INSIGHTS INTO GROUNDWATER SEEPAGE: EXAMINING THE DYNAMICS OF PHOSPHORUS LOADINGS AT MULTIPLE SPATIAL SCALES IN ONEIDA LAKE, NEW YORK.

A Dissertation

Presented to the Faculty of the Graduate School

of Cornell University

In Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

by

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August 2023

INSIGHTS INTO GROUNDWATER SEEPAGE: EXAMINING THE DYNAMICS OF PHOSPHORUS LOADINGS AT MULTIPLE SPATIAL SCALES IN ONEIDA LAKE, NEW YORK.

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Cornell University 2023

Excess loading of nutrients into lakes is one of the biggest threats to the quality of freshwater and the associated ecosystems. In general, phosphorus (P) is considered the limiting nutrient for primary productivity in freshwater systems and has been recognized as one of the main contributors to excessive algal growth in temperate lakes. Contributions by groundwater seepage are rarely addressed in conventional approaches to address nutrient loading to lakes, due largely to the logistical challenges of determining groundwater exchanges at the sediment-water interface. However, where studied, groundwater has been shown to be a key element of a lake's nutrient dynamics, with a direct and significant impact on littoral communities.

In this dissertation I investigated the role of groundwater seepage in the P loading dynamics along the shoreline of Oneida Lake, in central New York, during the summer seasons of 2017, 2018 and 2020. I first explored the potential of groundwater seepage to carry P into a 700m stretch of the shoreline associated with three different adjacent land uses, by directly measuring groundwater seepage flow using seepage meters, and collected groundwater samples to analyze for its P content using pore water samplers. Samples were analyzed for both Total Phosphorus (TP) and Soluble Reactive Phosphorus (SRP). Synthesizing these data, I estimated groundwater P loads into this segment of the Oneida Lake shoreline, and then analyzed the relationship between the observed loads and possible controlling factors, including precipitation, shore adjacent land uses, and distance from the shore. As the next step, I expanded the analysis throughout the entire Oneida lake shoreline, by using the same methods to estimate loads at ten representative locations around Oneida Lake’s 88 km long shoreline. Results indicated that groundwater seepage is a continuous source of dissolved P throughout the sediment-water interface of the entire Oneida Lake shoreline. SRP represented a very small fraction, but TP concentrations and loads were extremely high, suggesting that dissolved organic compounds were the primary source for groundwater P. Groundwater seepage flows and its loading were highly variable both across space and time, which was partially explained by adjacent land uses and precipitation patterns. This constant input in the littoral region of the lake has elevated the concentrations of P in the associated nearshore surface waters and may be influencing phytoplankton development including cyanobacteria, and another biota. Estimated loads were then integrated into a comparison of the groundwater phosphorus inputs, with surface water inputs associated with the five main tributaries to Oneida Lake to better understand the relative contributions from these two different sources. Results suggested that groundwater contribution of dissolved phosphorus, and specifically TP, to the lake shoreline is comparable to tributary contributions, particularly during baseflow conditions. My research concludes that groundwater seepage is a significant source of dissolved P to Oneida Lake and may be a crucial factor aiding to maintain summer primary productivity, and algal blooms in temperate lakes.

BIOGRAPHICAL SKETCH

Maria Sol Lisboa was born in Buenos Aires, Argentina, in 1986. She completed her first 10 years of education in Mendoza, and then moved to Israel where she completed the last two years of high school. She returned to Mendoza in 2005 and enrolled at the Universidad Nacional de Cuyo to study Natural Resources Engineering. She graduated in 2011 with an honor’s thesis investigating the influences of meteorological parameters on landslides’ occurrence in the Aconcagua Park, Argentina. After graduation she joined the Anaerobic Digestion Lab at the University of Maryland as a research assistant investigating manure co-digestion substrates for biogas production and wastewater treatment. Upon finalizing the internship, she moved to Buenos Aires and worked in an environmental consultant firm on various projects related to the oil and energy sector. During her years in Buenos Aires, she met Mariano who has been her partner since then. In 2015, through a Fulbright scholarship co-funded with the Argentinian Government, Mariano and Sol moved to the United States where Sol joined the Soil and Water Lab at the Biological and Environmental Engineering Department at Cornell University to conduct her graduate studies. In 2018, she obtained her master’s degree where she investigated the seasonal, land use and drought effects on phosphorus loading to Owasco Lake from small tributaries. At that moment Sol decided to continue into the PhD program and developed her research project to continue investigating the connections between hydrology and nutrients dynamics, but this time looking at groundwater resources. After completing all the required course and field work for the doctorate, Sol and Mariano welcomed into their family their first daughter, Lara, in April 2022.

This thesis is dedicated to my mom, who showed me the path and supported me with all the means to get here; and, to my daughter who inspired me to complete this work.

ACKNOWLEDGMENTS

I would like to first acknowledge my academic advisors. I want to thank Todd Walter, my main advisor in BEE for allowing me the opportunity to join his lab, and for the constant encouragement to keep going and pursue what interests me the most. To Rebecca Schneider, who over the years has not only become my academic advisor, but also my mentor. Rebecca, I am grateful for your dedication and patience toward my learning and growing process, both as a scientist and as a person. You truly are the definition of a female role model for women and mothers in STEM, and I will deeply miss our weekly conversations. To Lars Rudstam for joining me in this research with an open mind, and for the time discussing and teaching me about limnology. I am grateful for all the valuable perspectives and contributions to each chapter. Second, I want to thank my husband Mariano, who embarked with me on this adventure so far from home, for your strength and unconditional support – this is also your achievement. To my family (my parents, my sister, my aunt and uncle, and my cousins) for being there at every single step loving and supporting. Finally, to my daughter Lara, whose arrival made everything else much more significant.

I also want to thank Mark Sarvary and the BIO1500 staff, for giving me the opportunity to teach, and also for sparking my interest in pedagogy. The classroom was one of my anchors during many tough moments in my graduate life. To the Cornell Biological Field Station Staff for welcoming me and my family for over three summers, and for all the help and support provided to make fieldwork possible. To Peggy Stevens, who has helped with every administrative task and made everything happen. To the undergraduate interns that help with this research collecting data in the

field or running samples in the lab. Vivian Garcia for all the support during the first field season. To the Kieckhefer Foundation that provided part of the funds, and to all my advisors that always found ways to make ends meet when needed.

I also want to thank my lab mates at the Soil and Water Lab, and my friends at Cornell and elsewhere. Daniela Rosero and Sara Reynolds for the emotional support and the long enriching talks. Neelam and Mahnaz for keeping us company and for the good food. To the South American community at Cornell that helps us feel closer to home and were always there for us.

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Q: Seepage flow rate

ΔV: seepage bag volume change

A: Surface area covered by the seepage meter

t: Time

PREFACE

Excess loading of nutrients is still one of the biggest threats to lake water quality and ecosystems, despite big efforts to reduce nutrients inputs into lakes from the surrounding landscapes (Conley et al. 2009). In general phosphorus (P) is considered the nutrient limiting primary production in temperate lakes; excessive P loading has been identified as one of the main causes underlying nuisance algal growths (Carpenter et al. 1998; Schindler et al. 2016). In the 1970's, P loading into U.S. lakes was significantly reduced with the ban on P in detergents and the enactment of regulations, the foremost being the Clean Water Act. However, attention to P loading has risen again due to the increase in often toxic, blue-green algal blooms (Hazardous Algal Blooms or HABs). HABs not only negatively impact aquatic ecosystems but the toxins can also have direct impacts on human health (Backer and McGillicuddy 2006). The combined ecological, human health, and aesthetic impacts of HABs result in significant financial costs to local and regional economies by impairing water quality for recreation, fishing, and other uses (Dodds et al. 2009).

The main pathways for nutrients to get delivered into lakes include precipitation, tributary discharge, overland stormwater runoff, and groundwater discharge. Sources of nutrients can be classified as either point source (PS), i.e., typically discharged from a pipe, or non-point source (NPS), which refers to nutrients that cannot easily be tracked to a distinct source (Carpenter et al. 1998). Point sources of phosphorus, particularly those originating from sewage discharges, have been extensively addressed and significantly reduced over time, due to effective regulatory measures and wastewater treatment practices (Orderud and Vogt 2013). Recently, considerable research and management efforts have shifted the focus to identifying and controlling diffuse, non-point sources of pollution. Various land uses have been evaluated for their impact on water quality in rivers and lakes. Agricultural activities, and specifically chronic fertilizer and manure applications interacting with exposed and eroding soils, make this land use a primary source and pathway for P transport into water bodies (Heathwaite et al. 2000; Burt et al. 2008). Using a range of approaches from edge-of-field measurements or monitoring stream concentrations and flows, to watershed modeling, researchers have evaluated the factors that control phosphorus loading from agricultural and other land uses into tributary streams (Lisboa et al. 2020). The general consensus is that storm events, and the associated runoff, increasingly are dominating the hydrologic flowpaths in most watersheds, and stream phosphorus loads are primarily controlled by the quantity of sediment-bound P transported during storms. However, in many cases, even under strict watershed controls, issues related to excess P loading persist (Kleinman et al. 2015). Researchers and water resources managers are evaluating other potential sources and pathways of nutrients into lakes. Internal loading, which is the release of P from lakebed sediments during anoxic conditions, has gained a lot of attention in recent years with over 1,000 publications and studies relating lake summer trophic conditions with sediment P released, and highlighting the long-term impacts of legacy P (Boström et al. 1988; Nürnberg 2009; Orihel et al. 2017).

Another potentially significant external source of P into lakes is groundwater seepage, which is increasingly gaining attention. Nearly 150 studies have investigated groundwater seepage and quantified flow rates along lake shorelines, broadly focusing on its magnitude and timing (Rosenberry et al. 2015). Many fewer studies, though, have dealt with its nutrient contributions (Lewandowski et al. 2015). Rosenberry et al (2015) identified several reasons behind the disregard of groundwater seepage for water and nutrient budgets, highlighting the challenges associated with spatial and temporal heterogeneity, the lack of convenient methodology, and the difficulty to access the sediment-water interface, among others. In addition, dissolved P has traditionally been considered to be readily adsorbed to soil particles in the vadose zone, which would make it unavailable in groundwater (Edwards and Withers 2007). As a result, P contributions to lake systems by groundwater have been rarely studied. However, there is growing evidence that P can be transported by groundwater, and it is not necessarily immobilized in aquifers (Holman et al. 2008, 2010b; Nisbeth et al. 2019), and can even reach thresholds of ecological significance (Kilroy and Coxon 2005; Griffioen 2006; Holman et al. 2010; Kidmose et al. 2013).

