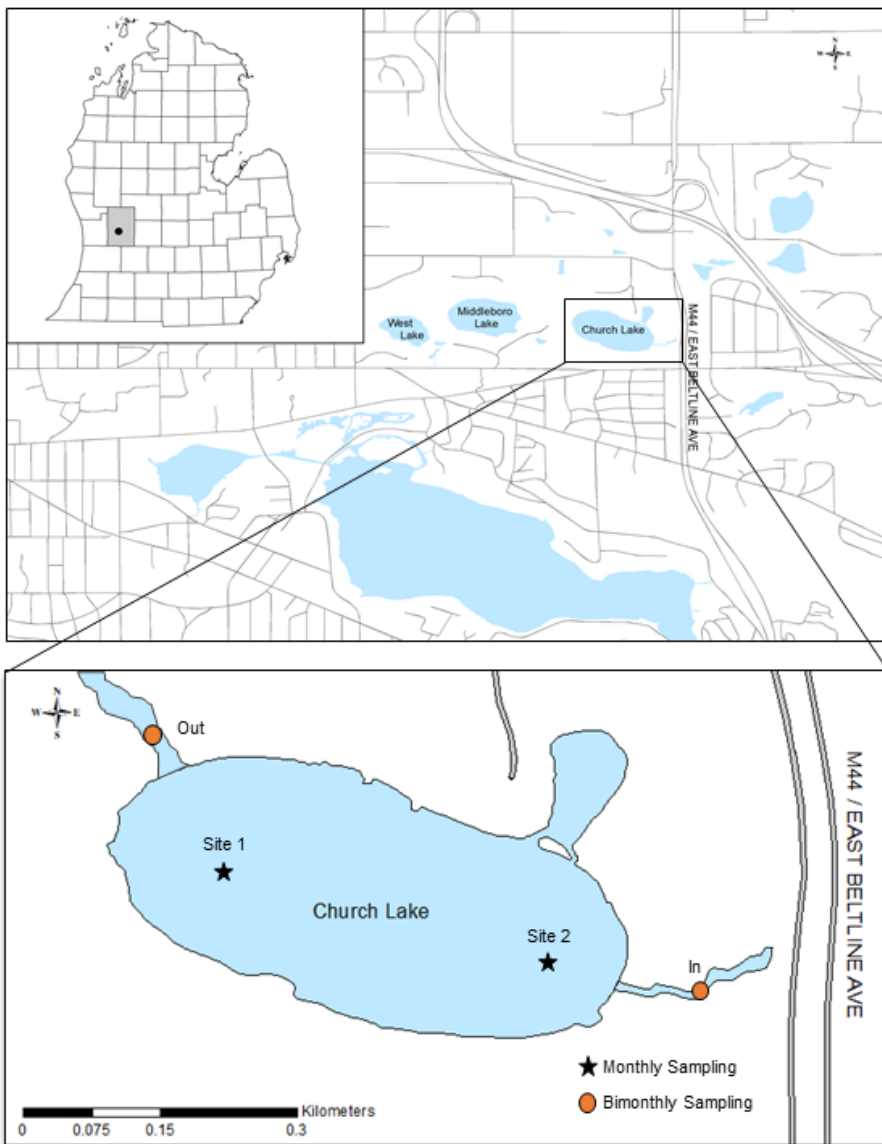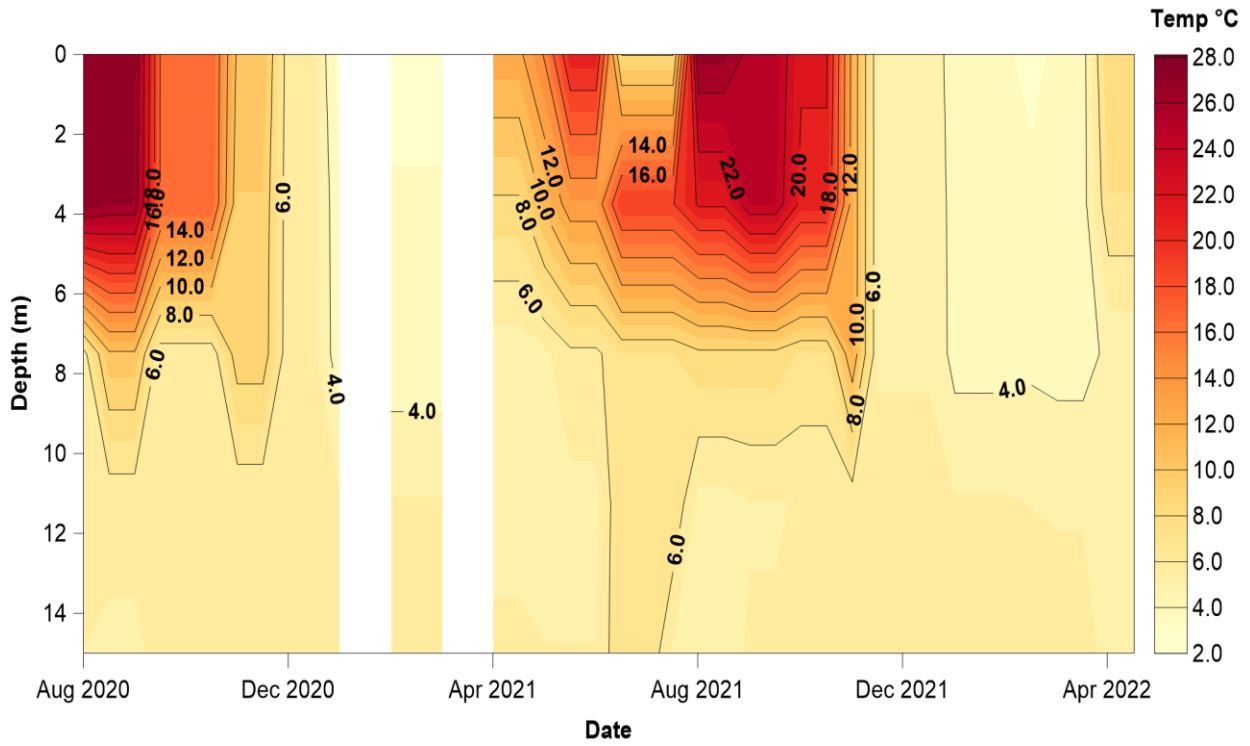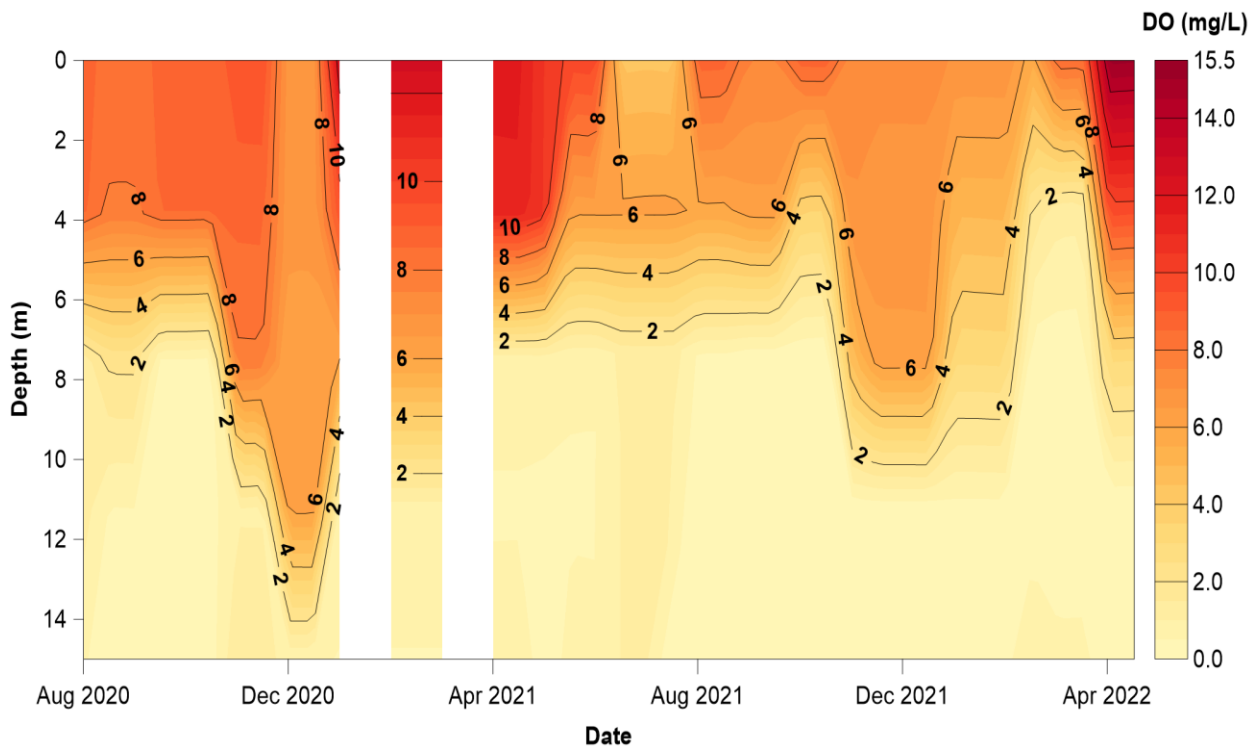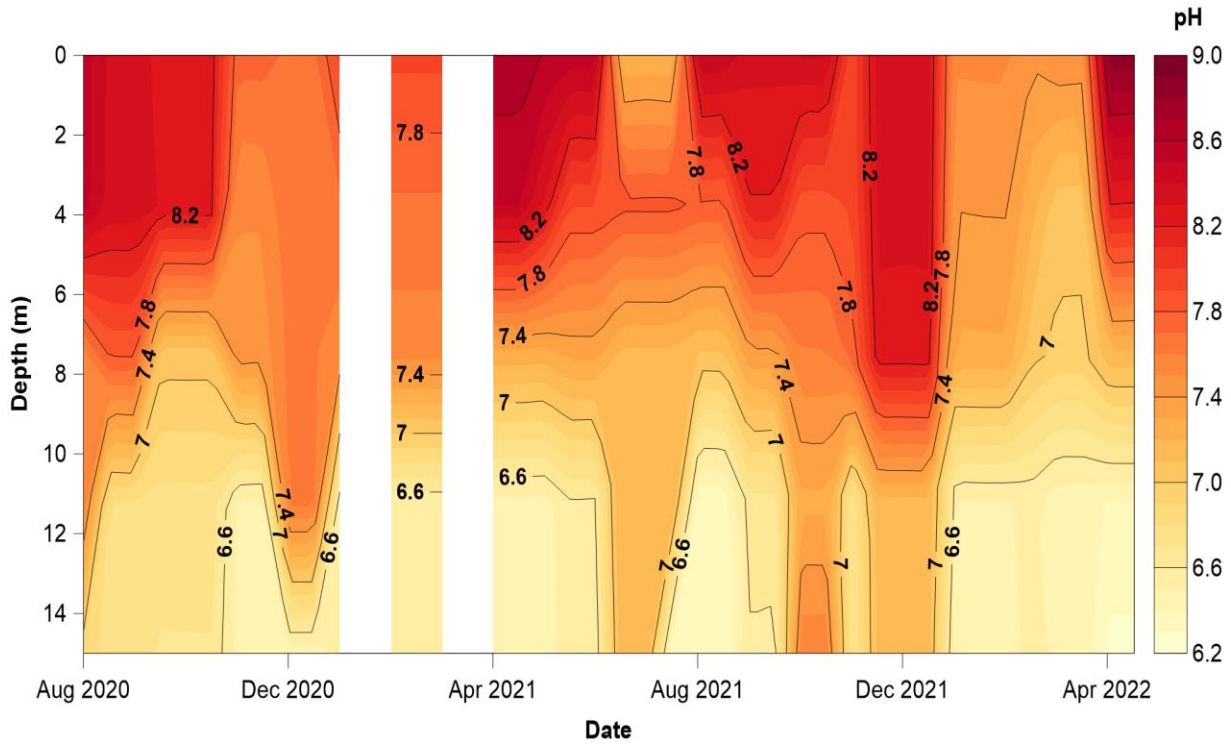
Fig. 2.4