Groundwater seepage discharge and its potential nutrient loading may be particularly important for the nearshore environment, the littoral zone of lakes. Research suggests that direct discharge of groundwater into lakes mainly occurs along shore areas where shallow local pathways interact with lakes. Population growth, and the intensification of land-use change, and human activity have severely affected and, in some cases, degraded nearshore areas. Moreover, many lakes now have offshore areas appearing meso to oligotrophic, and near shore areas exhibiting eutrophic conditions, including elevated nutrient concentrations, nuisance growth of filamentous algae and cyanobacteria blooms (Hecky et al. 2004; Makarewicz et al. 2012; Howell et al. 2014; Pothoven and Vanderploeg 2020). Historically, efforts to understand and mitigate nutrient conditions and their effect on a lake’s trophic status have focused on pelagic, open waters of the lake, with limited focus on the littoral zone. Recently, however, more research has centered on understanding shore conditions and ecology more systematically, especially in the Lauretian Great Lakes (Howell et al. 2012; Makarewicz and Howell 2012; Barton et al. 2013; Pothoven and Vanderploeg 2020; Chomicki et al. 2022). But groundwater seepage continues to be poorly studied for its potential as a source of nutrients to nearshore areas, and its role connecting terrestrial and lake biogeochemical processes.

This dissertation research investigates the role of groundwater seepage in the P loading dynamics along the Oneida Lake shoreline during the summer seasons of 2017, 2018 and 2020. Oneida lake is a large (207 km^2 in surface area), shallow, mesotrophic, polymictic lake located in central New York State with a large watershed (3,579 km^2, Schneider et al. 2016). Previous research has documented sub-surface groundwater flow along the entire shoreline of Oneida Lake (Schneider et al. 2005), but its nutrient contributions to the lake have not been studied to date.

In **Chapter 1,** I explored the potential of groundwater seepage to carry significant amounts of phosphorus into a 700m stretch of Oneida Lake shoreline associated with three different adjacent land uses, including an abandoned field, a wetland forest, and residential houses with septic systems in place. I directly measured the rates of groundwater flow using seepage meters and collected groundwater using pore water samplers. Water samples were analyzed for Soluble Reactive Phosphorus and Total Phosphorus using standard methods. A total of 384 seepage measurements were made over two summers (2017 & 2018), and 178 porewater samples and 180 lake water samples were analyzed for SRP and TP. These data were integrated to provide estimates of the rates of groundwater P loading into a portion of Oneida Lake shoreline during the summer season. I then analyzed the relationship between the observed loads and possible controlling factors, including precipitation, shore adjacent land uses, and distance from the shore.

In **Chapter 2,** I built on the findings from Chapter 1 and expanded the analysis throughout the entire Oneida lake shoreline, by estimating the concentrations, flows, and resulting loads of dissolved P transported by groundwater at ten representative locations around Oneida Lake's 88 km long shoreline. The goal was to assess the spatial and temporal variability of P loading, including SRP and TP by groundwater seepage along the Oneida Lake shoreline throughout the summer 2020. Over the course of nine weeks, 87 groundwater seepage flow measurements were made, and 87 pore water samples and 79 lake samples were collected. An evaluation of potential drivers of groundwater patterns was conducted using statistical models to a) assess the influence of precipitation prior to sampling events, b) compare dynamics among shorelines associated with each of the two large but different drainage basins, and c) compare P loading among shorelines differing in proximate adjacent land use.

In **Chapter 3**, I compared the groundwater phosphorus inputs determined in Chapter 2, with surface water inputs associated with the five main tributaries to Oneida Lake to better understand the relative contributions from these two different sources. Grab samples were collected from the tributaries simultaneously with the groundwater sampling throughout the summer of 2020. Stream flow rates were obtained from nearby U.S. Geological Survey gauging stations located on each stream and used to quantify stream P loads. In addition, automated ISCO water samplers were used to monitor stream water more continuously during several large storm events. Data was summarized to compare the relative importance of the two sources at different temporal scales, and during base flow conditions.

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CHAPTER 1

GROUNDWATER SEEPAGE: HIDDEN INPUTS OF PHOSPHORUS, WITH HOT SPOTS AND HOT MOMENTS, AT THE SEDIMENT-WATER INTERFACE ALONG LAKESHORES

1. Introduction

Excess loading of nutrients is one of the biggest threats to lake water quality and ecosystems. In general phosphorus (P) is considered the nutrient limiting primary production in temperate lakes and excessive P loading is one of the main causes of nuisance algal growth in such lakes (Carpenter et al. 1998; Schindler et al. 2016). In the 1970's, P loading into U.S. lakes was significantly reduced with the ban on P in detergents and the enactment of regulations, the foremost being the Clean Water Act. However, attention to P loading has risen again due to the increase in often toxic, blue-green algal blooms (Hazardous Algal Blooms or HABs). HABs not only negatively impact aquatic ecosystems but the toxins can also have direct impacts on human health (Backer and McGillicuddy 2006). The combined ecological, human health, and aesthetic impacts of HABS result in significant financial costs to local and regional economies by impairing water quality for recreation, fishing and other uses (Dodds et al. 2009).

In order to conduct effective nutrient management, it is important to quantify and evaluate the contribution of the various P sources and pathways to lakes. The main pathways for nutrients to get delivered into lakes is through precipitation, surface water discharge, overland stormwater runoff, and groundwater discharge. While nutrient loading through precipitation and surface water discharge have been widely studied, groundwater loading into lakes has been seriously overlooked (Lewandowski et al. 2015; Robinson 2015). Indeed, the linkage between a lake and its adjacent groundwater is one of the least studied factors in lake hydrology and ecology (Healy et al. 2007; Labaugh et al. 2009) even though the importance of groundwater seepage for lakes was already reported 60 years ago (Meyboom 1967). Conversely, other groundwater-surface water interfaces have been much more studied, such as the hyporheic zone (river-aquifer interface) (Cardenas 2015; Ward 2016) and the marine-groundwater interface (Moore 2010). Groundwater contributions to a lake's nutrient budget are difficult to quantify and characterize, mainly due to the heterogeneity of groundwater fluxes and composition across time and space. In addition, water composition is often altered as its flows across the sediment-water interface due to changes in biogeochemical conditions such as temperature, pressure, organic matter content, biological activity, and oxygen concentration, to name a few (LaBaugh et al. 1997; Carlyle and Hill 2001; Schuster et al. 2003; Moore 2010). As a result, direct groundwater nutrient loading estimates are scarce, and estimations based on groundwater composition from samples taken from wells or piezometers located in the vicinity of the lake's shore can be misleading (Krabbenhoft and Webster 1995; Griffioen 2006; Beck et al. 2007)

Traditionally, P has not been considered a major component of groundwater due to its tendency to bind to sediments and soil particles. Because of this, direct groundwater discharge has been overlooked as a source of nutrients to lakes. Research on P has focused on surface runoff with particular attention to storm and snowmelt events. However, in temperate areas, high flow events are dominant in winter and early spring, while primary productivity, with its associated biological demand for nutrients, peaks in late spring and summer when surface discharge is low and groundwater input may dominate. In addition, there is growing evidence showing that P can be mobile in groundwater under certain circumstances, for example when there is an excessive application of fertilizer (Domagalski and Johnson 2012; Roy and Malenica 2013). A review compiling historical data on P concentrations in groundwater in England found concentrations of phosphate above the regulatory threshold in many areas, with land cover as a significant predictor (Holman et al. 2008). They concluded that groundwater contributions to surface water may have the potential to trigger or sustain eutrophication (Holman et al. 2008). Groundwater inputs of phosphorus were found to be particularly critical in naturally nutrient- poor ecosystems, such as coastal pine barrens (Schneider 1994). Moreover, some studies have indicated that groundwater can be a significant source of nutrients even in lakes not dominated by groundwater flow inputs (Loeb and Goldman 1979; Shaw et al. 1990; Roy and Malenica 2013). Similarly, Grannemann et al. (2000) suggested that groundwater could have a significant impact on the Laurentian Great Lakes' water quality, sparking an interest in the matter that led to several recent publications about groundwater influences on water quality in the Great Lakes (Haack et al. 2005; Robinson 2015; Knights et al. 2017).

Research suggests that direct discharge of groundwater into lakes mainly occurs along shore areas where shallow local pathways interact with lakes. Population growth, and the intensification of land-use change, and human activity have severely affected and, in some cases, degraded nearshore areas. Moreover, many lakes now have offshore areas appearing meso to oligotrophic, and near shore areas showing eutrophic conditions, including elevated nutrient concentrations, nuisance growth of filamentous algae and cyanobacteria blooms (Hecky et al. 2004; Makarewicz et al. 2012; Howell et al. 2014; Pothoven and Vanderploeg 2020). Historically, efforts to understand and mitigate nutrient conditions and its effect on a lake's trophic status have focused on pelagic, open waters of the lake, with limited focus on the littoral zone. Recently, however, more research has centered on understanding shore conditions and ecology more systematically, especially in the Lauretian Great Lakes (Howell et al. 2012; Makarewicz and Howell 2012; Barton et al. 2013; Pothoven and Vanderploeg 2020; Chomicki et al. 2022). But groundwater seepage continues to be poorly studied for its potential as a source of nutrients and pollutants to nearshore areas, and its role connecting terrestrial and lake processes. Understanding of the interplay of hydrological, biogeochemical, and socioeconomical factors in these areas is a key component to improve our understanding of nutrient pollution, and to develop effective watershed-based approaches to lake management (Haack et al. 2005).

In this paper we investigated the potential of groundwater as a significant source of phosphorus to shorelines of Oneida Lake, a 207 km^2 mesotrophic, polymictic lake in central New York State with a large watershed (3,579 km^2, Schneider et al. 2016). Specifically, we aimed to: (1) directly estimate the rate of groundwater P loads into a portion of Oneida Lake shoreline during the summer season, and (2) analyze the relationship between the observed loads and possible controlling factors, including precipitation, shore adjacent land uses, and distance from the shore. Sub-surface groundwater flow has been documented along the entire shore of Oneida Lake (Schneider et al. 2005), but its nutrient contributions to the lake have not been studied to date.

2. Methods

2.1 Study Area

Our study was conducted at Oneida Lake (43°10′N, 75°52′W), located in central New York, 18 km east of the city of Syracuse. The lake is part of the Oswego River Basin which is part of the greater Lake Ontario basin. The lake runs from east to west dividing its 3579 km^2 watershed into similar sized halves, and our study is focused on a portion of the lake shoreline in the southern half. The lake is of glacial origin, with a consolidated sedimentary bedrock underlying the whole basin (Kantrowitz 1970), consisting of geological layers with high hydraulic conductivity. The basin consists of successive bedrock layers of limestone, shale, dolomite, and sandstone overlain by unconsolidated glacial till (Kantrowitz, 1970). The combined sedimentary bedrock and glacial deposits result in a high ability to store and transmit water creating an extensive system of aquifers that underly large portions of the watershed. The watershed is characterized by a continental climate with warm, dry summers and cold, snowy winters. The mean annual precipitation for the southern basin is 965 mm (USGS, 2010). Approximately 56 percent of the precipitation that falls in the watershed reaches the lake through surface inflow (Mills et al. 1978). The rest is redistributed through evaporation, transpiration by trees and plants, and groundwater recharge. Seven tributaries, three in the south, four in the north, contribute to the overland surface flow to Oneida Lake. Oneida River, on the western shoreline, is the lake’s only outflow. A greater amount of water comes in from the northern than southern tributaries, due principally to spring snowmelt as the northern basin receives the highest snowfall east of the Rockies. However, there are much higher nutrient concentrations in the southern tributaries (Schneider et al., 2016). The southern basin is dominated by agricultural land use, followed by suburban areas surrounding the city of Syracuse, woodlands, and a 2100 ha swamp (Cicero Swamp). The lake is extensively used for recreation, fishing, and general tourism, playing a large role in the local economy.