Fig. 2.5

Fig. 2.6

Fig.2.7

49
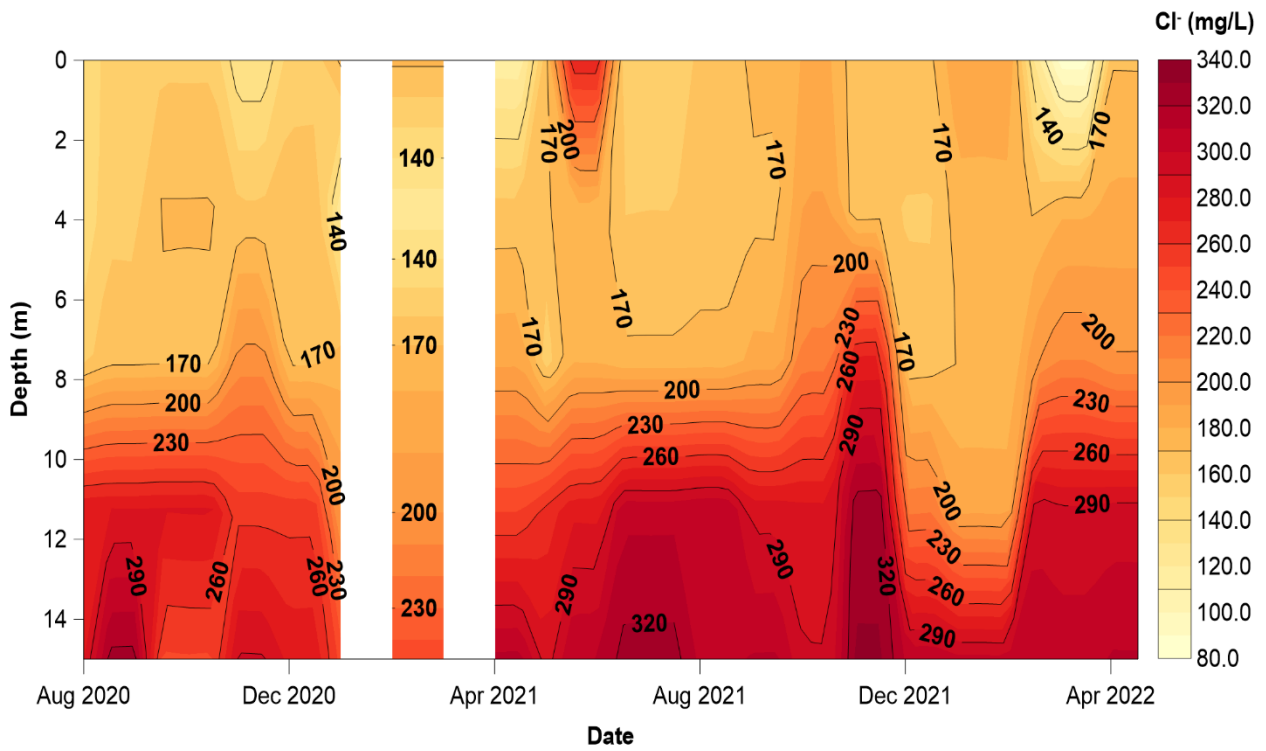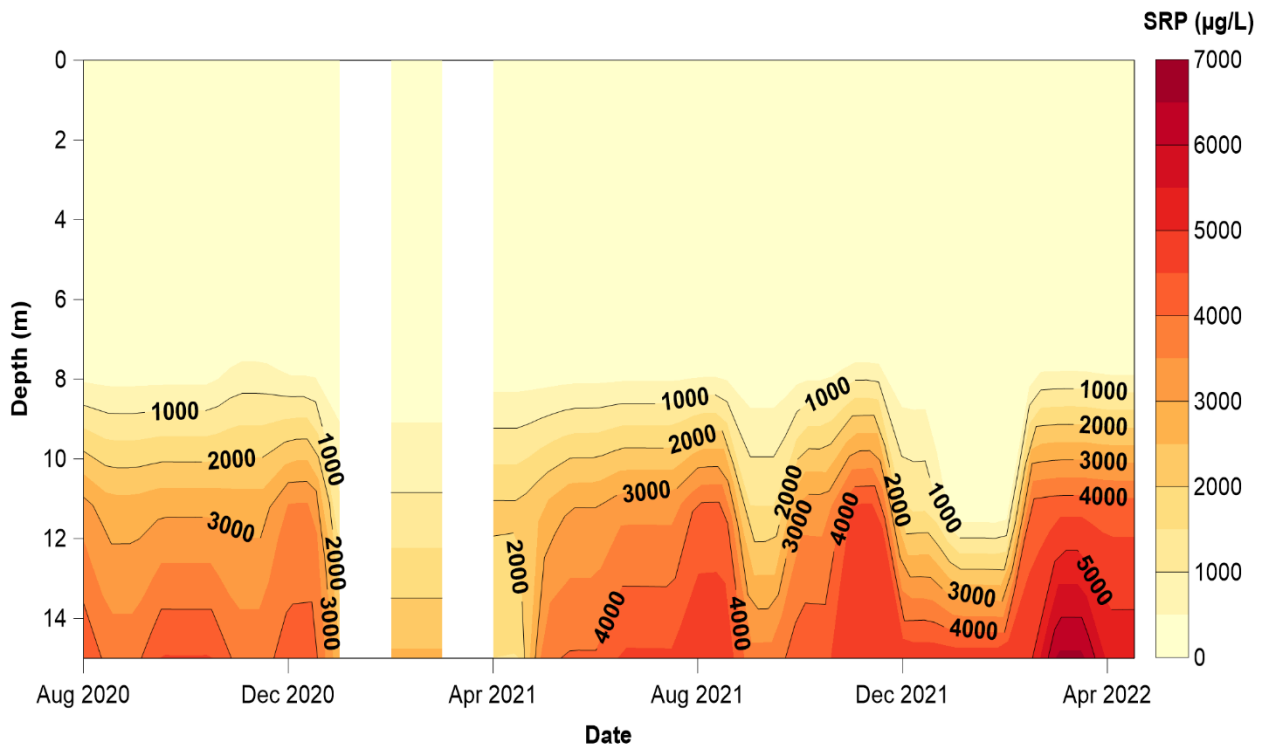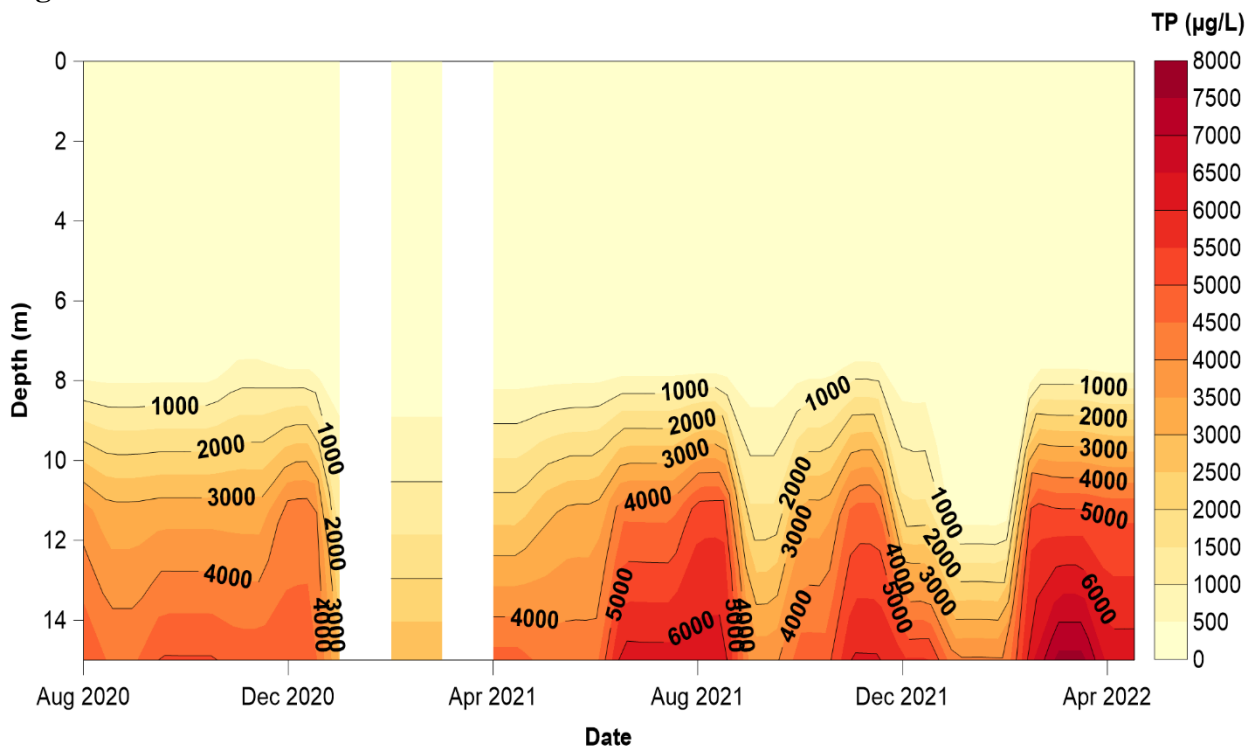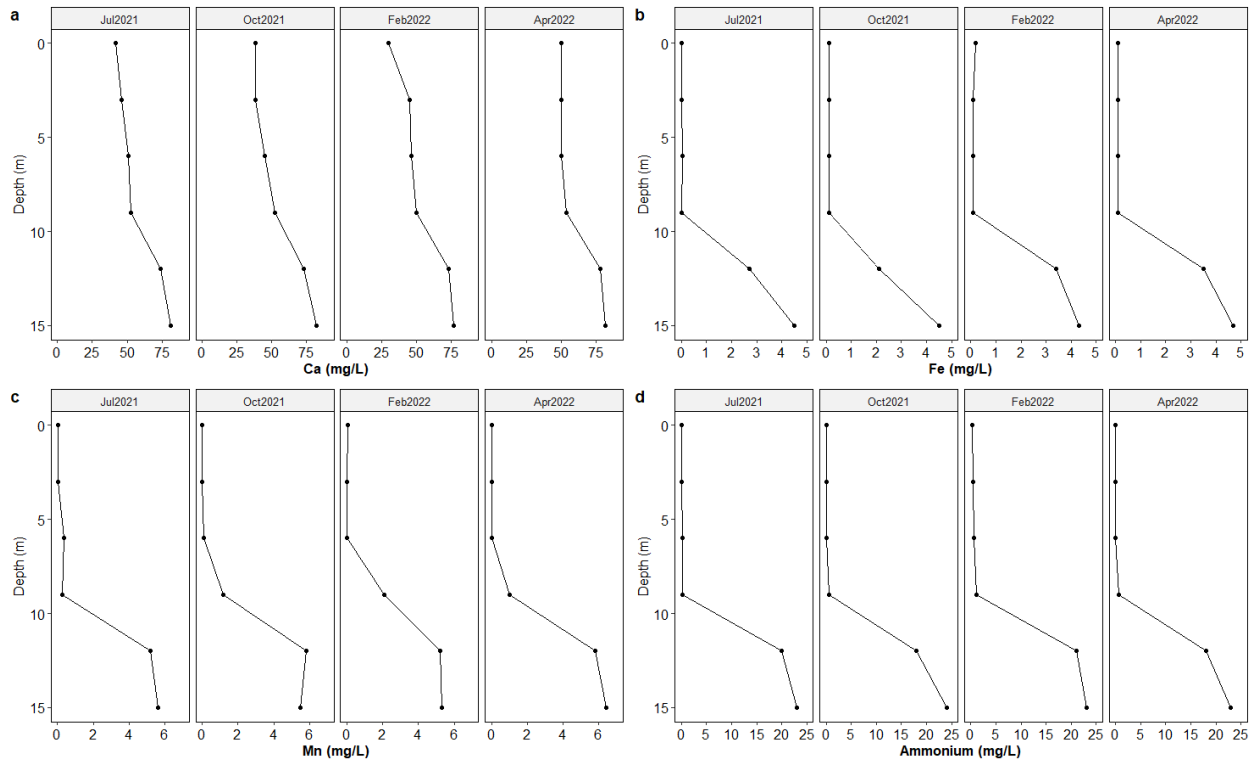
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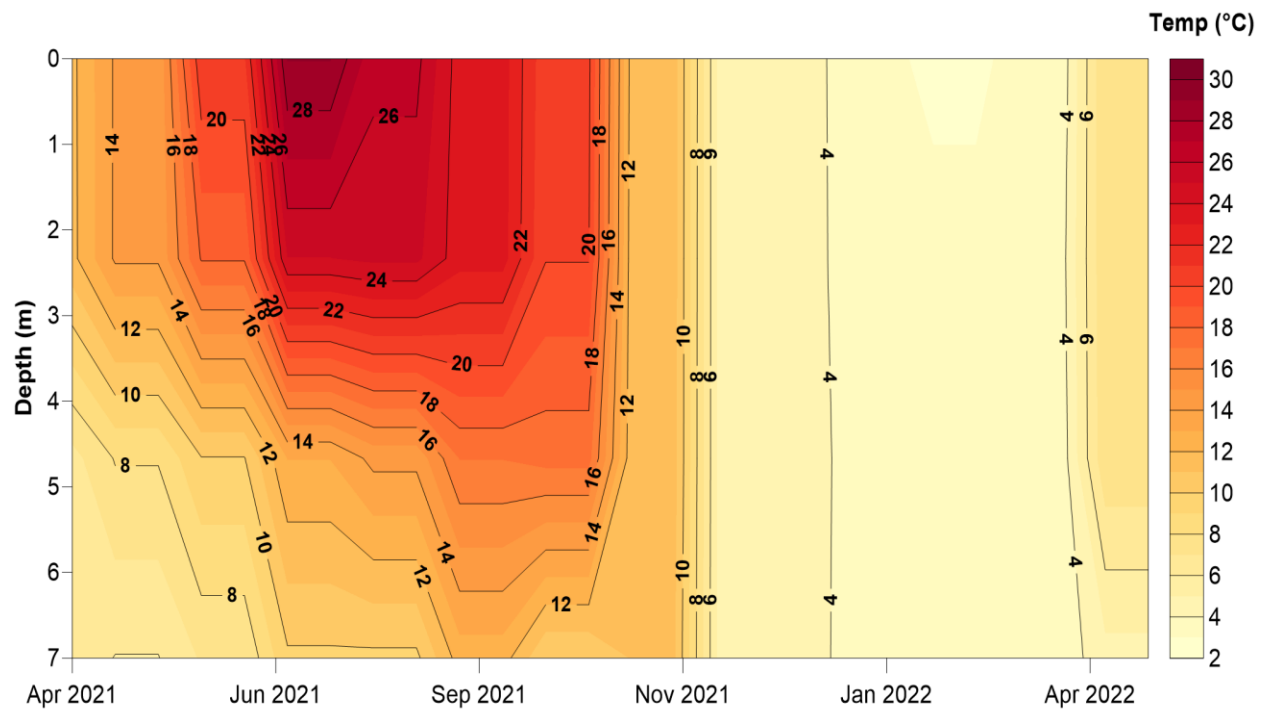
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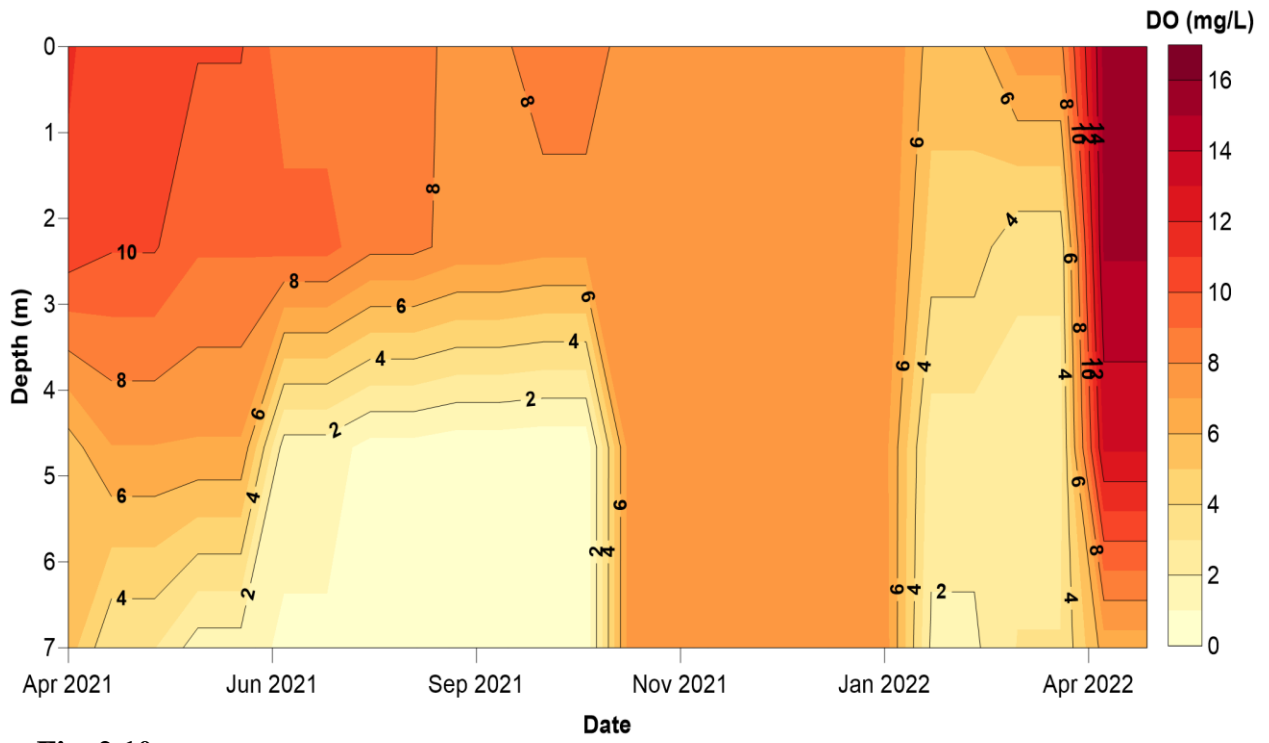
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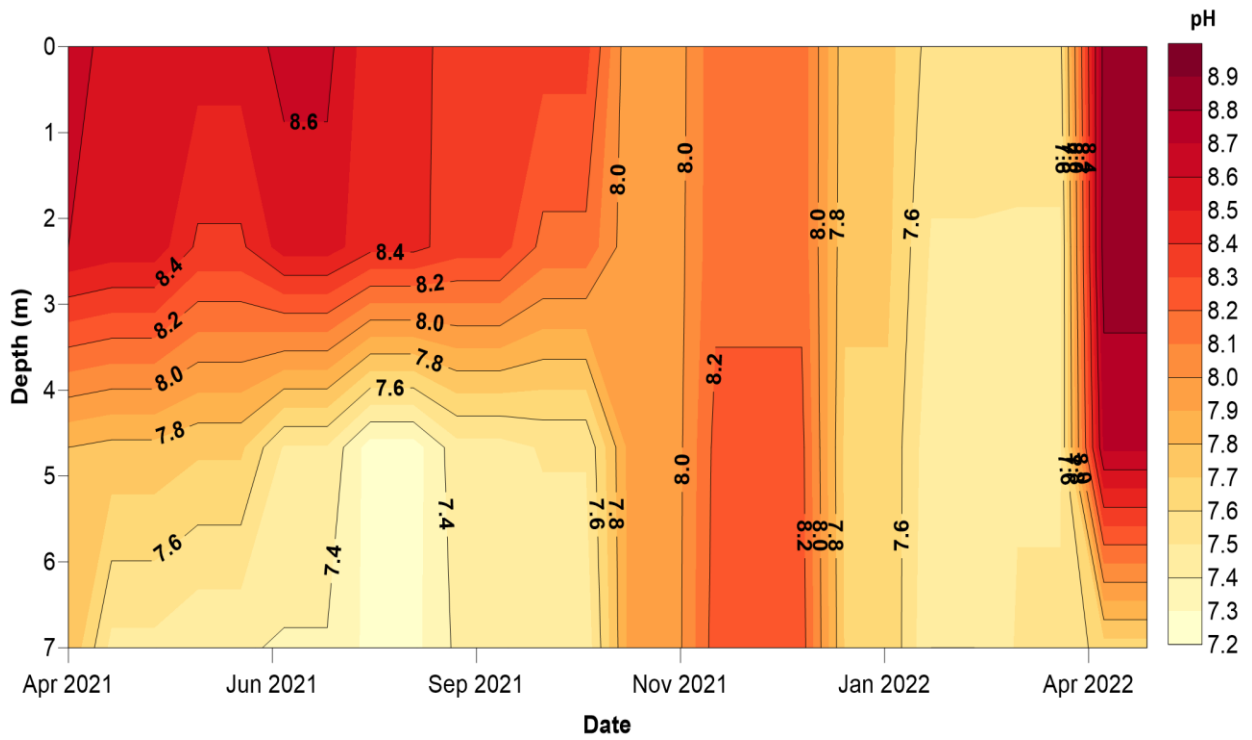
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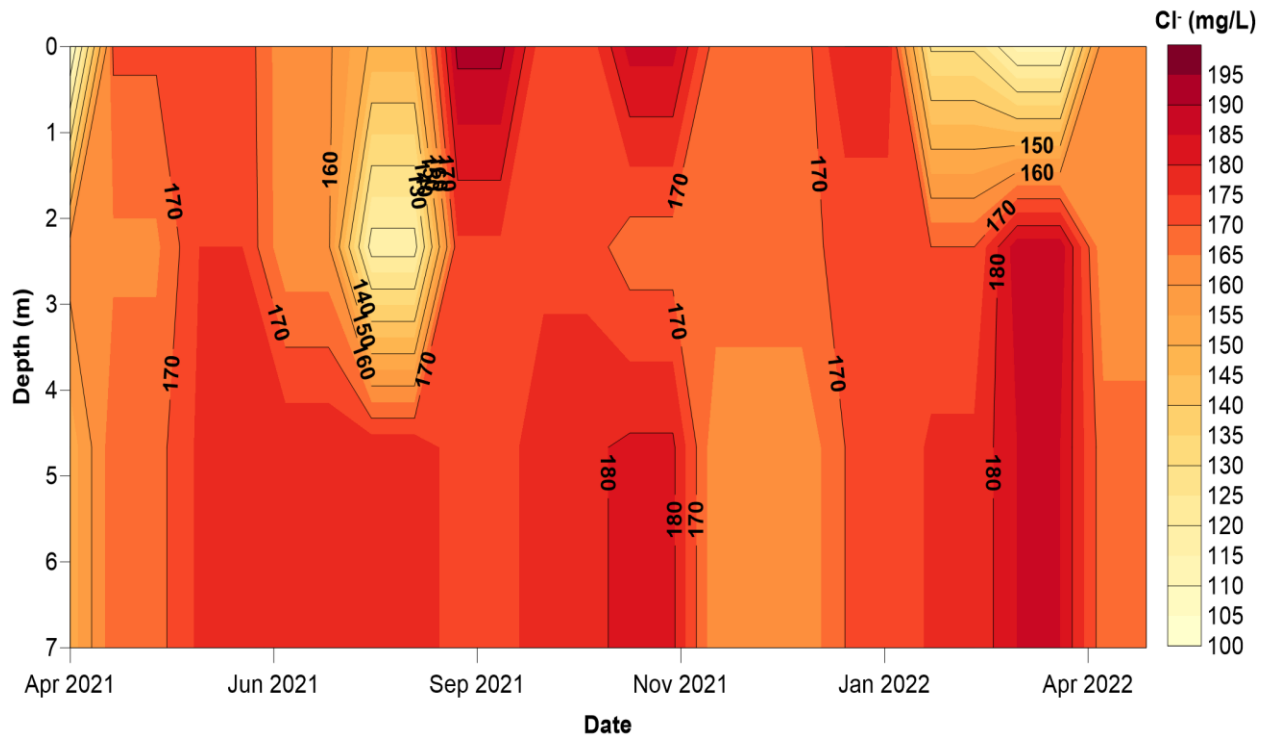
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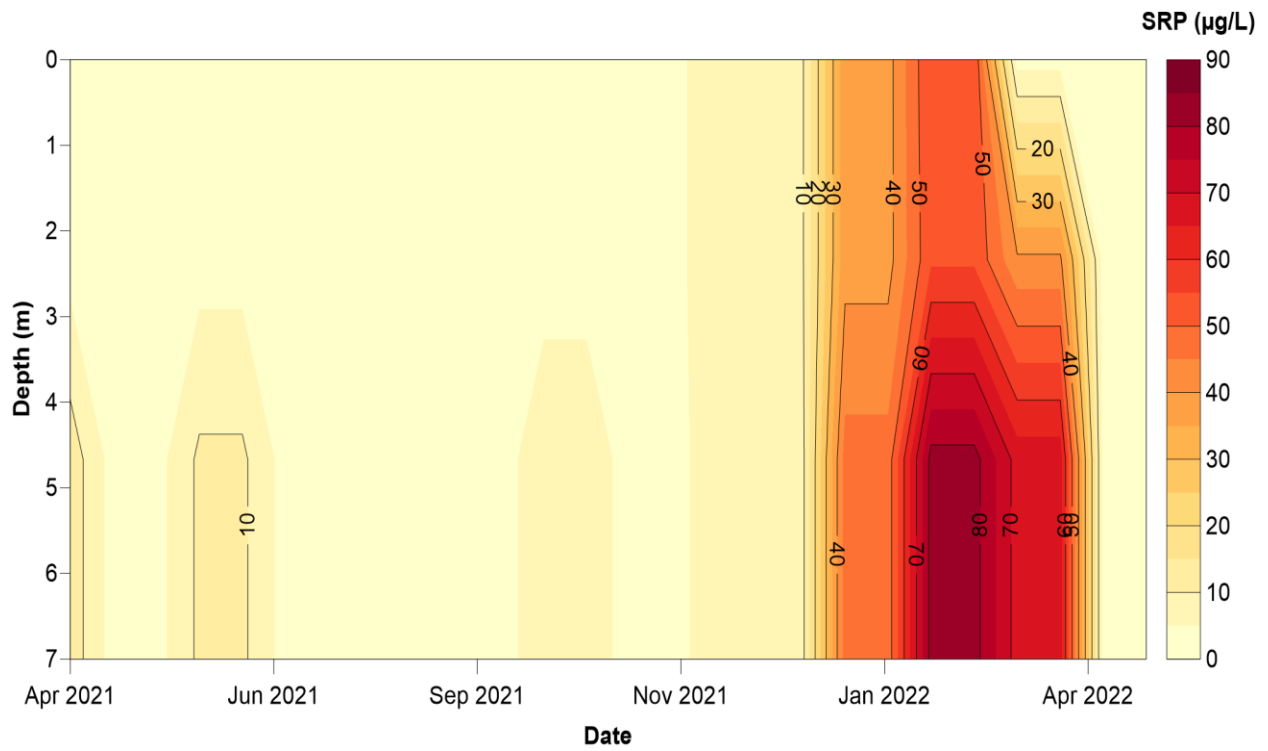
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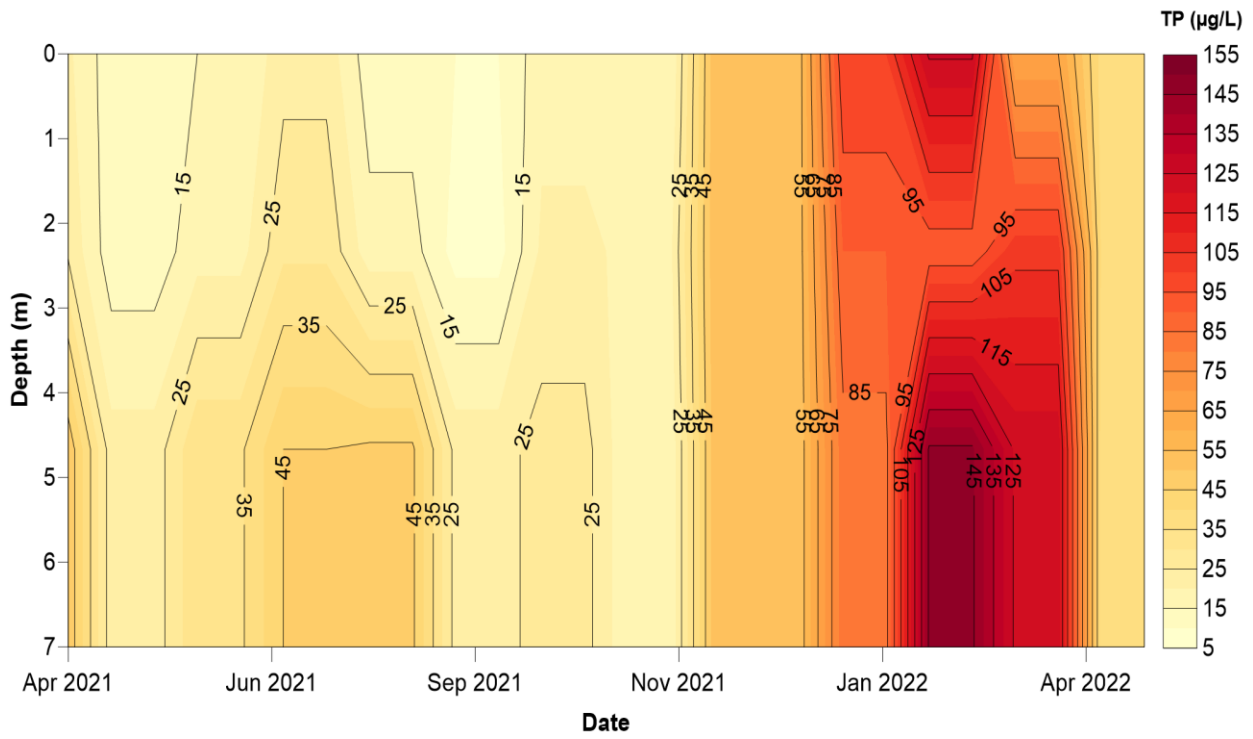
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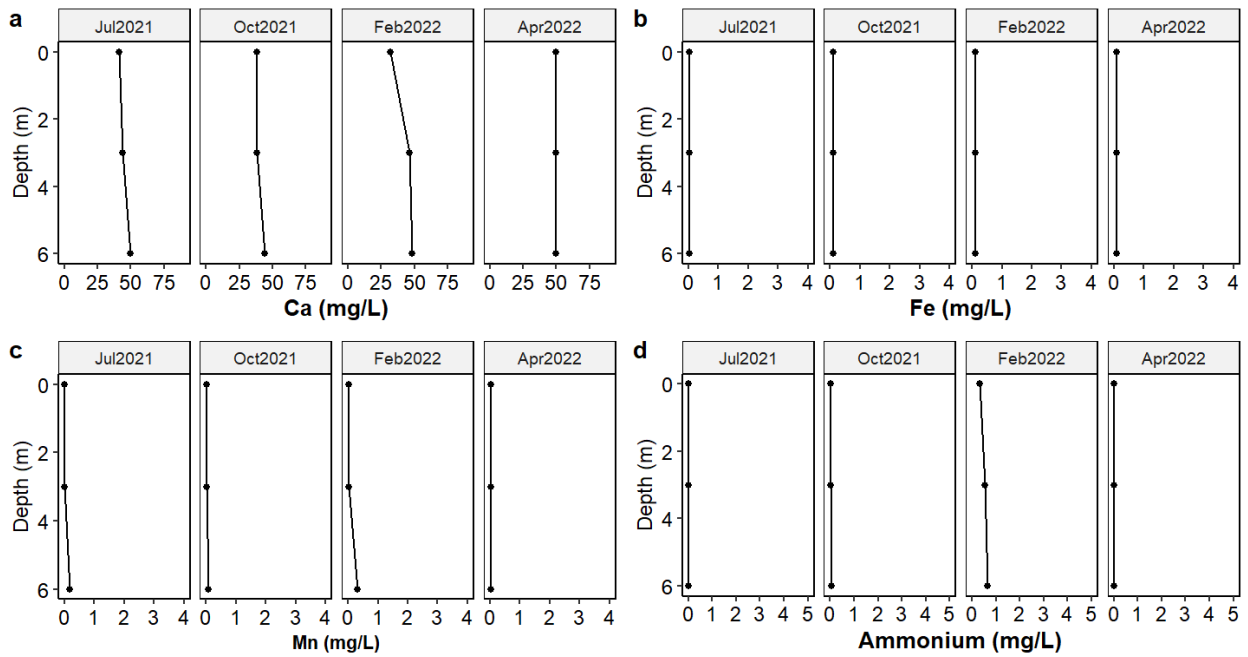
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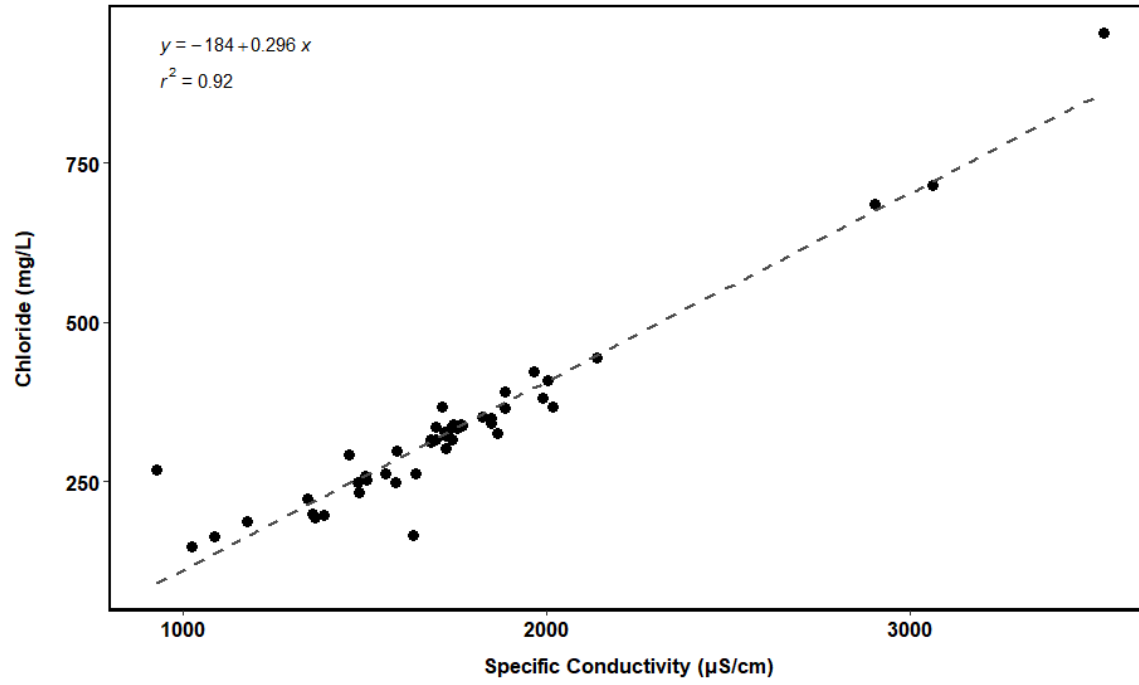
Fig. 2.16

Chapter 3

The Influences of Road Salt on Lake Sediment Phosphorus Release

ABSTRACT

Freshwater salinization from road deicing salts is a widespread environmental issue. Though the impacts of excess salt in freshwater lakes are well studied, there is minimal understanding of how high salt concentrations interact with additional aquatic stressors such as eutrophication. Our research seeks to address this knowledge gap by studying a chloride-impaired eutrophic lake in Grand Rapids, Michigan, USA. Previous water quality analyses have shown extremely high hypolimnetic concentrations of chloride and phosphorus and low dissolved oxygen, suggesting an absence of lake turnover and internal loading of nutrients from sediment phosphorus release. To further investigate the impacts of this high chloride on internal phosphorus loading, we collected sediment cores to measure phosphorus release under varying oxygen and chloride treatments. Mean maximum Total Phosphorus (TP) release was greatest in cores exposed to the high chloride/anoxic treatment ($1.71 - 2.23$ mg m^{-2} d^{-1}) compared to low chloride/ anoxic treatment ($0.83 - 1.42$ mg m^{-2} d^{-1}), suggesting that elevated road salt concentrations may exacerbate internal phosphorus loading. However, release of Soluble Reactive Phosphorus (SRP) was not consistent between treatments and was strongly influenced by the sediment source, indicating that P release from salinization is likely dependent on sediment composition. Management strategies in anthropogenically-impacted lakes should consider addressing both the elevated hypolimnetic phosphorus and chloride concentrations concurrently, as treating one problem without the other could promote continued nutrient release and hamper lake recovery.

INTRODUCTION

Human activity has greatly altered the chemical, physical, and biological properties of freshwater lakes (Conley et al. 2009, Reid et al. 2019). Recent studies have identified eutrophication and salinization as two prominent threats to aquatic ecosystems (Schindler 2012, Dugan et al. 2017, Reid et al. 2019). Eutrophication, resulting in part from excess phosphorus (P) in aquatic systems, causes substantive changes in productivity, biogeochemical functions, and socio-economic value (Schindler and Vallentyne 2008, Dodds et al. 2009, Isley et al. 2018). The process of P loading to lakes from anthropogenic sources is known as 'cultural eutrophication' and can cause a suite of problems in freshwater ecosystems, including harmful algal blooms, low dissolved oxygen levels, and unsightly aesthetics (Schindler 2012). Internal phosphorus loading (IPL) can exacerbate issues of eutrophication by releasing P from benthic sediments into the water column (Søndergaard et al. 2003, Steinman et al. 2004, Steinman and Spears 2020). During periods of hypoxia or anoxia at the sediment-water interface, dissolved P can diffuse out of the sediment and become available for uptake by organisms (Mortimer 1941, Steinman et al. 2004). Through this mechanism, IPL may continue to cause issues such as harmful algal blooms long after external loads have been reduced.