The watershed includes portions of six counties and 69 municipalities, with a human population of 262,164 based on the 2000 US Census, mainly aggregated in Onondaga County. The lake's shoreline extends for 88 km, is mainly used for recreational activities, and is characterized by both permanent and seasonal housing. Approximately 72 percent of the housing units in the Oneida Lake watershed are serviced by a public sewer system, with the remaining housing relying on septic systems for wastewater disposal. Most of the houses on the lake shoreline have been connected to a sewer system with a few houses still using septic systems. Changes around Oneida lake are being made annually, but at the time of this research, portions of the study shoreline were still using septic systems.

For this study we selected a portion of shoreline located in the southern basin. This area allowed us to sample from the three dominant shore land uses in the watershed, with easy and convenient access to the Cornell Biological Station (CBFS). The area encompassed 700 m of shoreline, where three distinct shore land uses were identified (Field, Wetland/Forest and Residential) (Figure 1). This section has ~260 m of shoreline adjacent to an abandoned agricultural field, followed by ~ 300 m of shoreline associated with a red maple swamp forest, which in turn was followed by 140 m of shore associated with nine houses (eight seasonal, one permanent) located within 50 m of the lakeshore edge. At the time of this study, none of these houses were connected to a sewer line, but instead relied on septic systems located within 50 m of the water's edge. This allowed us to directly observe and quantify the effect of septic systems on the lake's nearshore water quality. Hereafter, we will refer to the land uses for each of the areas as Field, Wetland and Residential.

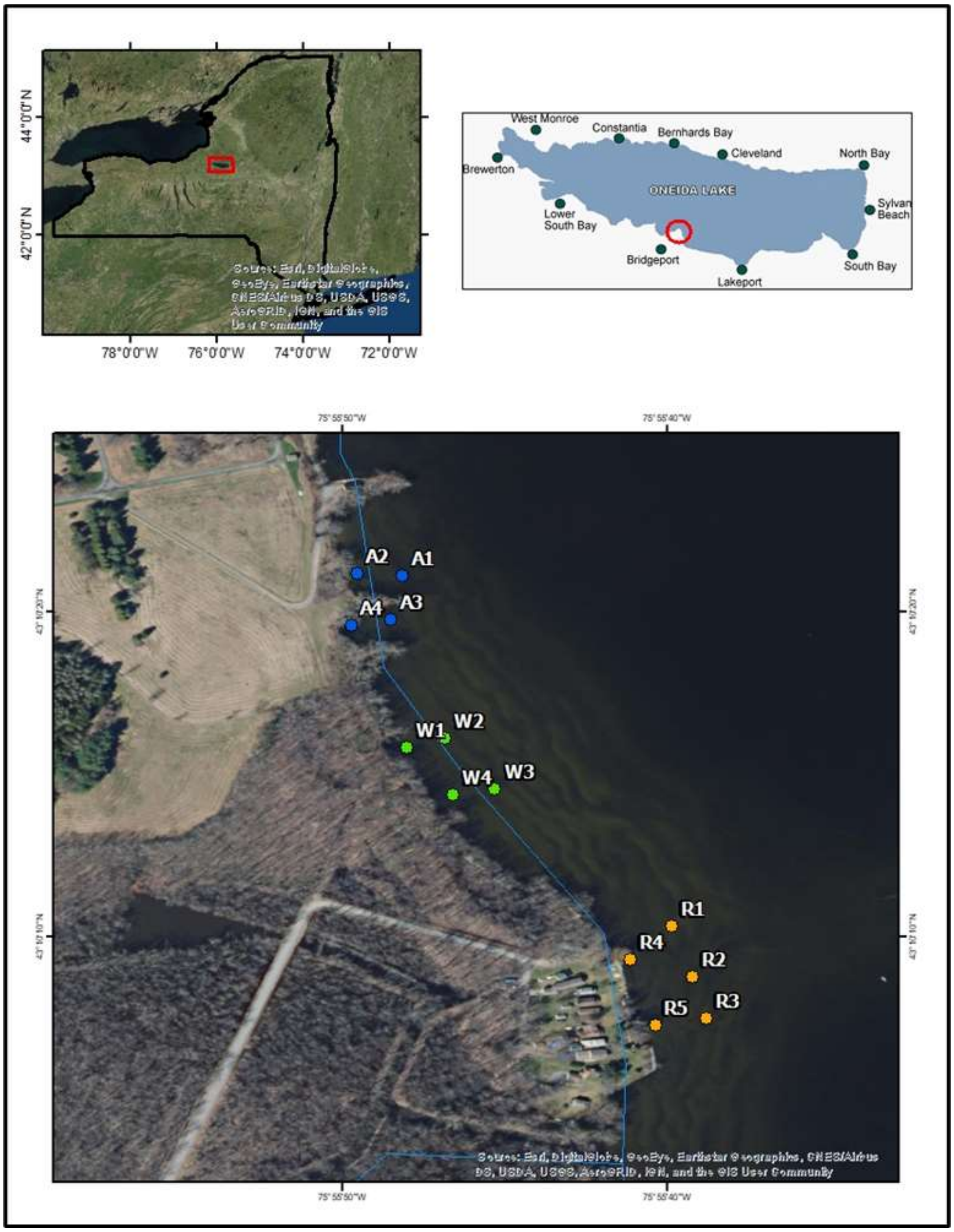

Figure 1. Oneida Lake location within NY State and sampling stations (points) at the South Shore of Oneida Lake. A1-4 represent sites located adjacent to the field land use, W1-4 wetland and R1-5 Residential.

2.2 Sampling design

During the summers of 2017 and 2018, 11 & 13 sampling stations, respectively, were installed along the 700 m southern shoreline of Oneida Lake, proximal to CBFS and coincident with reference sites used in previous studies (Schneider et al. 2005). Sampling stations consisted of a seepage meter modified from the design of Lee (1977), with the use of a plastic cover to reduce wave impact (Schneider et. al., 2005); and a porewater sampler (Schneider 1994) installed to a depth of ~40 cm into the lake sediments. The pore water samplers used in this study were designed by Dr. Schneider at Dr. Howarth's Lab in the early 90' and have been used to understand groundwater seepage solute concentrations in small freshwater lakes (Schneider 1994, Sebestyen and Schneider 2001, 2004). A pore water sampler consisted of a Luerlock valve connected to the above sediment end of a flexible plastic tube (0.32 cm diameter, vinyl) that passed lengthwise through a structural PVC pipe and terminated inside an 8 cm long pointed tip made of Delrin plastic. The below-sediment end of a tube was perforated (~1mm diameter) over 10 cm and wrapped in a polyethylene sponge filter that fit inside the permeable tip, with the purpose of preventing small clay sized sediments from interfering with sampling. A seal above the tip prevented lake water from infiltrating through the PVC tube to the sediments (Figure 2). The pore water samplers were pushed or pounded into the sediments. Sampling stations were equally distributed among the three land uses at two different distances from shore (10 and 38 m). This design was chosen to be consistent with previous studies from the early 2000s (Schneider et al. 2005) and thus facilitating comparisons. Seepage meters were monitored three to four times a week during the 2017 and 2018 seasons, and pore and lake water samples were collected once to twice a week during 2018. Lake samples were taken in the immediate vicinity of pore samplers with the purpose of comparing pore and lake water chemistry with a focus on P concentrations.

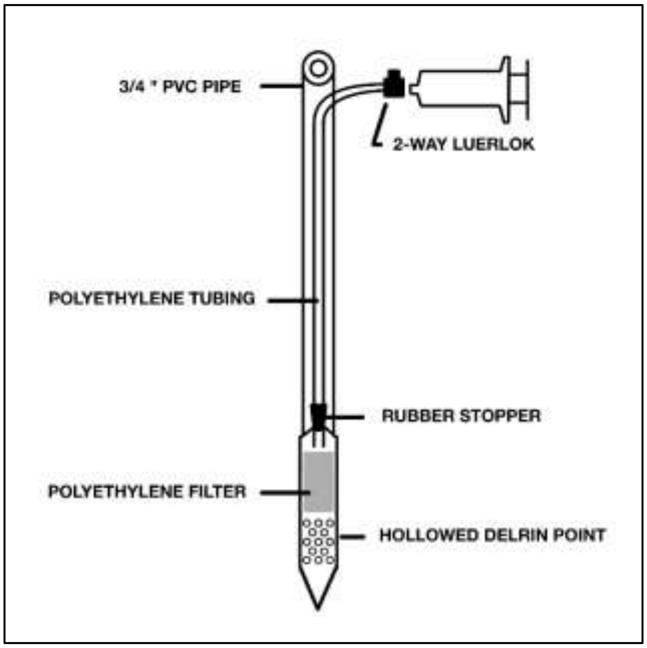

Figure 2. Pore water sampler schematic used for taking samples during this study.

2.3 Water sampling and analysis

Groundwater seepage was estimated at each site using seepage meters following the method established by Lee, (1977). Each bag was initially filled with 500 ml of water to avoid artificial bag inflation problems, and to allow for monitoring of recharging flow (Schneider et al. 2005). The bags remained attached to the meters for at least 24 and up to 72 hrs. After that time, the bags were removed, and volume change was determined using a graduated cylinder. Increases in volume indicated groundwater discharge into the lake, while volume loss indicated lake water recharging into groundwater. The seepage bags were replaced on a weekly basis to avoid over-expansion or leakage. Data was not incorporated in the analysis if either bags or meters covers showed signs of damage. Groundwater flow was calculated using the following equation:

$$Q = \frac{\Delta V}{Axt} \qquad \text{Equation 1}$$

where,

Q: Seepage flow rate

ΔV: seepage bag volume change

A: Surface area covered by the seepage meter

t: Time

During 2018, pore and lake water samples were collected for Total Phosphorus (TP) and Soluble Reactive Phosphorus (SRP) analyses. Before sample collection, pore samplers were first flushed two times when enough flow was available (~50 ml); however, toward the drier period of the summer only the first 20 ml of sample were discarded to ensure new water flowing into the device was collected. Water samples were collected in acid washed 60ml poly-propylene bottles, stored at 4 °C in a cooler, and transported to the nearby Cornell Biological Field Station laboratory. Once in the lab, each sample was divided into two portions for the various analyses. Approximately 15 ml were immediately filtered through a 0.45 μm filter (Supor Membrane Disc Filter, 25-mm diameter) and stored for SRP analysis. Additional unfiltered 25 ml subsamples were stored separately for TP analysis. All the samples were stored at 4 °C. To halt potential microbial cycling of nutrients, we decreased the pH to 2 by adding 30 % H_2SO_4 before storage (US EPA, 1978). After collection and preservation, nutrient analyses were run within one year at the Soil and Water Laboratory at Cornell University located in Ithaca, New York. Sample pH was checked monthly to ensure sample preservation. Phosphorus analysis was done on an automated wet chemistry analyzer (FS3000; Xylem Analytics O.I. Analytical, Beverly, Massachusetts) screening for phosphate anions (PO3 − 4) in SRP and TP samples. TP samples were first digested with persulfate and sulfuric acid (US EPA, 1978) and then filtered through a 0.45 μm filter (Supor Membrane Disc Filter, 25-mm diameter). Reagents for analysis were ammonium molybdate, ascorbic acid, sulfuric acid, and potassium antimonyl tartrate (US EPA, 1978). Each run was calibrated using 0.05, 0.1, 0.5, 1 and 5 ppm potassium phosphate standards, with all standard curve R^2 values between 0.998 and 0.999. If a given sample's P concentration was above the calibration range, the sample was diluted to ensure the quality of the data. In addition, during each sampling event, we measured dissolved oxygen concentrations (MW600; Milwaukee Instruments) in the lake and the pore water samples, directly in the field at the time of collection. Lake DO concentration was measured by inserting the probe in the top 10 cm of the lake water; for pore samples the DO probe was inserted in a special port created in the syringe used to collect the sample as soon as possible after suction to minimize sample oxygenation. Local precipitation was monitored daily using a manual rain gauge located 150 m from the shoreline in an open field.