Human activities in temperate regions have also contaminated freshwater ecosystems through the use of deicing salts. Increasing chloride (Cl⁻) levels associated with road salt have been observed in lakes throughout the temperate regions of the USA, including Michigan (Judd et al. 2005, Sibert et al. 2015, Wyman and Koretsky 2018). Road salt usage has substantially increased in the last five decades; in 1950, less than 1 million metric tons of salt were applied to U.S. roadways with the application increasing to over 24 million metric tons in 2014 (Lilek 2017). High Cl⁻ concentrations negatively impact ecosystems by increasing the mobility of heavy

metals in the water column, reducing biodiversity, expanding anoxic regions in lakes, and accumulating reduced solutes (Judd et al. 2005, Koretsky et al. 2012, Wyman and Koretsky 2018). High Cl^- levels can also create persistent density gradients in freshwater lakes, delaying or preventing seasonal turnover (Judd 1970, Novotny et al. 2008, Sibert et al. 2015). Without fall and spring turnover, lakes can become monomictic (mixing once per year) or meromictic (never mixing) with permanent hypoxic or anoxic conditions in the hypolimnion, a phenomenon observed in several Michigan lakes (Judd et al. 2005, Koretsky et al. 2012, Sibert et al. 2015).

Though eutrophication and salinization have been identified as two of the biggest stressors to freshwater systems (Dodds et al. 2009, Dugan et al. 2017, Reid et al. 2019), there is a lack of research on how the interaction of elevated Cl^- and P concentrations impact lakes. Due to the extensive use of road salt deicers in northern regions and the ubiquity of nutrient enrichment in temperate lake watersheds, it is important to understand the additive and synergistic effects of excess P and Cl^-.

The goal of this research was to investigate the impacts of high Cl^- concentrations on lake sediment P release. The higher Cl^- concentrations in the lake are a result of saline road deicer runoff from a nearby highway into the lake's tributary. This created a persistent dense salt layer in the lake bottom, preventing turnover and leading to low oxygen conditions. Several studies using wetland and stream sediments have seen increased P release after exposure to elevated salinity concentrations (Kim and Koretsky 2013, Bai et al. 2017, Haq et al. 2018), though the effects of redox state were not examined. It is well understood that excess Cl^- can prevent lake turnover and create permanent hypoxia near the sediment-water interface (Novotny et al. 2008, Koretsky et al. 2012) and that low oxygen conditions contribute to IPL (Mortimer 1941). However, the direct impacts of excess Cl^- concentrations on sediment-P release rates in lakes

have not been considered. Our research aims to understand if higher Cl⁻ concentrations can exacerbate IPL in freshwater lakes by looking at sediment P release under exposure to varying oxygen and salinity conditions. To our knowledge, our study is the first to look at how salt contamination affects IPL in freshwater lakes. We hypothesized that the redox condition would have a significant effect on sediment P release and that Cl⁻ concentrations would have minimal or no effect on IPL rates.

<div align="center">MATERIALS AND METHODS</div>

Study Location

Church Lake is located in eastern Grand Rapids in Kent County, Michigan, USA (Fig. 3.1). The lake's surface area is approximately 7.7 hectares and its maximum depth is 16 m. The watershed is predominately urbanized apart from low-lying wetlands adjacent to the lake. A small, unnamed tributary flows into the east side of Church Lake. The origin of the tributary is a 36-inch concrete culvert that diverts stormwater runoff from East Beltline Avenue into the stream. East Beltline Avenue (M-37/M-44) is a Michigan State Highway with a two-way annual average daily traffic count of 46,832 vehicles and considerable road salt use in the wintertime (GVMC 2018). Church lake has a small ephemeral stream that flows west out of the lake and through a wetland before reaching another lake downstream.

Sediment Core Collection

Sediment cores from two sites were collected on 26 August 2021. A total of 9 sediment cores were collected from each sampling site within Church Lake resulting in a total of 18 sediment cores. Sampling sites within the lake were chosen near the locations used for the water

quality surveys and were used to capture heterogeneity within the lake. Both sites selected were in the lake's previously established hypoxic zone.

Sediment cores were obtained using a modified piston coring apparatus (Fisher et al. 1992, Steinman et al. 2004). The coring device was assembled from a 0.6m long polycarbonate core tube with a 7cm diameter, a polyvinyl chloride (PVC) attached assembly, a piston made of two rubber stoppers and an eyebolt, a plastic-coated piston cable with a swivel clip, and aluminum driving rods (Ogdahl et al. 2014). The modified corer was positioned vertically at the sediment-water interface and carefully driven into the sediment to a depth of at least 20 cm. The core was brought to the surface and sealed with a rubber stopper before breaking the water surface. The stopper was secured with duct tape and placed in a vertical rack with the piston of the core bolted at the top to keep it stationary during transit. Sediment cores were placed on ice after collection until transportation back to the lab.

Field Water Quality Sampling

Prior to collecting sediment cores at each incubation, a YSI 6600 sonde (YSI Incorporated, Yellow Springs, OH) measured readings at the water surface and near-bottom of each site for DO, pH, temperature, and specific conductance. A Van Dorn sampler was used to take water samples at near-surface and near-bottom of each site for analysis of TP, SRP, and Cl$^-$ concentrations. For the experiment, 20L of near-surface water was collected from each site using 10L acid-washed carboys, which were placed on ice shortly after collection until transportation back to the lab. The water from each carboy was then sequentially filtered through a 1-µm filter followed by a 0.2-µm filter and stored at 4°C in acid-washed carboys.

Experimental Design

We used a $2 \times 2 \times 2$ experimental design with oxygen, Cl⁻, and site as the factors, each with two levels. This resulted in sediment cores being exposed to one of four treatments, which were randomly assigned: (i) oxic with hypolimnetic Cl⁻ concentrations (O + Cl⁻); (ii) oxic with surface Cl⁻ concentrations (O); (iii) anoxic with hypolimnetic Cl⁻ concentrations (AN + Cl⁻); and (iv) anoxic with surface Cl⁻ concentrations (AN). There were two replicate cores per treatment.

Initial Laboratory Processing

Once in the laboratory, sediment cores were adjusted to consistent depths of 20cm by removing excess sediment from the bottom of the core. The overlying water of each core was removed to within 2cm of the sediment surface using a peristaltic pump. A YSI 6600 multisonde probe was used to measure the specific conductivity of the water in each carboy. Conductivity was used as a proxy for Cl⁻ based on a linear relationship ($y = 0.296x - 184$; $r^2 = 0.92$; $n = 51$) previously established for the lake. Based upon the conductivity measurements, a total of 3 g of non-iodized table salt (NaCl) was added to one carboy from each site to reach the average Cl⁻ concentration estimated in the hypolimnion of the lake. After salt was added to the respective carboys, water samples were collected to measure the initial concentrations of the refill water for TP, SRP, and Cl⁻. The cores were then flooded with corresponding Cl⁻ or ambient water from each site until the water depth was approximately 20 cm in the core tube. We stored the remaining water in acid-washed carboys at 4ºC, which were used to refill core tubes after each sampling date during the experiment. The sediment from the remaining core from each site was used as a control for pre-experiment ash-free dry mass (AFDM), TP, and metals analysis.

Sediment Core Incubation

Sediment cores were placed in a darkened environmental growth chamber with the temperature and light set to match the ambient bottom conditions in the hypolimnion of the lake. Temperature accuracy within the environmental growth chambers was checked daily using an additional thermometer. Cores were exposed to either oxic or anoxic treatments within the chamber. For each oxic treatment, air was gently bubbled into the cores using aquarium pumps to maintain water column oxygen concentrations at 75–100% equilibrium with atmospheric oxygen throughout the incubation period. The water column of the cores with the anoxic treatment was bubbled with N_2 (with 350ppm CO_2 to buffer pH). All gasses were bubbled into core tubes at a uniform rate through tubing placed above the sediment surface; caution was taken to ensure bubbling did not disturb the sediment surface. DO concentrations in the water columns of each core were measured at the end of all experiments using a YSI Pro-DO sonde placed near the water-sediment interface.

During the incubation period, 60mL water samples were collected from each core tube at approximately 10 cm depth in the water column through a plastic sampling port at 0 h, 12 h, and days 1, 2, 5, 10, 15, 20, and 25. We used 20 mL of unfiltered water for TP analysis and filtered the additional 40 mL through an acid-washed 0.45- µm filter for a 20 mL subsample of SRP and Cl^-. Immediately after collection, TP and SRP samples were stored at 4ºC, and the Cl^- samples were frozen until analysis. TP and SRP were analyzed on a Seal AQ2 Discrete Analyzer (USEPA 1993) and values below detection were designated as one-half the detection limit to assign a numerical value above zero for analysis (Hornung and Reed 1990). Cl^- samples were analyzed by ion chromatography on a Dionex DX500 (APHA 1999). To maintain the original volume and concentration gradient in the core tubes, the 60 mL subsample was replaced with the filtered water from the corresponding lake site and Cl^- treatment.

Sediment Analysis and Fractionation

Following completion of the incubation (day 25), 50 mL of water was removed from the center of the water column of each core and filtered through a 0.45-µm filter for analysis of dissolved Fe. The cores were dewatered and the top 10 cm of sediment was removed from each core and homogenized. The sediment was homogenized and 25 g was subsampled, dried, and ashed at 550°C for 1 hour for AFDM and TP analysis. Additional 5 g subsamples of sediment were taken from each core, centrifuged to remove excess pore water, and sequentially fractionated to determine the major P compounds in the sediment following methodology modified from Hupfer et al. (2009). Sediment fractionation is a process that separates different forms of SRP, helping determine the amount that is available to be released (mobile) and the amount that is more stable, which has implications for IPL (Psenner and Pucsko 1988, Hupfer et al. 2009). Fractionation involved 25mL of each of the following extraction chemicals: 1M NH_4Cl shaken for 30 minutes extracting loosely-bound and pore water P; 0.11 M $NaHCO_3$ $Na_2S_2O_4$ (buffered dithionite, BD) shaken for one hour extracting Fe- bound and redox-sensitive P; 1M NaOH shaken for 16 hours extracting metal-oxide-bound P; and 0.5 M HCl shaken for 16 hours extracting Ca-bound P. All anoxic cores were processed in a vacuumed-sealed glove box filled with N_2. A separate pore water extraction was not possible due to limited porewater content. The remaining sediment from each core was dried and sent to Trace Analytical Laboratory where metals (Al, Ca, Fe, Mg) were analyzed using EPA method 6010b (USEPA, 1996).

Statistical Analysis

Maximum sediment core releases rates were calculated for each core using the following equation based on the methodology used in Steinman et al. (2004):

$$P = (C_t - C_\Theta) * V/A$$

Where P_{flux} is the rate of TP or SRP release in mg m^{-2} d^{-1}; C_t is the concentration of TP or SRP in mg/L at time t; C_0 is the TP or SRP concentration in mg/L at time 0; V is the volume of the overlying water column; and A is the surface area of the sediment. Flux calculations were based on the linear portions of the water column P concentration curves measured through time to capture the apparent maximum release rate. To avoid potential short-term bias, C_t and C_0 could not be based on only two consecutive dates. A multi-way analysis of variance (ANOVA) with 3-factors and two levels was used to test for differences in mean maximum apparent P release rates. Additionally, a multi-way repeated measures ANOVA with two levels of sediment source (Site 1 vs. Site 2), redox treatment (Oxic vs. Anoxic), and Cl$^-$ concentration (Low vs. High) was used to test for differences in water column P concentrations of our sediment cores throughout the duration of the incubation period. Time was used as the repeated measure. All statistical analyses were conducted using R software (R Core Team, 2020). Data normality was tested using the Shapiro-Wilk goodness of fit test. When necessary, data were transformed (ln, square root, reciprocal, power) to meet the assumptions of ANOVA. If the assumptions were not met and the transformation was unsuccessful, overlying core water column data were still analyzed using ANOVA and the results were noted as exploratory.

RESULTS

The water quality parameters varied slightly between Site 1 and Site 2 at Church Lake. The surface water specific conductivity and temperature were nearly identical at the two sites but

varied slightly with near-bottom measurements due to differences in depth (Table 3.1).

Additionally, the concentrations of TP, SRP, and Cl^- were similar at the surface of each site but

differed slightly at near-bottom depths, with Site 1 having higher concentrations of SRP and TP

than Site 2.

The Cl^- concentrations of the initial water added to the cores in the low Cl^- treatment

were 159 mg/L and 156 mg/L for Site 1 and Site 2 respectively, while the initial water for high

Cl- treatment was 321 mg/L for Site 1 and 307 mg/L for Site 2 (Table 3.2). The initial refill

water for each site and treatment had SRP concentrations below detection limits, whereas TP

ranged from 0.008 mg/L to 0.012 mg/L.

Phosphorus Release Rates

Phosphorus release rates were calculated in two ways. The first was as an overall mean

flux using release from day 0 through day 25. The second was as a mean maximum apparent

release rate based on the maximum linear increase over at least 3 sampling dates over the 25-day

incubation period.

The overall mean release rates for TP and SRP were higher in Site 1 sediment cores

compared to Site 2 cores (Fig. 3.2 and Fig. 3.3). All cores saw an initial decline in overlying

water P concentrations, likely due to initial disturbance and settling of sediment in the cores. The

means for overlying water TP concentrations over the 25-day study ranged from 0.032 mg/L to

0.178 mg/L and SRP concentrations ranged from 0.005 mg/L to 0.049 mg/L (Table 3.2). The

anoxic and Cl^- (AN + Cl^-) replicates at Site 1 had the highest TP and SRP concentrations while

anoxic (AN) only replicates had the highest SRP concentrations for Site 2. Overall TP release

differed significantly between sites, redox treatment, and Cl^- level and there were no significant

interactions between the treatments at the 0.05 significance level (Table 3.3). However, there were significant interactions between Site × Redox, Site × Cl⁻, and Site × Redox × Cl⁻ for the SRP concentrations (Table 3.3). The SRP accounted for ~25-45% of the TP being released from the sediment.

The mean maximum apparent release for TP was highest in the AN + Cl⁻ treatment at both sites (Fig. 3.4), but only redox had a significant effect (Table 3.4). Mean maximum TP release rates for sediment core treatments ranged from 0.19 mg m⁻² d⁻¹ to 1.71 mg m⁻² d⁻¹ at Site 1 and 0.007 mg m⁻² d⁻¹ to 2.23 mg m⁻² d⁻¹ at Site 2. Mean maximum apparent SRP release rates trends varied from those of TP. SRP was relatively low among the two sites under oxic conditions, ranging from -0.090 (suggesting SRP movement from the water column to the sediment) to 0.096 mg m⁻² d⁻¹. Mean maximum release rates varied between the two sites for the other three treatments, ranging from 0.295 to 1.053 mg m⁻² d⁻¹ for AN treatments, -0.004 to 0.468 mg m⁻² d⁻¹ for O + Cl⁻, and 0.058 to 1.595 mg m⁻² d⁻¹ for AN + Cl⁻ treatments. SRP maximum release rate was greatest in Site 1 cores exposed to the AN + Cl⁻ treatment, though Site 2 had the highest SRP maximum release in cores with just the anoxic treatment. Redox, Cl⁻, and site were all significant factors influencing the apparent mean maximum SRP release rate, though there was a significant interaction effect of site (Table 3.4).

Sediment Fractionation

Post-incubation fractionation results were relatively consistent among redox and Cl⁻ treatments but differed slightly between sites (Fig. 3.5). In all cores, very low amounts of SRP were found in the NH_4Cl fraction, which holds loosely-sorbed labile P. At Site 1, the greatest percentage of SRP was measured in the NaOH (metal-oxide-bound) fraction, ranging from

34.2% to 39.6% of the total sediment SRP (Table 3.5). Additionally, Site 1 had more SRP by

mass and percentage in the BD fraction (Fe- and redox sensitive-bound) compared to Site 2,

which is the fraction of P that can be mobilized under anoxic conditions. The greatest percentage

of SRP at Site 2 was measured in the HCl fraction (Ca-bound), with this fraction comprising

32.8% to 52.0% of the SRP in the sediment. The mean dry-weight sediment TP was lowest in the

AN + Cl$^-$ treatment at both sites (Table 3.5). On average, Site 1 had less dry-weight TP than Site

2. The percent organic matter (OM) ranged from 2.96-3.92% and there was no distinct pattern

between treatments or sites (Table 3.5)

Sediment Metals and Content

Ca was the most abundant element by mass found in the sediments of all the cores, followed

by Fe (Fig. 3.6). There was no clear pattern that emerged between the experimental treatments

and sediment metal composition, though similar to the P fractions, there were differences

between the sites. The Fe:P ratio by weight was high and ranged from 22 to 32, with the AN +

Cl$^-$ treatment having the highest mean Fe:P ratio at both sites (Table 3.6). Generally, the Fe:P

ratio was greater at Site 1 compared to Site 2 (Table 3.6).