2.4 Data and Statistical Analysis

The data analysis was structured in two phases. In the first phase we use a descriptive summary analysis to characterize and estimate groundwater flows, P concentrations, and P loads pattern into Oneida Lake along the south shore. P loads were calculated by multiplying P concentrations by average hourly groundwater seepage flow in the period between sample collection. For flow analysis we used the data collected during 2017 and 2018, while for concentrations and loads we used the data collected during 2018 season only.

In the second phase, we used linear regression modelling to evaluate relationships between environmental variables including precipitation, adjacent shore land use, and distance from shore on observed groundwater seepage flow, P concentration, and P loads. All response variables were $\log_e$ transformed to meet normality assumptions, and predictor variables with large absolute values were scaled in order to avoid inflated coefficients. In order to account for repetitive measurements over time at the same site we used linear mixed effect models (LMM) fitted by maximum likelihood using site as a random effect for the intercept. In addition, due to the longitudinal structure of the data set, we included time as a fixed effect (Bates 2009). As a result, we used the following null model for all the response variables:

$$\text{Response variable} \sim \text{Time} + (1|\text{Site}).$$

For each response variable, several LMM were developed using a forward selection approach. The final model selection was based on Akaike's information criterion (AIC) (Akaike 1992), and sequential F ratio testing (Wood 2006). Diagnostic plots of best-fit model residuals did not show major deviations from the assumptions of normality and constant variance. In addition, to understand the differences within categorical variables, we used a Type III Analysis of variance (ANOVA) using the Satterthwaite approximations to degrees of freedom. A comparison between pore and lake samples chemistry parameters was analyzed using two-sample Welch test; and Pearson correlation analysis was used to explore relationships between P concentrations and Dissolved Oxygen in the pore samples.

Results were considered significant when p-values <0.05. All statistical analyses were run in R software (R Core Team 2021). Mixed models were run using the lmerTest package (Kuznetsova et al. 2017)

3. Results

3.1 Groundwater Flows

A total of 384 groundwater seepage flow readings were made during the 2017 and 2018 summer seasons along the 700m shore section at Oneida Lake Southern shore: 170 during 2017, and 214 during 2018. The number of readings collected adjacent to each land use varied slightly over the period of the study with Field sites being more represented during 2017 (Table 1*)*. Across all sites, the mean groundwater flow for 2017 was 1.73 L/m^2 day (SD=3.68), and 1.05 L/m^2 day (SD=2.52) for 2018, with an overall mean of 1.35 L/m^2 day (SD=3.10) across both years. Comparison among land uses indicated that the highest average flow occurred at the Field sites during both years, with an overall mean of 1.77 L/m^2 day (Figure 3A). Residential sites followed Field sites, and Wetland sites exhibited the lowest flow rate during both years. Residential areas showed the largest range of individual flow values with a SD of 3.8, and also the highest recorded flow rate of 26.9 L/m^2 day. Wetlands areas showed the lowest range of values for flow rates during both seasons. All sites exhibited occasionally negative seepage values, which indicate that groundwater was recharging on occasion, although the duration and magnitude of these flows was low. A comparison of the flow patterns at two different distances from shore using the 2017 data indicated that sites that were closer to shore (10m) presented the highest mean flow (2.15 L/m^2 day), however the highest individual value (26.9 L/m^2 day) was observed at a site located farther from shore (38m). During 2018, the pattern was similar, with sites near shore still exhibiting higher mean flow (1.44 L/m^2 day) than sites farther from shore, which also showed the highest individual value (23.1 L/m^2 day). (Table 1, Figure 3)

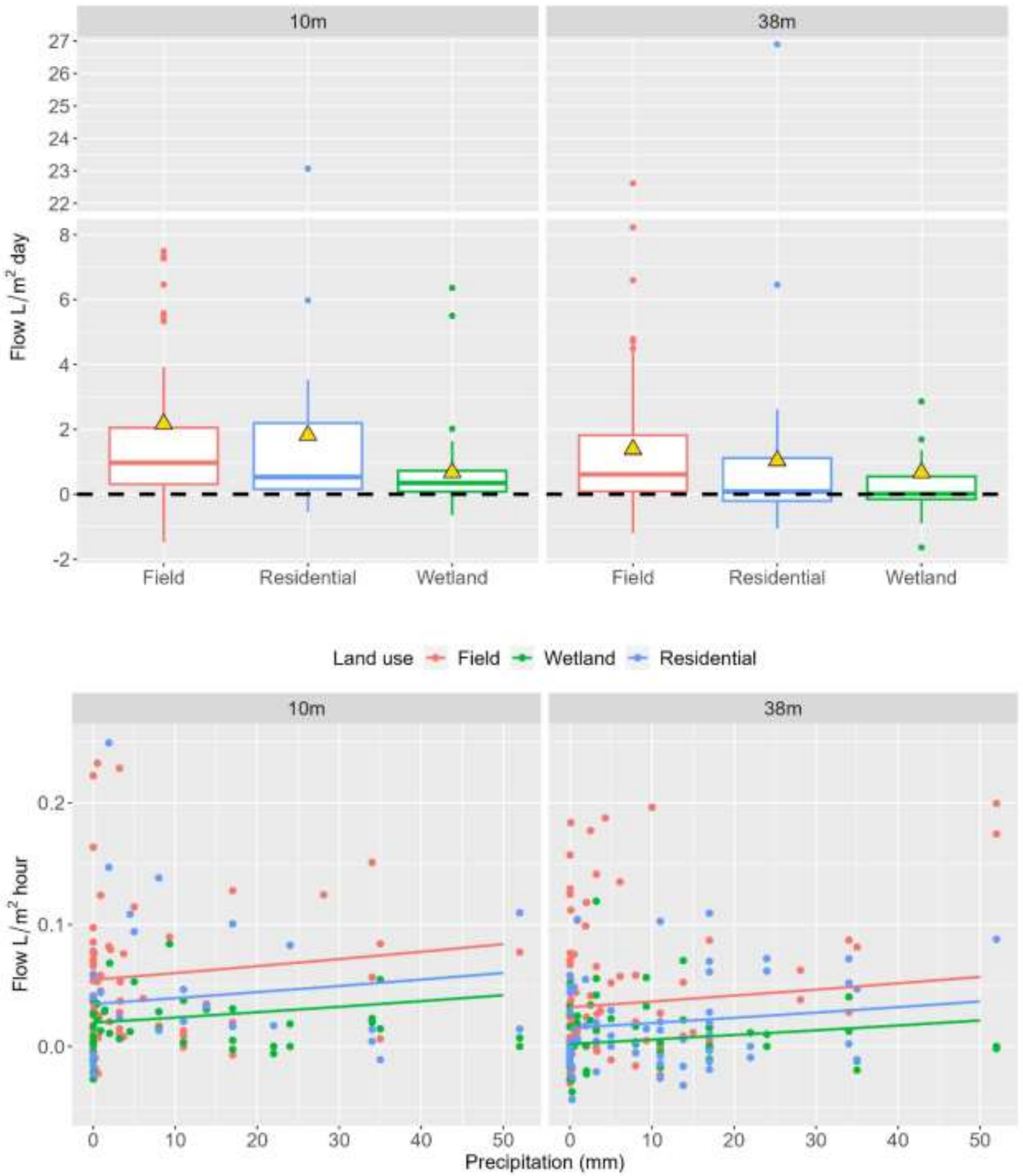

Figure 3A. Boxplots showing groundwater flow rates into Oneida Lake during 2017 and 2018 seasons at 10 m (left), and 38m (right) from shore, and three different land uses. Triangles represent flow means for each landuse, and dashed line showed the change from discharge into recharge. Notice that y-axis has been cut for illustrative purposes. Figure 3B. Flow rates in response to precipitation at two different distances from shore (10 m (left) and 38 m (right)) and three different land uses. Lines represent predicted flows from LLM, points represent data collected.

Table 1. Groundwater flow, pore water Total (TP) and Soluble Reactive Phosphorus (SRP) concentrations (mg/L), and Loads (mg/m^2-day) (mean, standard deviation, minimum and maximum) at Oneida Lake during summer 2017 & 2018 for each land use and distance from shore.

Parameter	Year	2018					
	Summary	per Land use			per Distance Shore		Total
	Category	Field	Residential	Wetland	Near (10m)	Farther (38m)	
TP mg/L	n	55	58	47	77	83	160
	Mean	2.26	2.63	1.31	1.62	2.57	2.11
	SD	3.57	3.03	1.38	1.86	3.57	2.91
	Min	0.11	0.08	0.10	0.10	0.08	0.08
	Max	25.93	18.75	6.00	10.79	25.93	25.93
SRP mg/L	n	59	61	58	86	92	178
	Mean	0.12	0.31	0.09	0.12	0.23	0.17
	SD	0.13	0.53	0.12	0.12	0.45	0.34
	Min	0.004	0.010	0.005	0.004	0.005	0.004
	Max	0.83	2.22	0.93	0.93	2.22	2.22
TP Load mg/m^2-day	n	55	58	47	77	83	160
	Mean	1.80	1.92	0.31	1.50	1.16	1.31
	SD	3.57	4.01	0.66	3.37	2.95	3.15
	Min	-0.12	-2.91	-0.23	-2.13	-2.91	-2.91
	Max	16.41	20.67	3.14	20.67	16.41	20.67
SRP Load mg/m^2-day	n	59	61	58	86	92	178
	Mean	0.19	0.17	0.03	0.15	0.10	0.12
	SD	0.47	0.40	0.09	0.37	0.36	0.36
	Min	-0.08	-0.04	-0.03	-0.04	-0.08	-0.08
	Max	2.40	2.41	0.64	2.40	2.41	2.41
Flow L/m^2-day	n	72	67	75	99	115	214
	Mean	1.50	1.19	0.49	1.44	0.71	1.05
	SD	2.35	3.04	2.03	3.01	1.95	2.52
	Min	-1.20	-0.55	-1.64	-0.65	-1.64	-1.64
	Max	10.40	23.07	16.12	23.07	16.12	23.07
Flow L/m^2-day	Year	2017					
	Summary	per Land use			per Distance Shore		Total
	Category	Field	Residential	Wetland	Near (10m)	Farther (38m)	
	n	109	37	24	62	108	170
	Mean	1.95	1.39	1.21	2.15	1.48	1.73
	SD	3.40	4.92	2.55	3.32	3.86	3.68
	Min	-1.48	-1.05	-0.89	-1.48	-1.05	-1.48
	Max	22.62	26.90	11.45	15.86	26.90	26.90

Flow L/m^2-day	**Year**	**2017 & 2018 combined**					
	Summary	**per Land use**			**per Distance Shore**		**Total**
	Category	**Field**	**Residential**	**Wetland**	**Near (10m)**	**Farther (38m)**	
	n	181	104	99	161	223	384
	Mean	1.77	1.26	0.67	1.71	1.09	1.35
	SD	3.03	3.80	2.18	3.14	3.05	3.10
	Min	-1.48	-1.05	-1.64	-1.48	-1.64	-1.64
	Max	22.62	26.90	16.12	23.07	26.90	26.90

LMM were used to further investigate the relationships between groundwater seepage flow and precipitation, land use, and distance from shore. Groundwater seepage flow differed significantly among the three land uses ($p<0.001$) and with distance from shore ($p<0.01$). Field sites exhibited significantly higher flows compared to Residential and Wetland areas. Distance to shore was also highly negatively correlated with flows, exhibiting significantly higher flows at sites near shore compared to sites located farther from shore. Precipitation in the previous 24 hr. was marginally correlated with flows ($p=0.06$). In addition, statistical models indicated that flows were predicted to increase as precipitation increases independent of land use type Table 2, Table 3 (See SM Table 1 for details on model selection).