DISCUSSION

Anthropogenic input from road salt deicers has large implications for the mixing

dynamics and biogeochemical cycles in lakes, including the potential to exacerbate existing

issues in eutrophic lakes (MacLeod et al. 2011, Lind et al. 2018, Wyman and Koretsky 2018).

Though excess nutrients and Cl$^-$ can be co-occurring problems, there is not a robust

understanding of how road salts alter processes such as P nutrient cycling, particularly in lakes

(Hintz et al. 2019). Several studies have seen reduced lake mixing as a consequence of higher Cl$^-$

concentrations, resulting in prolonged bottom water hypoxia (Novotny et al. 2008, Sibert et al. 2015, Wiltse et al. 2020) and it is known that low dissolved oxygen concentrations stimulate P diffusion in iron-rich sediments due to the release of P from ferric oxy-hydroxides (Mortimer 1941, Søndergaard et al. 2003). However, there have been no studies to our knowledge on whether the elevated Cl^- concentrations from road deicers can further promote mobilization of P out of lake sediments and into the overlying water column. Understanding how excess salt influences nutrient processes in lakes is important for informing management decisions, especially for northern temperate lakes where road salt and P are common pollutants. Here we show, based on results from laboratory experiments, that a high concentration of Cl^- in lakes has the potential to impact sediment phosphorus release and IPL rates.

Throughout the experiment, the mean concentration of TP in the overlying water column was greatest in cores exposed to the AN + Cl^- treatment. We saw similar results when calculating the apparent mean maximum release from cores, though the redox condition was determined to be the only statistically significant factor. The negative values for mean maximum flux measured in the oxic cores show that the Church Lake sediments have the potential to serve as a P sink when there is enough oxygen present. The overall highest mean TP release rates that we measured were slightly lower than what is typically seen under low oxygen conditions in eutrophic systems (Nürnberg and LaZerte 2004, Steinman et al. 2009). For example, sediments from Mona Lake, about 40 miles west of Church Lake, had TP release rates ranging from 0.8 - 15.56mg $m^{-2}\,d^{-1}$ under anoxic conditions (Steinman et al. 2009) while nearby Spring Lake had high release rates reaching 29.54 mg $m^{-2}\,d^{-1}$ (Steinman et al. 2004). The mean maximum release rate in the Church Lake sediments was measured for 1.71 mg $m^{-2}\,d^{-1}$. The lower temperature of the incubator, which was kept at 5.5 °C to simulate hypolimnetic conditions of Church Lake,

could have resulted in this overall lower release. Warmer temperatures have been shown to stimulate mineralization of organic-bound P, create microbial respiration-induced reducing conditions, and increase the rate of reactions and diffusion leading to more phosphorus mobilization out of the sediments (Jensen and Andersen 1992, Jiang et al. 2008). Additionally, while our methods were consistent with prior studies (Steinman et al. 2004, Steinman et al. 2009) and post-incubation measurements of the water column with a DO probe confirmed hypoxic conditions (< 2 mg/L) in cores from the 'anoxic' treatments, the DO concentration may have still been high enough to curb sediment P release (Wetzel 2001). Fe^{3+} is reduced and releases P when the redox potential drops below 200mv, which corresponds to oxygen concentrations of 0.1 mg/L (Steinman and Spears 2020). Due to the measured DO concentrations between 0.75 – 1.80 mg/L, low enough oxygen concentrations were likely not maintained to stimulate persistent P release from Fe-hydroxides, attributing to lower overall P release in the Church Lake sediment cores.

The apparent mean maximum release for SRP was significantly influenced by oxygen level, Cl^- level, and site, though there was a significant interaction effect of site with all factors. The results varied between TP and SRP; this was likely due to SRP being an extremely reactive and bioavailable form of P compared to sorbed and complexed organic and inorganic P forms (Welch and Jacoby 2004). Therefore, the amount of SRP mobilized is more influenced by the sediment composition, which varied between sites in Church Lake. P can bind to Al, Ca, Fe, and other minor elements in the sediment depending on the mineral composition and redox conditions (Hupfer and Lewandowski 2008). Site 1 had a higher concentration of metals in the sediment as well as a greater proportion of the SRP in the redox-sensitive Fe- bound fraction, whereas Site 2 had more SRP in the non-redox-sensitive Ca-bound fraction. This means that Site

1 had a higher capacity to both sorb P and have it subsequently mobilized under anoxic conditions, helping explain why Site 1 had higher overall P release rates compared to Site 2.

Given the small size of the lake and relatively uniform shape, it was surprising to see such differences in sediment composition and P release between the two sites, though the varying hydrology may contribute to the observed heterogeneity. Site 1 is located in the deeper west end of the lake in an area that is permanently stratified due to the salt gradient while Site 2 is located in a shallower basin near the inflow of the tributary that experiences biannual mixing. The spatial distribution of the sediment P pool is noted to be heterogeneous within shallow lakes due to variations in sediment transport, deposition, and resuspension processes (Mackay et al. 2012, Albright et al. 2022). Since Site 2 is shallower and located near the inlet of the tributary, the resuspension of the bottom sediment and sedimentation of suspended solids may have an impact on the local composition (Blom et al. 1992). Site 1 is deeper and likely not impacted by these processes, allowing for greater accumulation of nutrients and metals due to sediment focusing. Although more sediment sampling would be needed to assess overall variability in P release, these data suggest that a targeted mitigation strategy may be possible to address the higher releases occurring in the deeper area of the lake.

Though the differences in sediment composition help explain the variation in P release between the sites, there was still higher P release in sediment cores exposed to the $AN + Cl^-$ treatment for both the mean apparent maximum release and the average overlying water P concentrations, especially at Site 1. While there is little to no literature exploring the impacts of sediment P release from salinization in lake sediments, there have been several studies looking at the effects of road salt contamination on the mobilization of bioreactive elements, like SRP, in stream, wetland, and estuary sediments (Jun et al. 2013, Kim and Koretsky 2013, Bai et al.

2017). Incubations of stream sediments from different land-use gradients showed that salinization decreased sediment net SRP releases in all but the urban sites, which showed significant net P release 1.3 to 3.5 times greater than the control (Duan and Kaushal 2015). Generally, the reduced releases of SRP with increasing salinization were believed to be caused by changes in ionic strength and pH that decreased colloid stability, leading to flocculation with SRP (Green et al. 2008, Duan and Kaushal 2015, Haq et al. 2018). However, a few sites saw a net release of P, which was theorized to be a result of the reduction in oxygen concentration from microbial respiration during a concurrent release of labile dissolved organic carbon (DOC). A follow-up sediment incubation experiment from urban streams saw significant positive linear relationships between overlying water SRP concentrations and salinity in over half of their sites, though the exact mechanism behind the release was unknown (Haq et al 2018).

Another proposed mechanism for the increased P release from salinization is via anion exchange between Cl^- and phosphate ions (PO_4^{3-}). In studies of stormwater bioretention system soils, mass exports of P were observed from incubation columns exposed to periodic salt applications (McManus and Davis 2020, Goor et al. 2021). The authors speculate that this large release of P was a combination of excess salt altering exchange sites on clays, as well as desorption of PO_4^{3-} from anion exchange with Cl^-. Additionally, it was hypothesized that a threshold of salt accumulation in the media dictates the difference between P export and retention (McManus and Davis 2020). Although we did not measure the Cl^- concentrations in the Church Lake sediments, it is possible that saturation of Cl^- in the sediments was preventing adsorption of P, leading to increased P in the water column. Future studies may want to conduct similar P release experiments using 'naïve' or non-salt impacted sediments to gain more insight into the interactions of Cl^- on IPL.

Additionally, this study only measured Cl^- and did not measure sodium (Na^+) concentrations in the sediment or overlying water, though NaCl was used as the salt additive for the incubations. Na^+ is a less conservative element than Cl^- and undergoes processes of cation exchange within soils and sediments, displacing other positively charged ions including Ca^{2+}, Al^{3+}, and ammonium (Findlay and Kelly 2011, Duan and Kaushal 2015). Therefore, elevated concentrations of Na^+ can impact or interfere with processes associated with these compounds, such as P adsorption with Ca^{2+}. In our study, we saw less P in the Ca-bound fraction in cores from Site 1, which is located in the deeper part of the lake with consistently higher salinity concentrations. Though our shorter 25-day incubation may not have been able to capture the full effects of elevated salinity on ion-exchange processes, the persistent exposure of Site 1 sediments to elevated salinity concentrations in the lake could have influenced the P-binding capacity of Ca^{2+} in the sediments over the long-term.

While these mechanisms may help explain how elevated concentrations of salt could increase P loading, our study still saw the greatest P release in the AN + Cl^- treatment, and there was little difference in the release between O + Cl^- and O treatment cores, suggesting a larger P release from redox-sensitive fractions in the sediment. In some capacity, it appears that additions of NaCl may have increased the mobilization of Fe, a metal that can decouple from P under reducing conditions. Fe^{2+} mobilization has been seen along an increasing salinity gradient in the field and laboratory studies of wetlands and coastal floodplains due to reductive dissolution in combination with desorption (Klein et al. 2010, Wong et al. 2015). In column leaching experiments using roadside soils, greater addition of NaCl resulted in higher concentrations of Fe in the leachates, which the authors attributed to ligand and ion exchange processes and increased dispersion of organic matter (Amrhein et al. 1992). Under the low oxygen treatment in our study,

the elevated salinity could have enhanced mobilization of Fe and other elements sorbed onto the exchange sites, such as P. Further studies are needed to investigate the impacts of excess road salt on P cycling mobilization of other elements coupled with IPL in lakes, especially under various redox conditions.

Though P and Cl^- are common contaminants in temperate regions, there is limited research on how these stressors may interact in freshwater lake ecosystems. Both observational data and laboratory experiments should consider how excess salt can indirectly or directly influence lake nutrient processes like IPL, as this has implications for eutrophication and subsequent proliferation of algal blooms. Several studies have reported on the anoxic conditions created from prolonged stratification due to a salinity gradient from road salt runoff, with one study reporting sediment release of P (MacLeod et al. 2011, Koretsky et al. 2012, Wyman & Koretsky 2018). Additionally, our results suggest that elevated salinity may further promote IPL contingent on sediment composition, exacerbating the problems of eutrophication. It is important to understand how road salt runoff impacts nutrient processes in lakes so that informed management decisions are made; treating the P loading is only addressing a symptom of the larger problem of saline deicer runoff.

CONCLUSIONS

NaCl road deicers have the potential to increase IPL under anoxic conditions. Sediment cores were collected from two sites in a salt-impaired lake in Grand Rapids, Michigan and exposed to two levels of oxygen (oxic vs. anoxic) and Cl^- (high vs. low). Mean maximum apparent release of TP was greatest for the AN + Cl^- treatments, as was SRP at Site 1. However, there was a significant interaction effect of site, suggesting that differences in sediment composition may have influenced P release between sites. Several studies of stream sediments

have shown that elevated salinity concentrations may mobilize P out of sediments potentially via changes in redox, anion exchange, or alteration of clay adsorption sites, though there is no known consensus at this time. Similar mechanisms may be responsible for the increased P release in AN + Cl⁻ cores via mobilization of trace metals from higher salinity concentrations. Due to the increasing use of road salt in temperate regions, future studies should consider completing this experiment using naïve sediments or greater increments of Cl⁻ concentrations to see how rising salinities impact lake sediment biogeochemistry.

Hopefully, the results from this study shed light on the need to concurrently study the impacts of salinization and eutrophication of freshwater ecosystems so that effective and scientifically sound management and remediation decisions can be made for lakes experiencing elevated levels of nutrient and salt pollutants. For Church Lake, treating the high P concentrations in the hypolimnion prior to mitigating the elevated Cl⁻ concentrations will be important in reducing the potential for algal bloom formation should the salinity gradient break down and lake mix. Using a non-redox-sensitive chemical inactivant such as Alum or Phoslock would remove excess P from the water column and prevent further release from the sediment (Lürling et al. 2020). Due to both the direct and indirect impacts of Cl⁻ on sediment P release, removal of the salt-contaminated bottom water after P treatment, potentially via hypolimnetic water withdrawal, may also be necessary to mitigate further impacts from IPL. Ultimately, treatments for the elevated P and Cl⁻ will only be temporary fixes should the high amounts of saline deicers continue running off into the ecosystem.

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FIGURE CAPTIONS

Fig. 3.1 The sites of sediment core collection in Church Lake located in Grand Rapids, MI USA. *Upper left inset*: shows the study location (black circle) within Kent County, MI. *Upper Panel:* a view of the hydrologically connected Tri-Lakes next to M44/East Beltline Ave in Grand Rapids, MI. *Bottom Panel*: zoomed in view of the sediment core collection locations within Church Lake.

Fig 3.2 Mean (± SD, n = 2) concentrations of (**A**) TP and (**B**) SRP measured over the duration of the incubation in the overlying water of sediment cores collected from Site 1 in Church Lake. The letters in the legend refer to the redox state and chloride treatment (AN= anoxic condition; O = oxygen, oxic condition; + Cl = high chloride concentration). Note varying scales on the y-axis between TP and SRP graphs.

Fig 3.3 Mean (± SD, n = 2) concentrations of (**A**) TP and (**B**) SRP measured over the duration of the incubation in the overlying water of sediment cores collected from Site 2 in Church Lake. The letters in the legend refer to the redox state and chloride treatment (AN= anoxic condition; O = oxygen, oxic condition; + Cl = high chloride concentration). Note varying scales on the y-axis between TP and SRP graphs.

Fig. 3.4 Mean (± SD, n = 2) apparent maximum (**A**) TP and (**B**) SRP release rates of sediment cores of each treatment from Sites 1 and Site 2. Results represent the four treatment combinations simulating various redox and Cl^- concentrations in Church Lake. (AN= anoxic; O = oxygen, oxic; AN + Cl = anoxic with high Cl^-; O + Cl = oxic with high Cl^-). Note the different y-axis scales between TP and SRP release.

Fig. 3.5 Extractable SRP concentrations from each sediment cores at the end of incubation period. The letters correspond to the redox state and chloride treatment (AN= anoxic condition; O = oxygen, oxic condition; + Cl = high chloride concentration); the subsequent number refers to the core replicate (1-2). In the legend, NH_4Cl represents the loosely sorbed / labile P faction; B/D represents the reductant soluble P; NaOH represents the metal-oxide- bound P; and HCl represents Ca- and Mg- bound P.

Fig. 3.6 Mean (± SD, n = 2) metal concentrations of post-incubation sediments from each treatment at Site 1 and Site 2. The control sediments were not exposed to any treatment. The metals analyzed were Aluminum (Al), Iron (Fe), Calcium (Ca), and Magnesium (Mg), all of which can bind to P in the sediment. The treatment abbreviations refer to the redox state and chloride treatment (AN= anoxic condition; O = oxygen, oxic condition; + Cl = high chloride concentration).

Table 3.1 Summary of water quality measurements at the near-surface and near-bottom of each sediment core sampling site within Church Lake. Temperature (Temp), specific conductivity (SpCond), and dissolved oxygen (DO) were measured with a YSI. Water samples were collected for analysis of total phosphorus (TP) and soluble reactive phosphorus (SRP) concentrations.

Parameter	Site 1		Site 2	
	Surface	Bottom	Surface	Bottom
Depth (m)		10.3		6.4
Temp (°C)	27.72	5.96	27.9	11.01
SpCond (μS cm^{-1})	823	1256	824	1015
DO (mg/L)	8.86	0.39	8.4	0.33
TP (mg/L)	0.009	0.115	0.007	0.028
SRP (mg/L)	<0.005	0.042	<0.005	<0.005
Cl$^-$ (mg/L)	168	194	173	176

Table 3.2 Initial refill and mean (± SD, n = 2) water column concentrations of TP, SRP, and chloride (Cl⁻) for each treatment. AN= anoxic condition; O = oxygen, oxic condition; + Cl⁻ = high chloride concentration.