Table 2. Fixed effects models estimates. P-values estimated via t-test using Satterthwaite approximations to degrees of freedom. Estimates are presented in logarithmic scale. Significant p-values are bolded.

Response Variable	**Groundwater Flow (ln Flow (L/m^2 h)**			
Model	Flow ~ Precipitation + Land use + Distance Shore + Time + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	3.17	5.65	0.56	0.575
Time	-0.12	0.13	-0.89	0.374
Precipitation (mm)	0	0.001	1.83	0.068
Wetland Land use	-0.26	0.06	-4.46	**<0.001**
Residential Land use	-0.14	0.06	-2.42	**0.016**
Distance shore (38m)	-0.16	0.05	-3.4	**0.001**
Response Variable	**SRP concentration (ln SRP (mg/L))**			
Model	SRP ~ Time + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	-216.07	122.97	-1.76	0.081
Time	49.37	28.4	1.74	0.084
Response Variable	**SRP Load (ln SRP (mg/m^2 h))**			
Model	SRP Load ~ Precipitation + Land use + Time + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	-57.77	114.32	-0.5	0.614
Time	1.23	2.64	0.47	0.641
Precipitation mm	0.01	0.003	2.18	**0.031**
Wetland Land use	-0.32	0.13	-2.47	**0.015**
Residential Land use	-0.1	0.13	-0.82	0.412
Response Variable	**TP concentration (ln TP (mg/L))**			
Model	TP~ Time + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	-1019.91	208.22	-4.9	**<0.001**
Time	235.56	48.1	4.9	**<0.001**
Response Variable	**TPLoad (ln TP (mg/m^2 h))**			
Model	TP Load ~ Land use + Time + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	-1055.26	461	-2.28	**0.024**
Time	242.95	106.6	2.28	**0.025**
Wetland Land use	-1.48	0.47	-3.15	**0.002**
Residential Land use	0.07	0.47	0.15	0.882

Table 3. ANOVA (Type III Satterthwaite's methods) results for flow, Phosphorus (TP, SRP) concentration and loads against time, precipitation, land use and Distance from shore.

Response Variable / Independent Variable		**Time**	**Land use**	**Precipitation**	**Distance Shore**
Flow (2017-2018)	Sum squares	0.15	3.72	0.62	2.12
	F-value	0.79	10.13	3.36	11.57
	p-value	0.374	**0.001**	*0.068*	**0.003**
SRP Loads(2018)	Sum squares	0.07	1.89	1.41	NA
	F-value	0.22	3.17	4.75	
	p-value	0.641	*0.075*	**0.031**	
TP Loads (2018)	Sum squares	17.35	43.91	NA	NA
	F-value	5.20	6.57		
	p-value	**0.024**	**0.008**		
SRP concentration (2018)	Sum squares	1.06	NA		
	F-value	3.02			
	p-value	0.08			
TP concentration (2018)	Sum squares	19.35	NA		
	F-value	24.00			
	p-value	**2.44E-06**			

3.2 Phosphorus Concentrations

A total of 178 pore water samples were collected during the 2018 season across 13 sites distributed along 700m of Oneida Lake Southern shore. Mean pore TP concentration was 2.11 mg/L (SD=2.91). Individual values range from 0.08 to 25.93 mg/L, with the highest individual value observed at a site located along the Field land use. Mean pore SRP concentration was 0.17 mg/L (SD=0.34). In contrast to the pore TP concentration, the highest individual SRP value (2.22 mg/L) was observed at a site along the Residential area, while the lowest individual value (0.004 mg/L) was observed at the Field site (Table 1).

Comparing among land uses, mean TP and SRP were highest at the Residential area (2.63 and 0.31 mg/L, respectively), and lowest at Wetlands sites (1.31 and 0.09 mg/L, respectively), however maximum individual values for TP were observed at Field areas (25.93 mg/L); while SRP maximum (2.22 mg/L) was observed at the Residential area (Table 1).

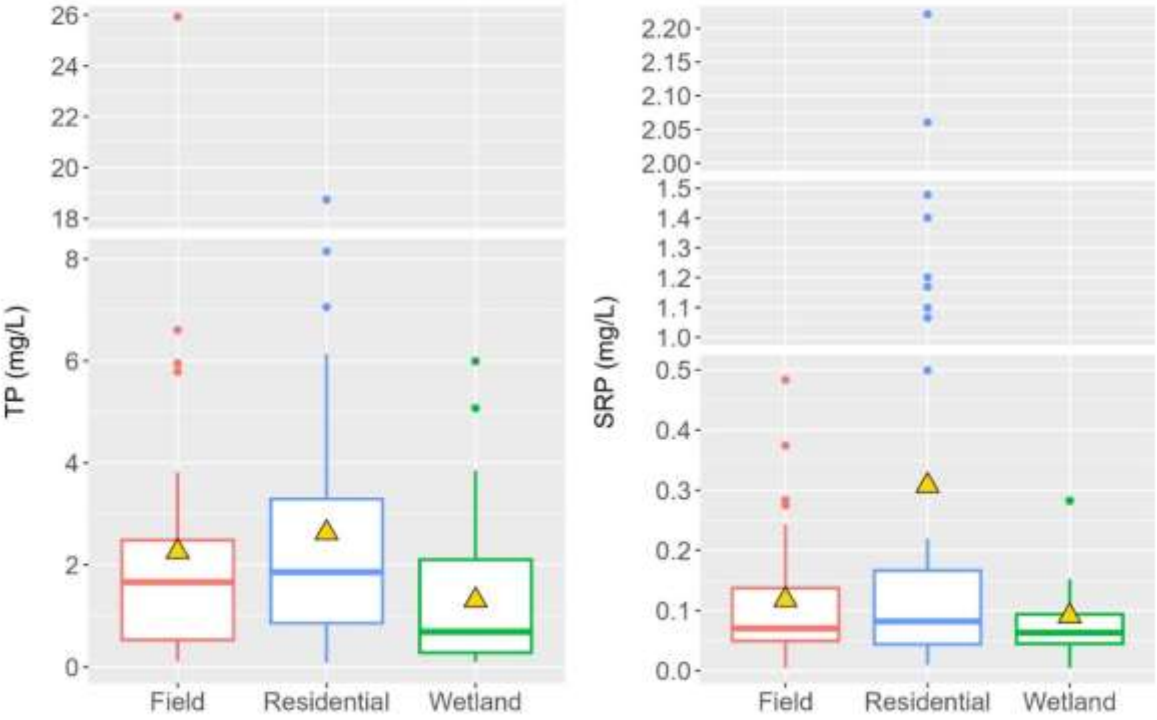

Figure 4. Boxplots showing pore water TP (left) and SRP (right) concentrations in mg/L during the 2018 season at two distances from shore (10 and 38 m) and three different land uses. Triangles represent flow means for each land use. Notice that y-axis has been cut for illustrative purposes.

For both TP and SRP concentrations, LMM was used to evaluate relationships with flows, precipitation, land use and distance from shore. Contrary to our initial hypothesis, none of the explanatory variables affected SRP concentrations. Surprisingly time had a positive effect on TP concentrations (p <0.001), indicating a strong seasonal increase of pore water TP concentrations (Table 2 & Table 3).

During 2018, a total of 214 samples of lake water were taken distributed among all sampling sites. TP concentrations of the lake water ranged between 0.04 and 10.2 mg/L, with a mean TP of 0.31 mg/L, which was six times lower than mean TP concentrations of the pore water samples. Similarly, SRP concentrations of lake samples range between 0.003 and 0.12 mg/L, with a mean value of 0.05 mg/L; three times lower than pore water concentrations (Table 4, Figure 5). Statistical analysis indicated that P concentrations (both TP and SRP) in lake samples were significantly lower than in pore samples (p-value <0.001) (Table 5).

Table 4. Descriptive summary of Total Phosphorus (TP), Soluble Reactive Phosphorus (SRP) and Dissolved Oxygen (DO) concentrations for lake and pore water samples.

Parameter	**Year**	**2018**		
	Summary			
	Category	***Lake (Off Shore)**	**Lake (at the Shore)**	**Pore**
TP mg/L	**n**	8	173	160
	Mean	0.009	0.31	2.11
	SD	0.003	1.17	2.91
	Min	0.005	0.04	0.08
	Max	0.015	10.20	25.93
SRP mg/L	**n**	8	180	178
	Mean	0.001	0.05	0.17
	SD	0.0003	0.03	0.34
	Min	0.001	0.0003	0.0044
	Max	0.002	0.13	2.22
DO mg/L	**n**	NA	186	184
	Mean		9.73	1.57
	SD		1.83	1.18
	Min		4.70	0.00
	Max		13.00	6.80

*Average over 8 sampling dates for 2018 summer months (June, July and August) of the composite samples across 4 open water stations at Oneida Lake (Rudstam, 2021).