Sediment Source	Treatment	TP (mg/L)	SRP (mg/L)	Cl⁻ (mg/L)
Site 1	Initial	0.008	< 0.005	159
	Initial + Cl⁻	0.012	< 0.005	321
	AN	0.161 ± 0.054	0.030 ± 0.009	188 ± 13
	AN+Cl⁻	0.178 ± 0.065	0.049 ± 0.021	370 ± 125
	O	0.092 ± 0.053	0.015 ± 0.012	184 ± 14
	O+Cl⁻	0.124 ± 0.074	0.024 ± 0.017	325 ± 15
Site 2	Initial	0.012	< 0.005	156
	Initial + Cl⁻	0.010	< 0.005	307
	AN	0.073 ± 0.030	0.011 ± 0.010	171 ± 22
	AN+Cl⁻	0.093 ± 0.046	0.007 ± 0.003	306 ± 18
	O	0.032 ± 0.023	0.005 ± 0.003	173 ± 25
	O+Cl⁻	0.048 ± 0.030	0.005 ± 0.004	309 ± 51

Table 3.3 Summary table of statistical results of an exploratory multi-way repeated measures ANOVA analysis of core water column TP and SRP concentrations measured over time during incubation. Bold values indicate statistical significance.

Factor	TP		SRP	
	F	*p*-value	F	*p*-value
Site	86.402	**< 0.0001**	135.34	**<0.0001**
Redox	39.269	**<0.0001**	40.478	**<0.0001**
Cl⁻	6.464	**0.0121**	10.236	**0.0017**
Site × Redox	1.288	0.2584	16.156	**<0.0001**
Site × Cl⁻	0.187	0.6658	16.156	**<0.0001**
Redox × Cl⁻	0.136	0.7134	0.892	0.3466
Site × Redox × Cl⁻	0.336	0.5629	3.995	**0.04763**

Table 3.4. Multiway ANOVA results for TP and SRP maximum apparent release rates depending on sediment source, redox conditions, and Cl⁻ treatment. Significant effects are in bold.

Factor	TP		SRP	
	F	*p*-value	F	*p*-value
Site	0.654	0.4421	12.743	**0.007**
Redox	9.716	**0.0143**	42.191	**<0.0001**
Cl⁻	0.351	0.5697	15.538	**0.004**
Site × Redox	1.304	0.2865	4.484	**0.002**
Site × Cl⁻	0.6	0.813	20.401	0.067
Redox × Cl⁻	0.472	0.5116	19.451	**0.002**
Site × Redox × Cl⁻	0.026	0.8766	8.181	**0.021**

Table 3.5 Mean (n = 2) extractable SRP, TP, and organic matter (OM) from post-incubation sediments of each experimental treatment from Site 1 and Site 2 in Church Lake based on dry weight. AN= anoxic condition; O = oxygen, oxic condition; + Cl⁻ = high chloride concentration.

| Site | Treatment | SRP- bound Fraction | | | | | | | | TP | OM |
| | | NH_4Cl | | BD | | NaOH | | HCl | | | |
		µg/g	%	µg/g	%	µg/g	%	µg/g	%	mg/kg	%
Site 1	AN	2.25	0.72	98.60	31.6	106.90	39.3	104.49	36.7	877.89	3.37
	AN + Cl⁻	2.49	0.63	119.47	30.0	145.54	36.6	130.58	32.8	818.13	2.96
	O	0.29	0.09	73.56	23.9	121.15	34.2	113.14	33.5	819.20	3.75
	O + Cl⁻	0.29	0.09	84.99	26.6	117.35	39.6	116.47	45.9	891.67	3.45
Site 2	AN	0.24	0.07	71.09	16.3	95.52	36.8	108.33	36.5	920.19	3.74
	AN + Cl⁻	0.19	0.06	57.09	17.8	110.20	44.9	167.32	52.0	823.94	3.92
	O	0.19	0.06	44.99	14.4	123.51	39.3	143.13	36.7	890.64	3.83
	O + Cl⁻	0.21	0.06	59.70	19.1	129.70	36.6	183.02	32.8	904.35	3.88

Table 3.6 Mean (± SD, n = 2) dry-weight metal concentrations from post-incubation sediments of each experimental treatment from Site 1 and Site 2 in Church Lake. AN= anoxic condition; O = oxic condition; + Cl⁻ = high chloride concentration.

Sediment Source	Treatment	Al (g/kg)	Ca (g/kg)	Fe (g/kg)	Mg (g/kg)	Fe:P (by weight)
Site 1	AN	21.0 ± 5.00	19.0 ± 2.00	23.5 ± 2.50	7.8 ± 0.80	29.17 ± 2.22
	AN+Cl⁻	26.0 ± 2.00	31.0 ± 3.00	25.5 ± 0.50	9.9 ± 0.10	30.71 ± 2.24
	O	20.0 ± 5.00	25.0 ± 7.00	23.5 ± 0.50	8.15 ± 0.05	28.62 ± 2.19
	O+Cl⁻	19.5 ± 1.50	29.0 ± 6.00	23.5 ± 0.50	8.15 ± 0.05	26.44 ± 1.31
Site 2	AN	18.5 ± 4.50	31.0 ± 0.00	22.5 ± 2.50	13.0 ± 1.00	22.87 ± 1.77
	AN+Cl⁻	17.5 ± 2.50	22.0 ± 3.00	21.0 ± 1.00	10.45 ± 1.55	30.72 ± 2.25
	O	14.0 ± 1.00	23.0 ± 4.00	20.5 ± 0.50	9.60 ± 1.40	25.26 ± 2.78
	O+Cl⁻	19.5 ± 0.50	19.5 ± 5.00	19.0 ± 1.00	9.65 ± 0.15	22.97 ± 2.36
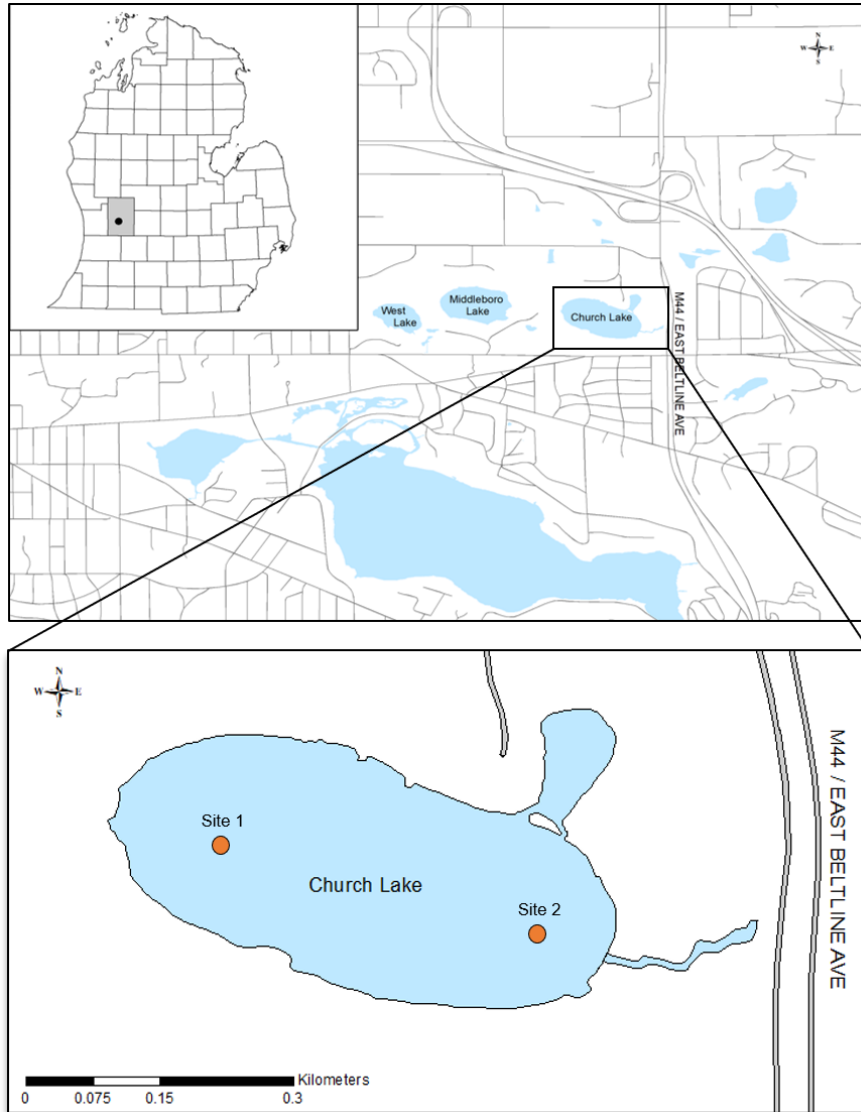
Fig. 3.1
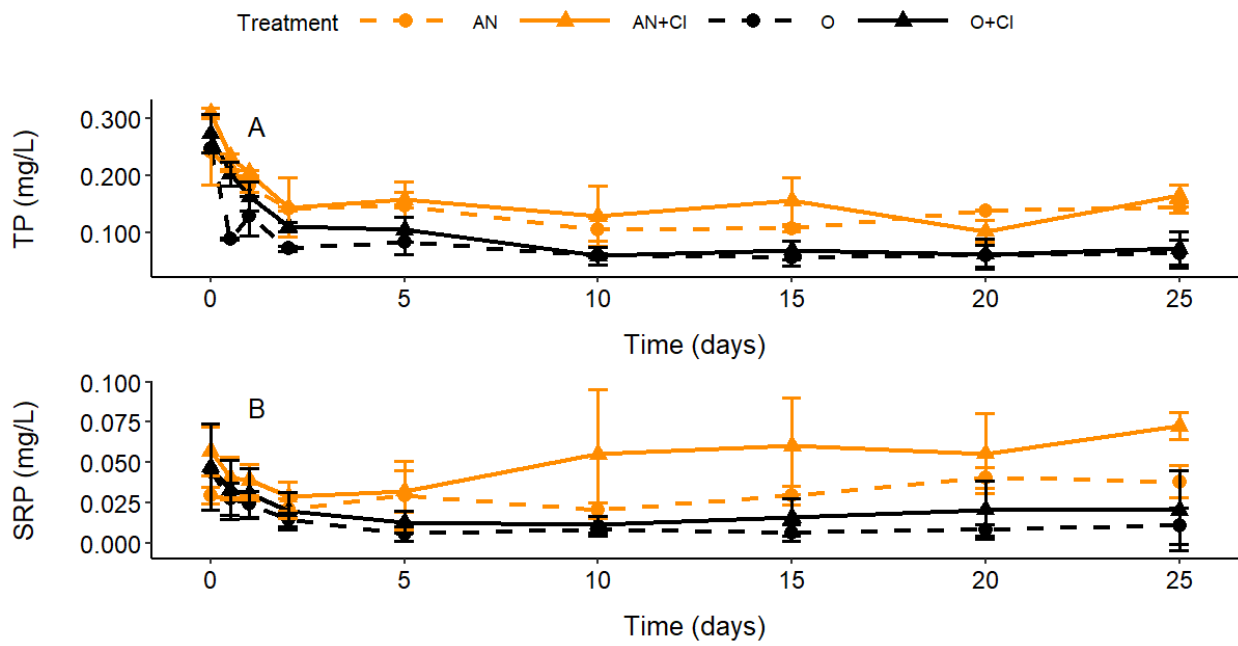
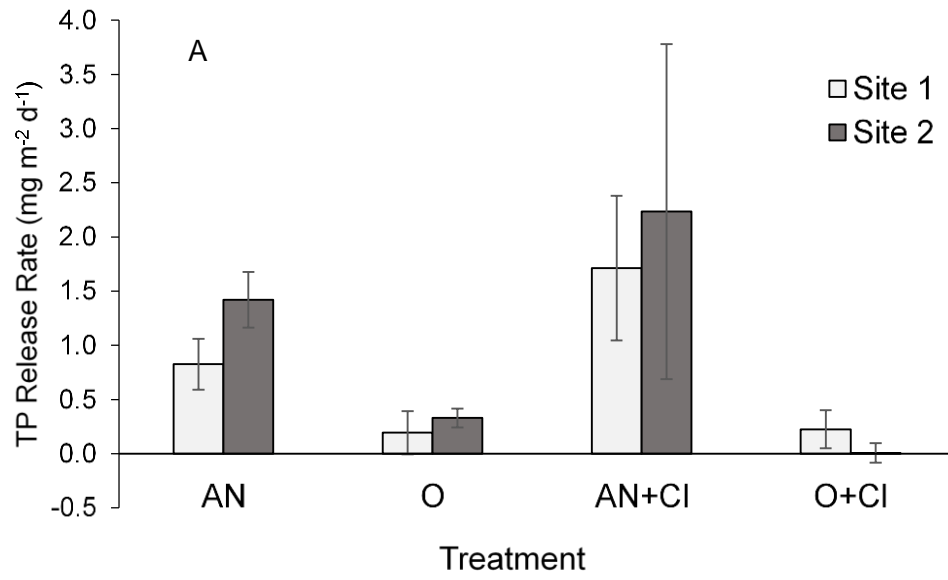**Fig 3.2**
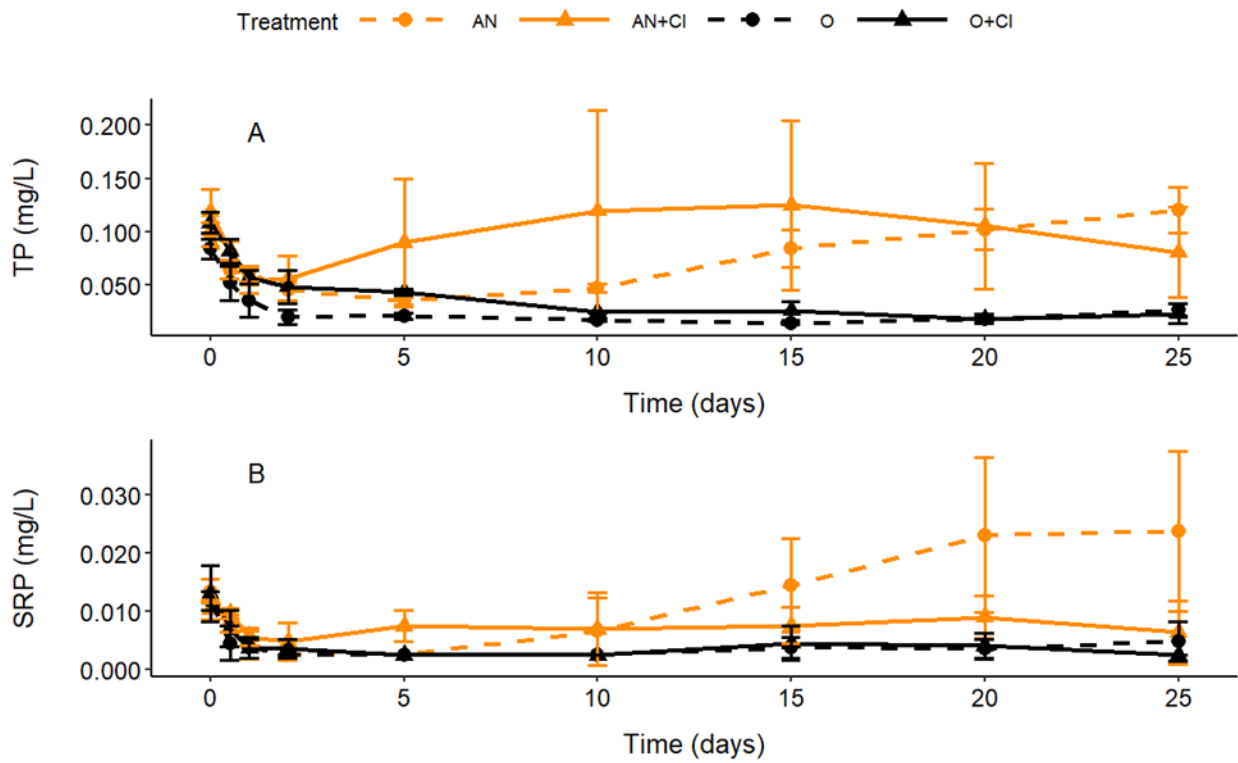
Fig. 3.3
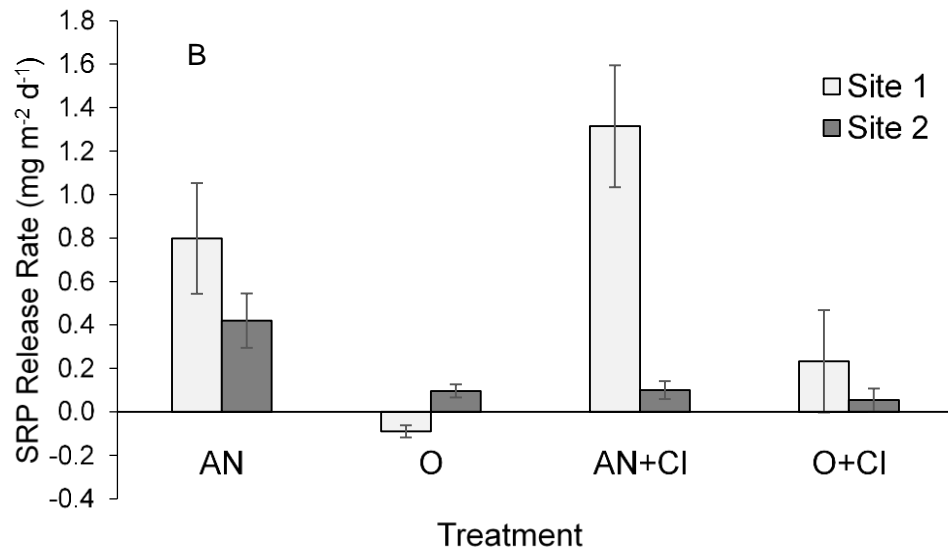
Fig. 3.4
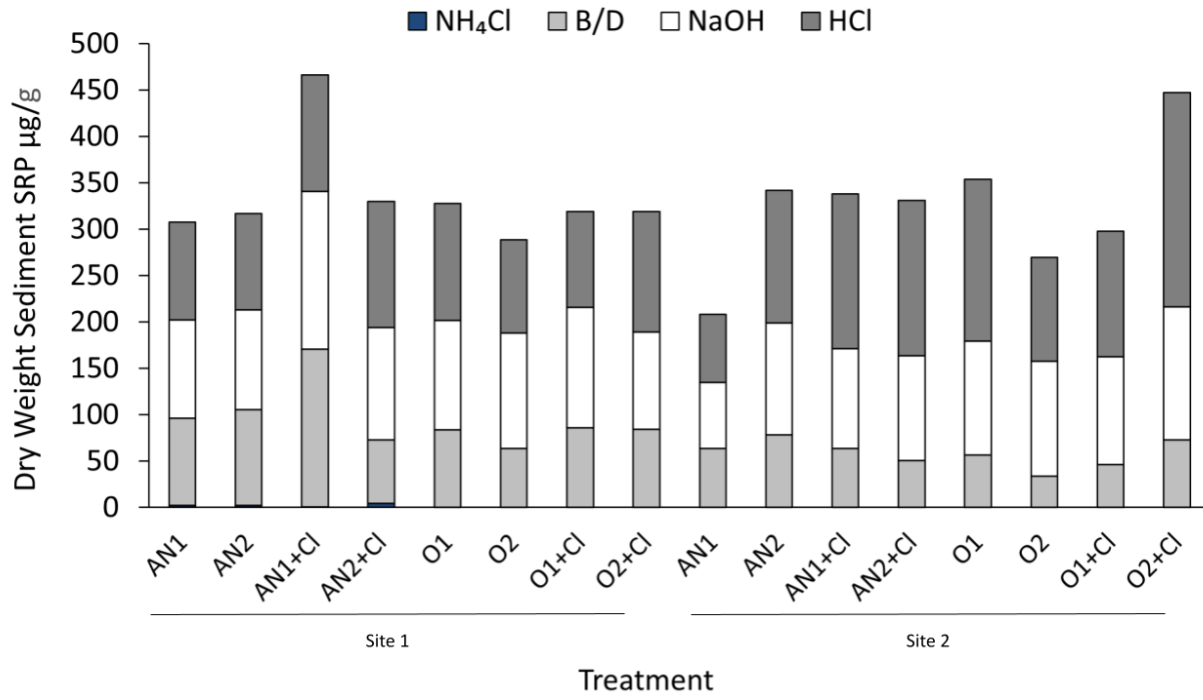
Fig. 3.5
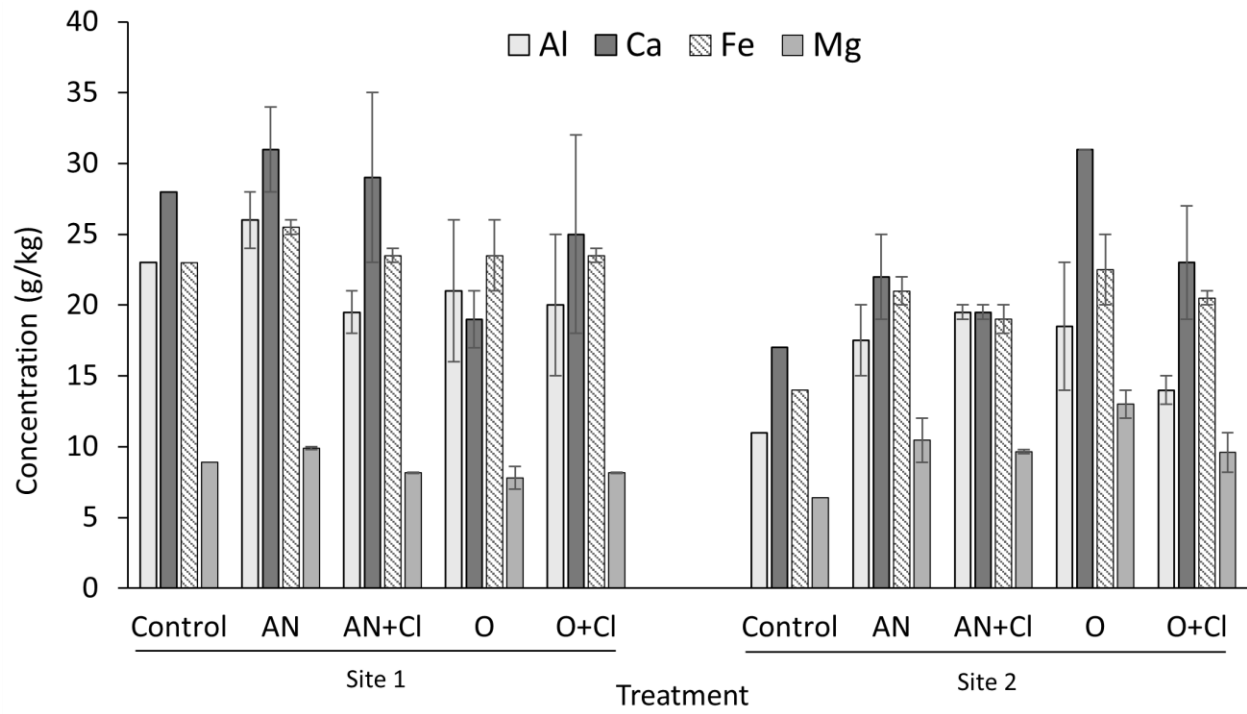
Fig. 3.6

Chapter 4

Synthesis and Conclusions

The salinization of freshwater ecosystems is a prominent threat to freshwater reserves around the globe (Hintz and Relyea 2019, Reid et al. 2019). Though salinization can occur through natural processes, such as weathering of rocks and minerals, salinization from human activities is largely responsible for the rising ion concentrations observed in freshwaters around the world. Salinization from anthropogenic sources includes agriculture, dewatering, sewage and effluent, industrial activities, and climate change (Cañedo-Argüelles et al. 2013, Le et al. 2018, Kaushal et al. 2021). One prominent source of salinization in temperate regions of the world is runoff from road deicing salts. In the U.S. alone, the amount of road salt applied annually has increased by 24 million metric tons over the last half-century (Lilek 2017). Lakes in urban areas are particularly susceptible to salinization from road salts, with as little as 1% impervious land cover in a lake catchment showing long-term increasing trends in chloride (Cl^-) concentrations (Dugan et al. 2017).

Elevated Cl^- concentrations in freshwater bodies are known to negatively impact the ecological and biogeochemical properties of these ecosystems. Studies have shown decreases in species reproduction and growth, shifts in community structure, and declining biodiversity in ecosystems exposed to high salt concentrations (Hintz and Relyea 2019, Arnott et al. 2020, Mausbach and Dzialowski 2020). Elevated Cl^- concentrations also affect abiotic processes and can cause mobilization of heavy metals, release of dissolved organic carbon (DOC) from sediment, and prolonged stratification and reduced mixing in lakes (Novotny et al. 2008, Duan and Kaushal 2015, Schuler and Relyea 2018).

Though salinization is recognized as an emerging problem in freshwater ecosystems, there is little research on the interactions of excess salt with other aquatic stressors such as eutrophication. External inputs of nutrients such as phosphorus (P) can lead to eutrophication of water bodies, causing substantive changes in aesthetics, productivity, biogeochemical functions, and socio-economic value of the ecosystems (Schindler and Vallentyne 2008, Brownlie et al. 2022). P is known to be a limiting nutrient in many aquatic ecosystems, and high concentrations can lead to the proliferation of algal blooms (Schindler et al. 2016). Legacy P in lake sediments can contribute to internal phosphorus loading (IPL), a process that can continue to release P into the water column even after external loads have been reduced (Steinman and Spears 2020). Currently, there is limited research on how higher concentrations of road salt alter processes such as P nutrient cycling in lakes. Given the ubiquity of eutrophication and salinization in northern temperate aquatic ecosystems, further research into the combined effect of excess P and Cl^- is necessary to help inform management strategies for lakes experiencing elevated concentrations of these contaminants. To fill this knowledge gap, I studied the water quality of road salt-impaired lake and sediment P dynamics under elevated Cl^- concentrations to assess how deicing runoff impacts P biogeochemistry.

Impacts of Chloride on Lake Water Quality

The results from my field observation study of Church Lake were similar to research conducted on other urban lakes in southwest Michigan (Judd et al. 20015, Sibert et al. 2015, Wyman and Koretsky 2018). Cl^- concentrations in Church Lake increased with depth, likely altering lake stability and raising the energy required to fully mix the lake. Below 10 m depth, the Cl^- consistently exceeded the EPA chronic toxicity threshold of 230 mg Cl^-/L (USEPA 1988), at times reaching 331 mg/L. The deepest site of the lake did not completely mix during

periods of expected turnover when the lake was isothermal, suggesting portions of the lake have become meromictic. Typically, non-shallow lakes in temperate areas are dimictic and undergo complete vertical mixing of the water during the spring and fall when the lake temperature and density are uniform across depths (Fig. 4.1) Oxygen is then redistributed throughout the lake, and DO concentrations are relatively high throughout the entire water column. During the summer and winter, differential heating and cooling of the surface water creates a density gradient that stratifies the lake. Decomposition of organic matter consumes oxygen during respiration, and DO concentrations in the hypolimnion drop since the oxygen in the deep, stratified layer cannot be replenished by atmospheric exchange. In lakes contaminated with road salt, the high Cl^- concentrations increase the density of the bottom water, introducing a chemical density gradient that can prevent the complete mixing of the lake, even during isothermal conditions (Fig. 4.2). The differences in chemical composition between the surface and bottom waters, as well as the prolonged low DO conditions, suggest that Church Lake did not have complete turnover during all periods of isothermality. A switch from dimictic to monomictic or meromictic conditions has been previously observed in other lakes with hypolimnetic concentrations of 180 – 241 mg/L of Cl^- (Hintz and Relyea 2019), which are within the range of concentrations observed in Church Lake.

This prolonged stratification in Church Lake has led to persistent hypoxic conditions in the hypolimnion at Site 1, with dissolved oxygen (DO) concentrations below 0.5 mg/L at the near-bottom. Under these low oxygen conditions, P can accumulate in the hypolimnion through redox-induced IPL, when P is released from Fe-hydroxides in the sediment into the overlying water column (Mortimer 1941). In non-salt-impaired dimictic lakes, IPL is observed during summer stratification, when the decomposition of organic matter causes low DO concentrations

near the sediment-water interface (Fig. 4.1). Extremely high P concentrations were measured year-round in the hypolimnion of Church Lake, suggesting that IPL may be perpetually occurring and accumulating at the lake bottom. The total phosphorus (TP) concentration was measured at over 7,500 µg/L at the deepest site, which is more than two orders of magnitude greater than the Michigan state eutrophic classification of 25 to 50 µg/L of P (Michigan EGLE 2012). The concentration of soluble reactive phosphorus (SRP), the bioavailable form of P, is also substantial, with measurements exceeding 6,500 µg/L. The high amount of SRP in the hypolimnion indicates there is limited biotic uptake of P deep in the lake; however, these high concentrations could have significant ecological implications should the SRP mix into the surface waters where there are enough resources for algal blooms to form.

Elevated hypolimnetic P concentrations due to IPL have been a proposed consequence of road salt contamination in lake ecosystems, but this phenomenon has been measured in only a few other lakes (Sibert et al. 2015, Wyman and Koretsky 2018). Often, studies examining salt contamination in lakes have not explored the potential responses of other important water quality parameters such as nutrients (Hintz and Relyea 2019). However, elevated concentrations of Cl^- can have an effect on processes that impact the biogeochemical cycling of nutrients, as seen here with Church Lake. Therefore, it is important to consider how the co-occurring contaminants of excess salt and nutrients interact with each other within freshwater lakes; their interaction response will help inform management strategies, which will increase the likelihood that lake ecosystems will be successfully remediated.

Elevated Chloride and Sediment Phosphorus Release

The elevated Cl^- concentrations resulting from road deicing runoff into Church Lake have prevented complete vertical mixing in the water and have led to consistent hypoxia in the

hypolimnion. Under these low DO concentrations, P can be released from ferric oxy-hydroxides to the overlying water column and induce IPL (Mortimer 1941). Though there is a clear, indirect mechanism for how road salt can lead to sediment release of P, there has been little consideration on whether elevated Cl^- concentrations can directly impact IPL rates and further promote the mobilization of P out of the sediments and into the overlying water column of lakes. In our study, we wanted to address this knowledge gap by looking at P release from sediment cores exposed to varying oxygen and salinity conditions.

Our results showed that elevated concentrations of road deicers have the potential to increase IPL under low oxygen conditions, though the sediment composition and location within the lake appear to impact the effects of Cl^- on P release. Sediment cores collected from two sites within Church Lake were exposed to two levels of oxygen (oxic vs. anoxic) and Cl^- (high vs. low), with sediment P release measured over the course of 25 days. Apparent mean maximum TP release was greatest in cores exposed to the high Cl^- /anoxic treatment (AN + Cl^-) (1.71 – 2.23 mg m^{-2} d^{-1}) compared to the low Cl^-/anoxic treatment (AN) (0.83 -1.42 mg m^{-2} d^{-1}). The mean maximum release of SRP was greatest in the AN + Cl^- treatment at Site 1 (1.595 mg m^{-2} d^{-1}); at shallower Site 2, the anoxic treatment again had the highest mean maximum SRP release (0.058 mg m^{-2} d^{-1}) but in this case, it was under the low Cl^- condition. These release rates were lower than the mean maximum fluxes measured in other eutrophic lakes in Michigan. Under anoxic conditions, sediments from Mona Lake, about 40 miles west of Church Lake had TP release rates ranging from 0.8 – 15.56 mg m^{-2} d^{-1} (Steinman et al. 2009) while nearby Spring Lake had high release rates reaching 29.54 mg m^{-2} d^{-1} (Steinman et al. 2004). The lower release of P measured in the Church Lake sediments may be a result of the lower incubation temperature of the sediment, as temperature can influence release rate (Steinman et al. 2009), as well as not

achieving complete anoxic conditions in the core tubes during the experimental period. Even so, the lower release rates do not fully account for the extremely elevated P concentration measured in the Church Lake hypolimnion. Therefore, some of the P in the lake bottom waters are likely a result of external loads and decaying organic matter that has been building up over a period of time due to the lack of mixing and biological uptake.

The differences in sediment release between sites may be explained by sediment composition. Site 1 had a higher overall concentration of metals such as Al, Ca, and Fe in the sediments, which are common elements that bind to P. Additionally, Site 1 had a greater proportion of the sediment SRP in the redox-sensitive Fe-bound fraction, whereas Site 2 had a greater percentage of SRP in the more stable Ca-bound fraction. These differences may help explain why Site 1 had greater P release rates, as the sediments at this site had a greater capacity to sorb P to metals and have the P subsequently mobilized under low oxygen conditions.

Though there were differences in sediment P release between sites, the highest P release was still measured in cores exposed to the AN + Cl⁻ treatment. There are currently no studies of sediment P release from salinization in lake sediments, but other studies of salt-contaminated stream and wetland sediments have seen increased P mobilization after exposure to elevated Cl⁻ concentrations (Kim and Koretsky 2013, Haq et al. 2018, McManus and Davis 2020). Proposed mechanisms for this P release from salinization include reduced oxygen from dissolved organic carbon release, anion exchange, and the alteration of clay adsorption sites (Duan and Kaushal 2015, McManus and Davis 2020, Goor et al. 2021). Additionally, the Cl⁻ appears to have an influence on redox-sensitive fractions of P, since there was little difference in P release between high and low Cl⁻ treatments in the oxygenated cores. Elevated salinity has been observed to increase the mobilization of Fe, also potentially displacing other elements sorbed onto Fe

exchange sites such as P (Amrhein et al. 1992). However, there is currently not a robust understanding of elevated salt concentrations and sediment nutrient release and therefore no definitive explanation on the cause of the increased release of P under high Cl^- concentrations.