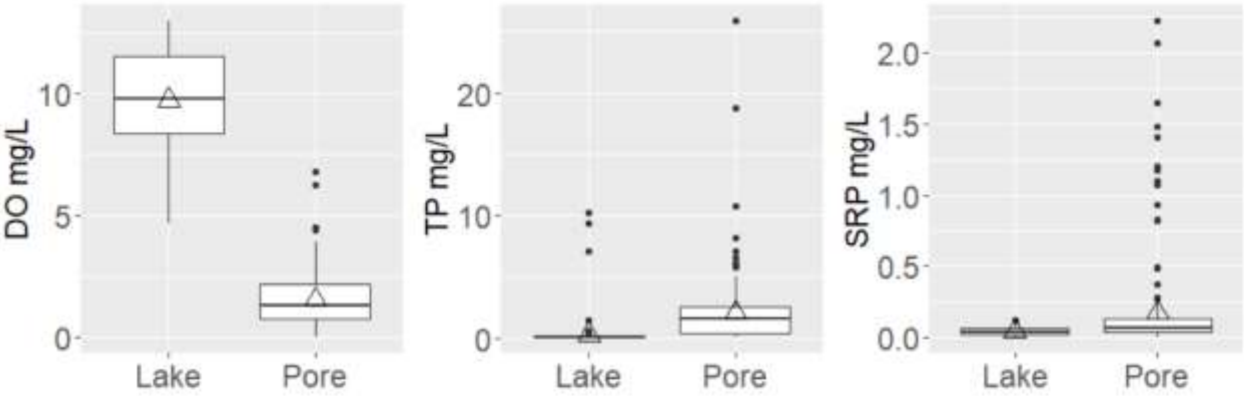

Figure 5. Dissolved Oxygen, TP and SRP in mg/L at shore lake water vs. pore water samples during the 2018 season.

Table 5. Statistical analysis comparing TP, SRP and DO of pore vs. lake water samples collected at the lake's nearshore.

Statistical analysis for Lake vs.Pore P and DO Welch Two samples t-test			
	TP	**SRP**	**DO**
t-value	7.30	4.98	37.64
p-value	6.21E-12	1.48E-06	2.20E-16
Pearson Correlation test pore P concentration vs. pore DO concentration			
	TP~DO	SRP~DO	
rho value	-0.13	0.1	
p-value	0.11	0.18	

In conjunction with the water sample collection, a total of 370 DO measurements were made during 2018. DO in pore water samples ranged from 0 to 6.8 mg/L, with an average of 1.15 mg/L. More than 90% of the pore samples exhibited DO values below the biological limit of 4 mg/L (Young et al. 2011). DO for lake samples were in general much higher, ranging between 4.7 and 13.0 mg/L, with a mean of 9.73 mg/L (Table 4, Figure 5). Statistical analysis indicated that DO was significantly higher in lake samples than in pore samples at all sites ($p<0.001$). Unexpectedly, pore DO concentrations were not significantly correlated with pore TP (rho=-0.13, p=0.11) or SRP (rho= 0.1, p= 0.18) concentrations (Table 5).

3.3 Phosphorus Loads

Mean TP loads across all sites was 1.31 mg/m^2 day (SD=3.15), with individual values ranging from -2.91 to 20.67 mg/m^2 day. SRP loads also showed broad variability ranging from -0.08 to 2.41 mg/m^2 day at individual sites and averaged at 0.12 mg/m^2 day (with a SD of 0.36 mg/m^2 day) (Table 1, Figure 6A). Comparing loads among the three land uses, mean TP loads were four times higher at Field and Residential sites (1.80 and 1.92 mg/m^2 day respectively), compared to Wetland sites (0.31 mg/m^2 day). The maximum TP load value was registered at a Residential area site (20.67 mg/m^2 day). SRP loads followed a similar pattern, such that average loads from the Field and Residential sites (0.19 and 0.17 mg/m^2 day, respectively) were seven times higher than Wetland area average (0.03 mg/m^2 day) (Table 1, Figure 6A). Both mean TP and SRP loads were higher at sites closer to shore compared to sites farther from shore.

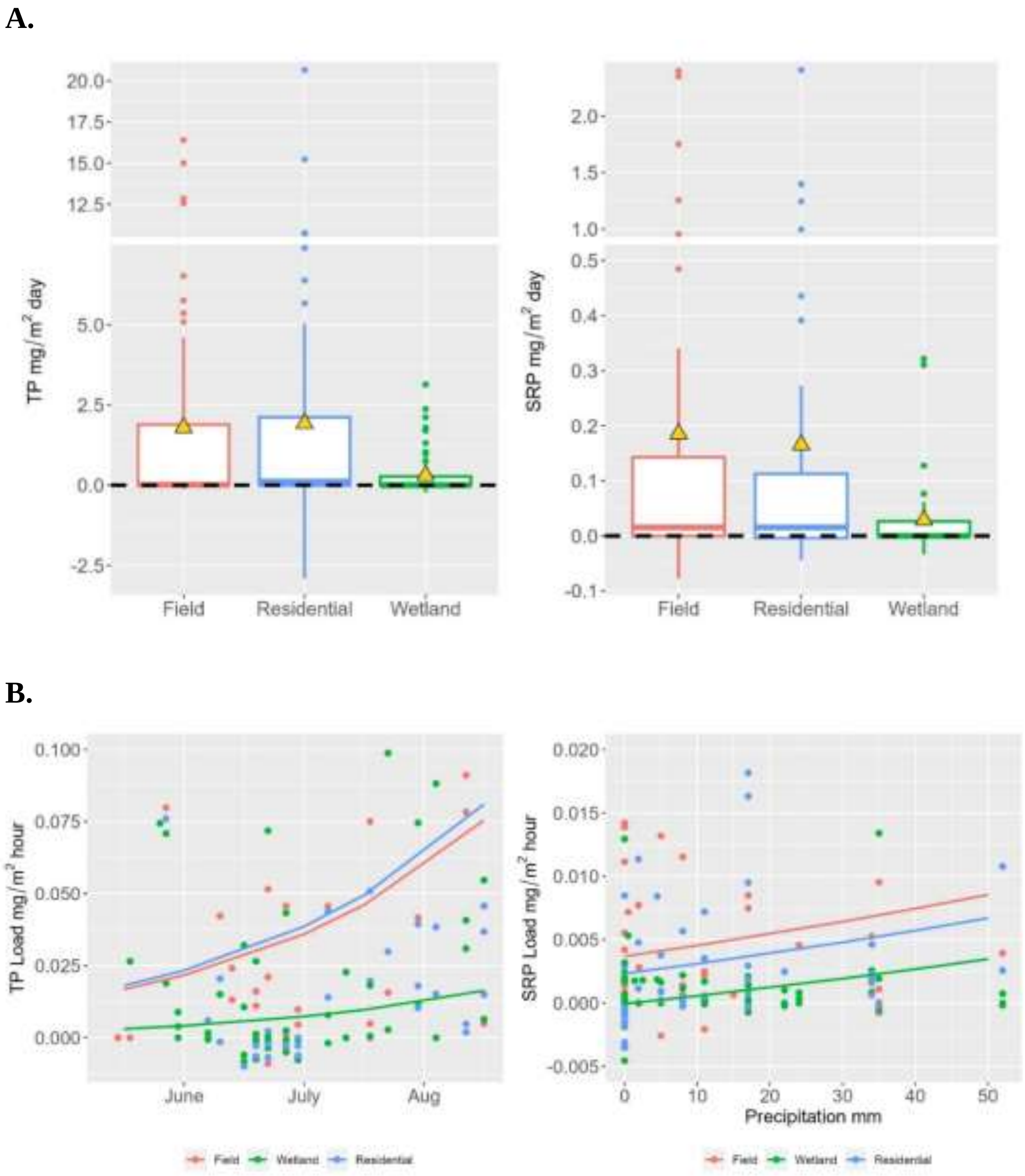

Figure 6. (A) Boxplots showing TP (left) and SRP (right) Loads in mg/m^2 hour during the 2018 season at three different shore adjacent land uses. Triangles represent flow means for each land use, and dashed line showed the change from infiltration to exfiltration. Notice that y-axis has been cut for illustrative purposes. (B). TP loads in response to season progression (time) at three different land uses (left). SRP Loads in response to precipitation at three different land uses (right). Lines represent predicted flows from LLM, points represent data collected.

For P loads, LMM were used to evaluate its relationship with precipitation, land use and distance from shore. TP loads to Oneida Lake were highly correlated with time, exhibiting higher loads as the summer season progressed (p=0.02). Land uses also exhibited significant influences on TP loads (p=0.008), with Wetlands contributing significantly lower loads than Field and Residential areas (Table 2, Table 3, Figure 6B). On the other hand, variability in SRP loads were not related to time but were highly correlated with precipitation in the previous 24 hr., with loads predicted to increase as precipitation increases (Figure 6B). Overall land uses had a marginal effect on SRP with Wetland sites exhibited marginally smaller loads than the Field site.

4. Discussion

Results of this research demonstrate the hidden but important contributions of groundwater seepage to phosphorus dynamics in lake shorelines, with critical implications for algal blooms and lake nutrient dynamics. Over the two years of this study, groundwater seepage was a continuous source of dissolved phosphorus discharging through the sediment and into nearshore waters of Oneida Lake, New York. The actual loading amounts were a combined function of flow rate and concentrations, both of which varied spatially and temporally along the 700 m stretch of shoreline. Higher groundwater flow rates were documented at sites closer to shore compared to those farther from shore, and also immediately following rain events. Comparison of phosphorus concentrations among the three differing adjacent land uses was also insightful. SRP concentrations ranged from 0.004 mg/L to 2.2 mg/L among sampling sites, with highest concentrations adjacent to the residential homes, and near zero concentrations next to the wetland. TP concentrations ranged between

0.08 and 26 mg/L, and overall increased with summer's progression. Combining flow rates and concentrations, dissolved SRP phosphorus loadings into the lakeshore averaged 0.12 mg/m^2-day, with a high of 2.4 mg/m^2-day, while TP loading averaged ~ten-fold higher, at 1.3 mg/m^2-day, with a high of 20.7 mg/m^2-day. These loadings are comparable to those reported in the literature for internal phosphorus loading from benthic sediments. However, the critical difference is that in our study the phosphorus is being transported into the lake shoreline from external watershed-based sources. Dissolved oxygen concentrations in the pore water were consistently lower than 3.0 mg/L which will maintain phosphorus in solution until it crosses the sediment-lake interface (Foster and Fulweiler 2019). This biogeochemical transformation has important implications directly at the sediment-water interface and deserves further research. More broadly, the chronic inputs of dissolved phosphorus are likely driving the higher concentrations documented in the overlying lake waters close to shore. Nearshore lake water P concentrations were approximately 10 times higher than water column averages at four standard sampling stations in the open waters of Oneida Lake (Table 4). Both the phosphorus dynamics at the sediment interface and the greater availability of dissolved phosphorus in lakeshore waters may be contributing to periodic nuisance benthic algal blooms observed along Oneida Lake shorelines. These findings have relevance to lakes elsewhere as it indicates that there can be a consistent source of P associated with groundwater seepage into the littoral habitat.