Potential Solutions

Results from this study can be used to help inform a remediation management plan for Church Lake, which may ultimately be transferred to other lakes impacted by road salt runoff and elevated nutrient concentrations. Though reducing the amount of road salt runoff entering Church Lake is the ultimate goal for improving the system, mitigating the extremely high P concentrations in the hypolimnion should be the initial focus of the restoration strategy. While the dense saline layer at the lake bottom reduced lake turnover and created anoxic conditions that led to a buildup of P in the hypolimnion, the Cl^- stratification is also preventing most of this P from mixing into the upper layers of water. If even a fraction of the 6,500 µg/L concentration of bioavailable P were to reach the surface, there could be sufficiently high nutrient concentrations to stimulate devastating algal blooms on Church Lake. Though this P is currently trapped in the hypolimnion, the lake does appear to mix to approximately 9 m depth during isothermal conditions in the fall. A warmer winter with reduced road salt application could lead to a weaker chemical density gradient in the water column, where wind mixing would be sufficient to turn over the lake when it is a uniform temperature. Therefore, treatment of the elevated P concentrations should be addressed promptly to reduce the potential for algal blooms.

Methods to reduce IPL may include treatment with chemical inactivants such as Phoslock, or Al, Fe, or Ca salts, which precipitate P in the water column and trap it in the sediments (Lürling et al. 2020). Phoslock is a relatively new bentonite-based product with a lanthanum salt as the active P-binding agent. It has a P binding capacity of approximately 12 g

kg^{-1} and is effective in removing SRP from the water column, though there are concerns with toxicity and slow settling rate (Gibbs and Hickey 2018). Alum (aluminum sulfate) is the most commonly used P-inactivation agent and can bind SRP in the water column, flocculate suspended solids, and become a cap over the sediment preventing further sediment release of P (Steinman et al. 2004, Gibbs and Hickey 2018). However, low pH values can cause the alum to disassociate and release Al^{3+} ions that are highly toxic to aquatic organisms, so a reduced dose rate or a buffer may need to be used (Paul et al. 2008). Sediment dredging has seen significant reductions in sediment P concentrations and release (Oldenborg and Steinman 2019, Lürling et al. 2020), though it has a more expensive upfront cost (Welch and Cooke 2005) and requires a location for deposition. Further, sediment dredging is extremely disruptive to benthic habitat.

Another method may be hypolimnetic water withdrawal, which would remove both the elevated P and Cl$^-$ concentrations in the bottom waters. There have been marked improvements in the water quality of lakes that underwent hypolimnetic water withdrawal treatment, including decreased surface and hypolimnetic P concentrations, increased water transparency, and decreased bottom water anoxia (Nürnberg 2020). However, the removal of the colder bottom water could lead to increases in sediment P release under the warmer temperatures and counteract the restoration goal of reduced P. Additionally, there are concerns about what to do with the hypolimnetic water, as relocating this untreated water could negatively impact other surface and groundwater supplies.

For IPL mitigation strategies to work over the long-term, the external loading of nutrients has to be reduced. Fortunately, Church Lake appears to have curbed external inputs of P, and the issues of elevated P in the hypolimnion are likely a result of legacy P building up over an extended period of time due to the lack of mixing. The tributary flowing into Church Lake had

moderate concentrations of P measured throughout the year, though SRP was below detection limits in many of our samples. Correspondence with the Church Lake homeowners revealed that most homes are on city sewer and do not rely on septic. Additionally, a majority of the properties maintain a vegetated riparian buffer that may help deplete nutrients in runoff from fertilized lawns before entering the lake. Therefore, continuing to monitor and reduce the P concentrations in the tributary will likely be a beneficial strategy for minimizing external P inputs.

However, treating the elevated P concentrations in Church Lake is only addressing the consequences of the larger problems caused by excess road salt into the ecosystem. Reducing the amount of saline deicing runoff into Church Lake is the only way to help the lake achieve full recovery, as the removal of excess Cl^- in the hypolimnion will help reinstate the dimictic mixing patterns of the lake. The most direct way to reduce inputs of Cl^- to the lake would be to alter the discharge location of the storm drain to not have water runoff directly from a state highway into the lake. Unfortunately, the large investments in infrastructure from municipal or state funds are a likely hurdle for this action to occur. Another physical option may be to plant vegetation or reroute the tributary through a retention pond or wetland, which may slow down the larger flushes of salt into the system, though a plume of Cl^- can still enter the groundwater from retention systems and the salt-laden soils adjacent to the tributary, leading to slow and steady salinization of the lake (Snodgrass et al. 2017).

Proactive measures that minimize the salt application or use of non-chloride-based solutions on roadways can help reduce the overall amount of Cl^- contaminating fresh surface and groundwater. The city of Grand Rapids and the Kent County Road Commission employ pre-wetting practices that dose the rock salt with a "liquid chloride solution" prior to application (Kent County Road Commission 2022). Pre-wetting quickens melting and improves material

adherence to the road surface, lessening the need for reapplication and reducing the amount of salt applied. For example, the Wisconsin Transportation and Information Center states that a conventional application of dry salt wastes about 30% of the material due to the wind- and traffic-induced scatter (WTIC 2005), yet this waste can be reduced to only 4% by pre-wetting the material before spreading it (O'Keefe and Shi 2005). However, the pre-wetting brine still contains Cl^- that can runoff into the lake and alter the density gradient. Instead, Grand Rapids could look into replacing part of the Cl^- based brine with organic deicers like beet and corn derivatives for the prewetting material. There are still tradeoffs associated with increased input of organic deicers, including increases in microbial and primary productivity and decreases in DO with the breakdown of the organic matter; hence, balancing the tradeoffs between traditional Cl^- deicers and organic additives should be taken into consideration when implementing deicing strategies (Schuler et al. 2017).

Currently, there are no ecologically and economically favorable replacements for saline road deicers (Hintz et al. 2022). Magnesium and calcium chloride ($MgCl_2$ and $CaCl_2$) are common alternatives to traditional NaCl that work in lower temperatures but have been noted to be more toxic to aquatic organisms and are more costly by weight (Szklarek et al. 2022). Sand is an abrasive that is often applied to increase vehicle traction, though runoff into surrounding waterways can increase turbidity and sedimentation (Terry et al. 2020). However, the use of road deicing agents is all but essential for driving in the colder months. Studies have shown that road salt can reduce wintertime automobile accidents by nearly 80% compared to roadways without deicers (Usman et al. 2010, Hintz and Relyea 2019). Ensuring human safety with the application of deicers comes at the cost of ecological impairments to freshwater ecosystems. Continuing to explore alternatives to road salt, using best management practices, and engaging stakeholders on

the impacts of saline deicers can help minimize harm to freshwater systems while keeping people safe on the road during the wintertime.

CONCLUSIONS

Overall, excess road salt was seen to alter the water quality and phosphorus dynamics of Church Lake by reducing lake turnover, increasing bottom water hypoxia, causing sediment release of P into the water column, and accumulating reduced solutes in the hypolimnion. Additionally, excess road salt could further mobilize P from the sediments and exacerbate IPL within the lake, though mechanisms causing this release require further examination. The biogeochemical impacts have implications for entire ecosystems as the alteration of water quality may cause algal blooms and reduce viable habitat for aquatic organisms.

This research can be used to help inform a lake management strategy for Church Lake, and other lakes that may be impacted by both excess salt and nutrients. Simultaneously investigating P and Cl^- concentrations in the lake, as well as sediment P release, shed light on the interactions of these two stressors in the ecosystem and demonstrated the need to treat the high P concentrations in the hypolimnion prior to mitigating the elevated Cl^-. Specifically for Church Lake, application of Alum or Phoslock would be beneficial for removing P from the water column and creating a cap to trap the P and prevent release from the sediment. Hypolimnetic water withdrawal or a created retention basin for road runoff could be used to remove the salt-contaminated bottom water after the P treatment, though these would be only temporary solutions if the inputs of Cl^- from the tributary were also not concurrently reduced.

While the conditions in Church Lake are quite exceptional, several other studies have seen similar responses in lakes with road salt contamination (Sibert et al. 2015, Wyman and Koretsky 2018). Excess nutrients and road salt are prominent threats to freshwater ecosystems,

though there is little consideration for what the combined effects of these contaminants are on lakes. This study highlights the need for research on how other major threats to freshwater ecosystems, such as eutrophication, will interact with road salts. In Michigan, a statewide survey of Cl$^-$ and P concentrations in lakes is a necessary step to understand the extent of co-occurring pressures of eutrophication and salinization, and evaluate current management practices for lakes that could be experiencing these issues.

Fig. 4.1 A conceptual model for the mixing regimes and sediment phosphorus dynamics of a non-chloride-impaired dimictic lake. White arrows represent mixing (with larger arrows showing greater mixing extent). The yellow P represents phosphorus.
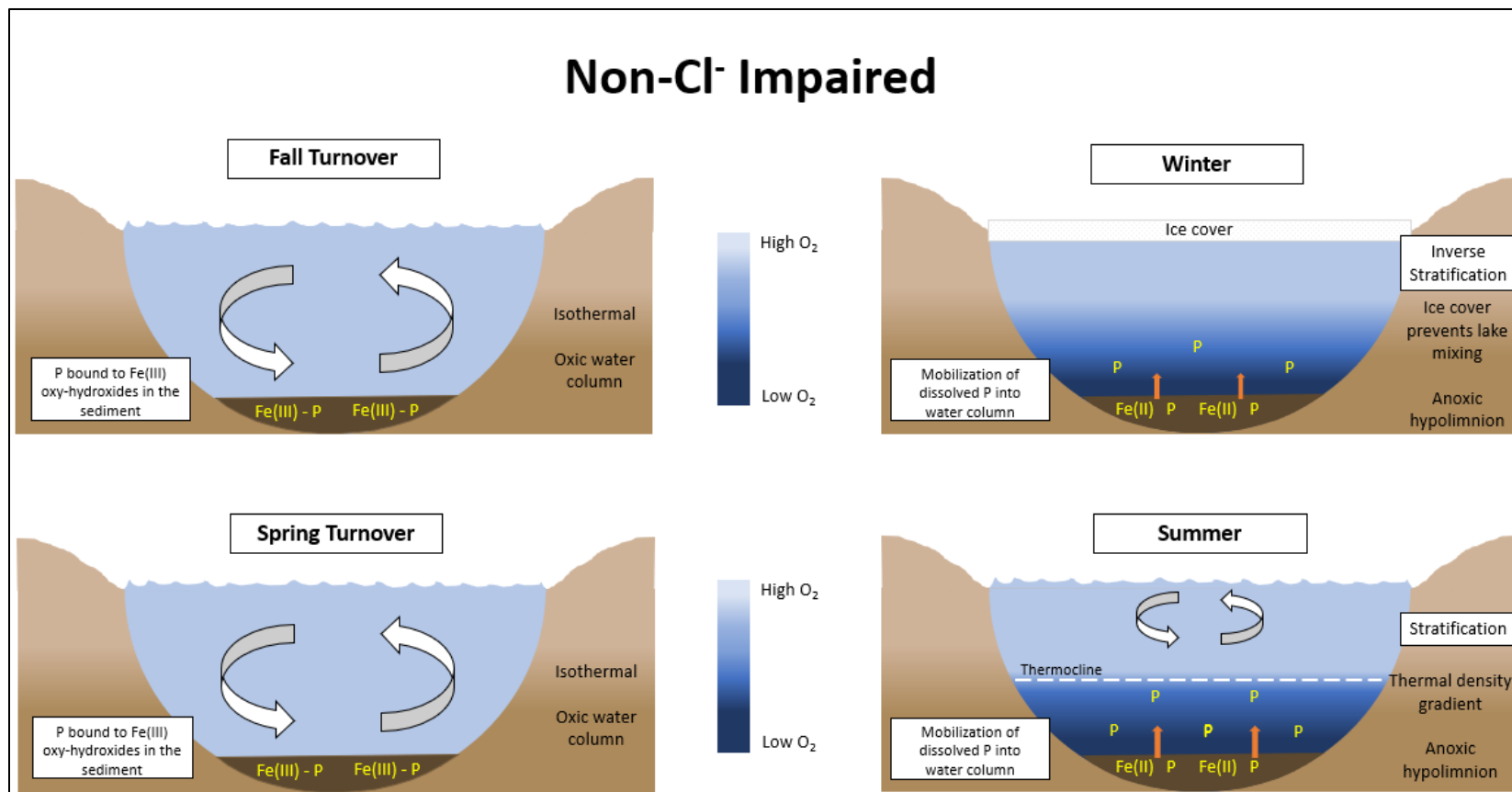
Fig. 4.2 A conceptual model for the mixing regimes and sediment phosphorus dynamics of a chloride-impaired lake that has shifted to a meromictic mixing regime. Thicker black arrows represent larger quantities of salt input.
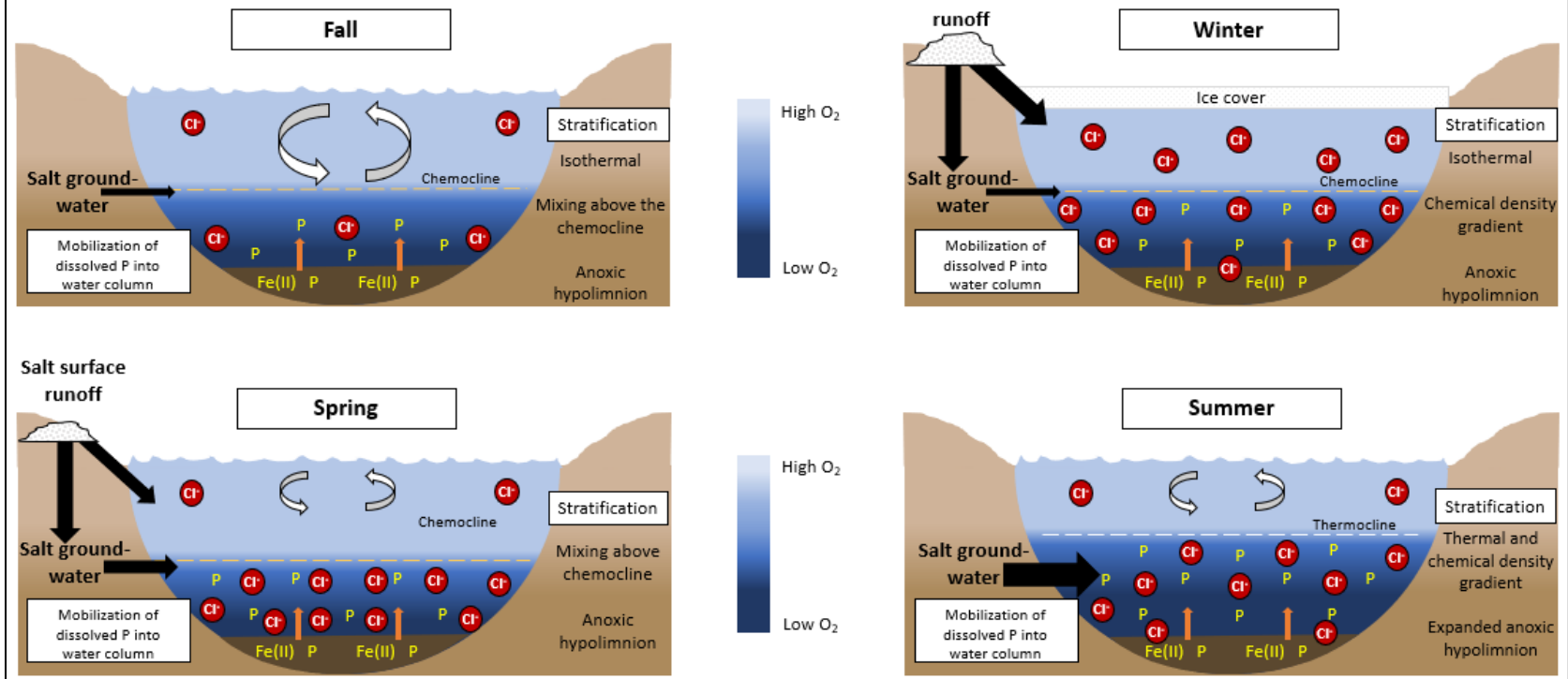
Fig. 4.1

Fig. 4.2

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