An overall mean of 1.35 L/m^2 day of subsurface flow into Oneida Lake South Shore was observed across the two summer seasons in which this study was conducted. Schneider et al. (2005) reported an overall average rate flow of 1.73 L/m^2 day into a subset of our study site, i.e. the shoreline stretch area adjacent to the abandoned field land use across three summers between 1997 and 1999. This rate is effectively identical to the flows recorded from the same sites averaged for summers 2017 and 2018 (1.77 L/m^2 day), two decades later. During 2017 the overall average flow rate was higher than during 2018 (1.95 vs 1.50 L/m^2 day). These rates are comparable to other studies (Lillie and Barko 1990; Shaw et al. 1990), although both much higher (Menheer 2004; Kidmose et al. 2011), and much lower rates have been reported (Sebestyen and Schneider 2001). Rosenberry et al. (2015) compiled data for 108 lakes around the world and reported seepage rates ranging from 0.05 to 1140 L/m^2 day, with a mean of 7.4 L/m^2 day (Table 6)

On a finer scale, flow rates were highly variable temporally across the period of study. The statistical analysis indicated that flow rates were weakly correlated with local precipitation amounts measured in the previous 24 hrs at CBFS. It is expected that rainfall of sufficient magnitude to recharge groundwater increases near-shore seepage rate (Winter 1983), however this relationship is thought to be complex and in general dominated by a delay effect. Thus, an increase in precipitation may not always translate into an immediate groundwater flow peak. A recent study that looked at seepage dynamics in eight lakes across the United States demonstrated that in areas where shallow subsurface pathways dominate, groundwater seepage could respond to local rainfall within minutes, while in others the response could take days or longer (Rosenberry et al. 2013). Most studies have focused on the shallow nearshore pathways, and only a few studies have been able to document the larger, longer scales of deeper flow paths for groundwater which might result in longer lag times (Cherkauer and Nader 1989; Schafran and Driscoll 1993).

In general, the predominant pattern among the sites was of groundwater discharging into the lake, including the greatest flow rates and most frequent direction of flow. However, on a few occasions we measured negative flow rates, indicating groundwater recharge. Other studies have documented a seasonal shift in dominant flow patterns from discharge to recharge, following spring snowmelt (Sebestyen and Schneider 2001), but that was not observed here. In other studies, portions of lakes exhibit recharge as the dominant process, usually in the vicinity of outflowing creeks (Belanger and Kirkner 1994; Healy et al. 2007; Rosenberry and Winter 2009), as was observed at the western end of Oneida Lake around the outflowing river (Schneider et al. 2005).

Spatial variability of seepage has been widely reported, although the reasons underlying such variability are less well understood (Keery et al. 2007; Kikuchi et al. 2012). Our observations are consistent with other studies in that we observed high spatial variability in seepage fluxes among sampling stations. A significant contributing factor to the variability in groundwater seepage flow rates could be explained by shore land uses, with the Field site showing significantly higher flow than the Wetland and Residential site. The Wetland site exhibited the lowest but more constant flow. Our results suggest that the Wetland area is retaining or transpiring water during the summer at Oneida Lake, a process that has been reported for other natural and constructed wetlands (Hunt et al. 1999; Ackerman et al. 2015). In addition, flow rates were significantly higher at sites closer to shore as compared with sites farther from shore. This finding contradicts the observation made by Schneider et al. (2005) where average groundwater flow rates did not decrease with increasing distance from shore. However, it does agree with studies elsewhere that also reported lower rates for sites farther from shore (Harvey et al. 2000; Knights et al. 2017). The diverse characteristics of hydrometeorological events that occurred every year, could help explaining the discrepancy between the observations in previous studies at Oneida South shore and this study, and with different patterns reported elsewhere. Precipitation events of smaller magnitude will activate shallow pathways that will result in high flow in sites closer to shore, while regional events or more intense event are needed to activate deeper pathways that will results in flows increasing at sites farther from shore (Rosenberry et al. 2015). The South portion of the Oneida Lake watershed has a surface area of ~ 600 km^2 with the underlying aquifer materials of sandstone and limestone having high hydraulic conductivities (Schneider et al. 2016), which could result in lakebed discharge from regional groundwater flow paths, in addition to shallow, local pathways.

Pore water P concentrations (TP: 2.11± 2.91 mg/L ; SRP: 0.17 ± 0.34 mg/L) were consistently higher than shore lake water concentrations (TP:0.31 ± 1.17 mg/L ; SRP: 0.05 ± 0.03 mg/L) in 2018, with TP and SRP mean values that were seven and three times higher, respectively. This result suggests groundwater is a potentially significant contributor of phosphorus, and likely other chemical compounds to the lake. Many other studies have reported pore water nutrient concentrations significantly higher than lake or adjacent streams waters (Sebestyen and Schneider 2004; Haack et al. 2005; Su et al. 2014; Knights et al. 2017). In addition, lake water concentrations at near shore areas were one to two orders of magnitude higher than lake water concentration in the deep off-shore areas (Rudstam 2021) (Table 4). A similar disparity between near and offshore waters has been reported for many of the Great Lakes (e.g. Hecky et al. (2004) for Lake Erie, Makarewicz and Howell (2012) for Lake Ontario, Pothoven and Vanderploeg (2020) for Lake Michigan, and Howell et al. (2014) for Lake Huron). In the Great Lakes system, higher nearshore P concentrations have been attributed to several drivers. From the physical/chemical perspective, Makarewicz and Howell (2012) hypothesized that excess nutrient loading into the near shore from tributaries' discharge, coupled with nutrient entrapment on the shore side due to the spring thermal bar, and wind induced currents that spread tributaries plumes parallel to the shores are among the main drivers for shore P enrichment. Additionally, Hecky et al. (2004) hypothesized that the invasion of dreissenid mussels may have a significant impact on P dynamic by retaining P in the nearshore (the nearshore shunt hypothesis). Our results suggest that groundwater seepage is an additional significant contributor of P to the nearshore environment, which interact with all the above-mentioned drivers to enhance near-shore eutrophication.

Pore water TP concentrations ranged between 0.08 to 26 mg/L, and SRP concentrations ranged between 0.004 to 2.22 mg/L. Similar averaged SRP concentrations were reported by Knights, et al., (2017) for pore water at Lake Erie's Western Basin, and Shaw et al. (1990) also reported similar SRP concentrations for pore water at Lake Alberta in Canada. Others, (Sebestyen and Schneider 2001; Hagerthey and Kerfoot 2005) have reported smaller but comparable concentrations for other temperate lakes in the US (Table 6). Much lower SRP concentrations were detected in the shoreline pore waters of two ponds located in the Pine Barrens of Long Island, New York, which are notable for their oligotrophic conditions which support a high diversity of endemic plant species (Table 6)(Schneider 1994). Reports of groundwater seepage TP concentrations were otherwise scarce in the literature.

Interestingly, TP concentrations were observed to increase with summer progression and the drivers for this increase are not known. We hypothesize that it may be related to an increase in mineralization rate or microbial activity in the surrounding watershed as summer progresses and temperatures increase. In general, literature on internal P loading report an increase in hypolimnetic TP concentrations, which is commonly attributed to an increase in P release rate from sediments, as temperature increases affecting DO concentrations in stratified lakes (Nürnberg et al. 2013b). We believe our observations of an increase in ground water TP through the season is an important result that needs further investigations to better understand the seasonal P dynamics at the sediment-water interface.

Overall, the sites located in the Wetland area exhibited TP concentrations two times lower than the Residential and Field areas. SRP concentrations were similar in the Field and Wetland sites, but concentrations in the Residential area were two to three times higher. Due to limited sample sizes and high variability in the data, the differences in average P values were not statistically significant among the three land uses. However, the trends provide important insights into possible causes and impacts. Wetlands are recognized as a natural solution for many water quality issues, including filtering and nutrient removal (Ackerman et al. 2015). Wetlands can decrease water nutrient concentrations through multiple mechanisms, including adsorption onto soil organic matter, vegetation uptake, sedimentation, and microbial transformation. For example, Ackerman et al., (2015) showed that a constructed wetland in Illinois significantly decreased SRP and Nitrate concentrations in the groundwater seepage outflowing the wetland compared to the wastewater inflow. Conversely, lakeshore residential development has been linked to increased pollutant discharges into lakes, both from surface runoff and from septic leachates (Macintosh et al. 2011; Timoshkin et al. 2018). Except for the research on septic system’s impact on downstream ground and surface water quality (Humphrey et al. 2010; Oosting and Joy 2011; Flanagan et al. 2020), we were not able to find articles that explicitly study the impact of adjacent shore land uses on groundwater seepage and its P concentrations discharging into lakes. At the residential sites, all the houses located in this stretch of the shore used septic systems at the time of this study. However, the high concentrations of SRP were mostly driven by the concentrations at Site R1, which were constantly between two and four times higher than at the rest of the sites. Interestingly, Site R1 is located 38 m offshore from the only house that was permanently occupied. Having whole year occupancy likely influences the state of the septic system, the amount of pollutants entering the system, and the discharging concentrations. This result suggests this site is acting as a Hot Spot (Mcclain et al. 2003) or as a permanent control point (Bernhardt et al. 2017) for P export through groundwater seepage, which highlights the importance of further studying the effect of septic system at shorelines sediment-water interface, in relationship to groundwater seepage P loading.

Table 6. Summary of groundwater flow, pore P concentrations and P Loads into temperate lakes reported in the literature using similar estimation and sampling methos as in this study.

Location	**Reference**	**Average Flow (L/m2 day)**	**Trophic State**	**Pore P concentration mg/L***	**P Load mg m2 day***	**Sampling Details****
Sparkling Lake, Wisconsin	Hagerthey and Kerfoot 1998	-	Oligomesotrophic	0.001-0.065	0.0007-0.0455	SRP
Lake Hampen, Denmark	Ommen et al., 2012	-	Oligotrophic	0.004-0.05	0.024-0.3	SRP at 10-50cm
Narrow Lake, Alberta	Shaw et al., 1990	-	Mesotrophic	0.175	0.063	TDP-Point estimate
Lake Mendota, Wisconsin	Brock et al., 1982	-	Eutrophic	0.27	0.486	Soluble PO4 at 4cm
Lake Erie Western Basin, Ohio	Knight, et al 2017	-	Mesotrophic	0.12 (0.01-0.3)	0-12.94	TDP at 25cm
Pine Barrens Ponds, NY	Schneider, 1994	-	Oligotrophic	0.01	0.06-0.17	SRP at 10&50cm
Oneida Lake - CBFS	Schneider et al 2005	1.72	-	-	-	-
Lower Sylvan Pond, NY	Sebestyen and Schneider 2001	0.05	-	-	-	-
Pine Barrens Ponds, NY	Schneider, 1994	11.05	-	-	-	-
Devils Lake, Wisconsin	Lillie and Barko 1990	3.4	-	-	-	-
Narrow Lake, Canada	Shaw and Prepas 1990	2.6	-	-	-	-
Lake Hampen, Denmark	Kidmose et al 2011	15	-	-	-	-
Long Lake,Minnesota	Menheer 2004	130	-	-	-	-
108 lakes	Rosenberry et al 2015	7.4	-	-	-	-
		(0.05 - 1140)	-	-	-	-
Oneida Lake, South Shore	**This study**	**1.05 (-1.6 - 23)**	**Mesotrophic**	**0.17 (0.004-2.22)**	**0.12 (0-2.41)**	**SRP at 30-40cm**

* Single values represent means, while values in parenthesis represent a range (min-max)

** Type of P analyzed and sample depth collection

Most of the pore water samples consistently exhibited hypoxic conditions, less than 4 mg/L DO and frequently as low as 1 mg/L. Dissolved oxygen levels lower than 3.0 mg/L in the porewater samples will maintain phosphorus in solution (Foster and Fulweiler 2019), until it crosses the sediment-lake interface. However, pore water phosphorus concentrations were not correlated with dissolved oxygen concentrations. Traditionally, oxygen control on P has been considered as the main mechanism driving P release at the sediment-water interface. Under oxic conditions P is sorbed to Iron or Manganese compounds, that return into solution under reduced conditions (Mortimer 1942). Although many experiment and field observations show strong correlations between oxygen depletion and P release (Boström et al. 1988; Nürnberg et al. 2013a; Foster and Fulweiler 2019), there are also studies that are challenging the universal validity of this mechanism and suggest that there could be several alternative processes underlying P release at the water-sediment interface (Hupfer and Lewandowski 2008). Other mechanisms driving P flux from sediments to overlying water include pH-mediated P release (Jensen and Andersen 1992; Golterman 2001) and organic matter decomposition through microbial activity, which may dominate during summer months (Moore et al. 1998; Wang et al. 2013). Moreover, Hupfer and Lewandowski, (2008) postulate that in addition to oxygen availability, P release is controlled by a complex coupling of sediment composition, external load, catchment hydrology, lake morphometry and biogeochemical reactions.

Combining flow rates and concentrations, phosphorus loadings into the lakeshore averaged 0.12 mg/m^2-day, with a high of 2.4 mg/m^2-day for SRP, and 1.31 mg/m^2 day, with a max of 20 mg/m^2 day for TP. Similar groundwater SRP Loads values were found for other lakes where similar methodology were used to estimate groundwater P fluxes (Table 6). Knights et al., (2017) reported TDP loads ranging between 0 to 12.94 mg/m^2-day for Lake Erie's Western Basin. Similarly, Ommen et al. (2012) reported SRP loads ranging between 0.024 to 0.3 mg/m^2-day for Lake Hampen in Denmark. Others have reported smaller, but comparable values (Shaw et al. 1990; Hagerthey and Kerfoot 1998). We were not able to find groundwater seepage TP load values for comparison in the literature. However, TP loadings estimated in this study are comparable to those reported in the literature for internal phosphorus loading from benthic sediments. Orihel et al. (2017) reviewed P internal loading along water bodies in Canada and reported TP fluxes that ranged from -27 to 54 mg/m^2-day. Similarly, Carter and Dzialowski (2012) predicted internal loading for 17 reservoirs in the Central Plain region of the US and reported mean TP loading values between 6 to 26 mg/m^2/day.

Conditions that favor internal loading, such as lake stratification and anoxic conditions in the sediments, occur during late summer and early fall when stream inputs are the lowest and phytoplankton productivity is the highest. Hence, when lake P concentrations and chlorophyll patterns cannot be explained by stream inputs, anoxic P release from the sediments (internal loading) is believed to be the main driver for the observed patterns. Indeed, evidence suggest that internal loading is in many cases the main driver of primary productivity during the summer and is a significant and widespread process in temperate lakes (shallow bays of Lake Champlain (Isles et al. 2015), Lake Simcoe (Nürnberg et al. 2013b)). Our study suggests that groundwater seepage could be an alternative and/or complementary process that is independent of, and may occur simultaneously with, internal P loading. The magnitude of groundwater seepage loading observed in this study is comparable to that reported for internal loading in many lakes and could be a significant contributor to the P dynamics of lakes during low flow periods. Groundwater seepage should not be overlooked in water quality models and P mass balance budgets.

Given the implications of groundwater seepage to the P dynamic in the near shore area, this phenomenon could potentially have significant ecological implications for the littoral environment. Our study suggests that groundwater seepage provides a significant and continuous amount of dissolved P to the sediment water interface, which could be a sustained P source to the benthic communities in the littoral areas. Considering the shift from off-shore pelagic to near-shore benthic primary productivity that many lakes (including Oneida Lake) are experiencing in temperate regions after the establishment of the invasive dreissenid mussels (Zhu et al. 2006; Higgins and Vander Zanden 2010; Mayer et al. 2014), this source of P could become highly relevant with implications for the nearshore ecology. Groundwater seepage is a ubiquitous phenomenon that occurs in many lakes, including the Great Lakes (Rosenberry et al. 2015; Robinson 2015) but studies of groundwater seepage are limited and fragmented. Although dreissenid mussels are recognized as an engineer species that has significant impacts on a lake’s nutrient dynamics and benthic and water column communities and productivity (Li et al. 2021; Karatayev et al. 2023), the presence of dreissenids often is not enough to explain shoreline eutrophication processes in the absence of localized P enrichment (Higgins et al. 2012; Bootsma et al. 2015). Phenomena like the resurgence of nuisance benthic algae, such as *Cladophora*, whose growth rates are strongly P limited (Bootsma et al. 2015; Howell 2018) could be explained at least in part by groundwater seepage and its P loading (Barton et al. 2013). Harmful cyanobacterial blooms could similarly be linked to this P source as many of these species exhibit a meroplantonic life cycle, in which individuals spend an initial period of development in or on top of the sediments (Barbiero and Welch 1992). There are a few studies that suggest that an increase in P concentration in the water-sediment interface may be the mechanism underlying cyanobacterial blooms in low-nutrient lakes (Carey et al. 2009, 2014). Our findings suggest that groundwater seepage could have implications for nearshore nutrients dynamic and food web structure that deserve more attention and need to be integrated into the current discussion about nutrients dynamic and management.

5. Conclusion

This study documented that groundwater seepage along Oneida Lake shoreline is a consistent source of new dissolved phosphorus entering the lake. It is comparable in magnitude to internal loading but originates from an entirely different, external source in the watershed. It influences the entire lakeshore littoral zone, elevating the P concentrations in both the entire water column and at the sediment water interface. Groundwater seepage may thus be playing a key role, along with the mussel invasion in the shift from pelagic primary production to benthic primary production that has been observed in many temperate lakes including Oneida Lake. Our results showed that land use along the shoreline influences groundwater flow rates, P concentrations, and P loadings. Wetlands acted to filter out P thereby decreasing P loadings into the lake, whereas residential areas with septic systems were a hotspot for P loading through groundwater seepage. The result of this study has important implications for all lakes that deal with nutrient pollution and its consequences, including recent increases in algal blooms.

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Supplementary Materials

SM. Table 1. Model Comparisons using AIC criteria.

Response Variable	Model ID	Model	AIC
Flow	FM0	Flow ~ Date + (1|Site)	557.00
	FM1	Flow ~ Precipitation + LandUse + DistanceShore + Date + (1|Site)	445.70
	FM2	**Flow ~ Precipitation + LandUse + DistanceShore + Precipitation * DistanceShore Date + (1|Site)**	**443.80**
	FM3	Flow ~ Precipitation + LandUse + DistanceShore + LandUse * DistanceShore Date + (1|Site)	448.80
	FM4	Flow ~ Precipitation + LandUse + DistanceShore + Precipitation * DistanceShore Date + (1|Site)	447.00
SRP Load	SL0	SRP Load ~ Date + (1|Site)	311.4
	SL1	SRP Load ~ Precipitation + LandUse + DIstanceShore+ Date + (1|Site)	307.1
	SL2	**SRP Load ~ Precipitation + LandUse + Date + (1|Site)**	**307.7**
	SL3	SRP Load ~ Precipitation + LandUse + Precipitation*LandUse + Date + (1|Site)	310
	SL4	SRP Load ~ Precipitation + LandUse + DistanceShore + Precipitation*LandUse + Date + (1|Site)	309.6
TP Load	TL0	TP Load ~ Date + (1|Site)	497.5
	TL1	TP Load ~ LandUse + DistanceShore + Precipitation + Date + (1|Site)	493
	TL2	**TP Load ~ LandUse + Date + (1|Site)**	**491**
TP Load	TL3	TP Load ~ LandUse + Precipitation + Date + (1|Site)	492
	TL4	TP Load ~ LandUse + DistanceShore + Date + (1|Site)	493
	TL5	TP Load ~ LandUse + Precipitation + LandUse * Precipitation + Date + (1|Site)	493

CHAPTER 2

GROUNDWATER SEEPAGE AS A DRIVER OF PHOSPHORUS LOADING AND BIOGEOCHEMICAL INTERACTIONS AT THE SEDIMENT-WATER INTERFACE IN THE SHORELINES OF ONEIDA LAKE

Introduction

Groundwater flow is an invisible but critical link between terrestrial and aquatic ecosystems that is slowly gaining recognition for its key roles in biogeochemical cycling. The complex connections between groundwater and streamside or riparian ecosystems have been the most extensively studied (Brunke and Gonser 1997; Brunner et al. 2017), with more than 1000 studies focused on soil microbial denitrification as the primary mechanism responsible for removing nitrate from groundwater. The hyporheic zone is a special subset of this environment, where the intermingling of ground water and stream water within the substrate influences energy cycling, nutrients and organic compounds, as well as water temperatures (Fernald et al. 2006; Vidon et al. 2010). Most recently, the interface of fresh groundwater with seawater along estuarine and ocean coastlines has gained attention, which has widely broadened the discipline to include groundwater interactions with diurnal tidal pumping and saline-freshwater biogeochemical interactions (Taniguchi et al. 2002; Moore 2010; Sekar et al. 2022); and these interactions have also been recognized for their role in coastal nutrient dynamics (Burnett et al. 2003; Gallardo and Marui 2006). Surprisingly, the study of the biogeochemical interactions between lakes and their adjacent aquifers remains incipient and fragmented.

That groundwater flows through lake shorelines has been recognized for almost a century (Meyboom 1967), but largely discussed in the anecdotal context of lakeshore owners and the potential impacts of their septic system leachates (Gilliom and Patmont 1983; Chen 1988). Nearly 150 studies have investigated groundwater seepage and quantified flow rates along lake shorelines, broadly focusing on its magnitude and timing (Rosenberry et al. 2015). Fewer studies have dealt with its nutrient contributions (Lewandowski et al. 2015). Studying biogeochemical processes has been made challenging by the complexity of groundwater-surface water exchange processes that can alternatively facilitate the transport and / or the retention of nutrients and pollutants across the sediment-water interface. Additionally, there has been a general perception that phosphorus (P) is immobile in subsurface water and aquifers, due to its tendency to bind to sediment particles or precipitate with metal complexes either in the vadose or saturated zone (Heiberg et al. 2010; Holman et al. 2010a; Kjaergaard et al. 2012; Prem et al. 2015).

Traditionally, surface hydrological pathways have been considered the main transport routes for external P into lakes, and river discharge is the main pathway integrated in lake management assessments and plans when dealing with eutrophication. As a result, P contributions to lake systems by groundwater seepage have been rarely studied, with the exception of a few small lakes where groundwater seepage is a major input source of water (Shaw et al. 1990; Buso et al. 2009). However, there is growing evidence that P can be transported by groundwater, and it is not necessarily immobilized in aquifers (Holman et al. 2008, 2010b; Nisbeth et al. 2019). Many factors are involved in the fate of P through the unsaturated and saturated zones of sediments. The geochemical conditions, such as redox potential and iron concentrations, are recognized as the principal mechanisms underlying P mobility and sorption (Walter et al. 1995; Szilas et al. 1998). However, other factors, such as the sorption potential of the aquifer matrix, the degree of P saturation, and the time of contact between groundwater and the aquifer matrix, as driven by the flow rate and hydraulic conductivity of the aquifer (Griffioen 2006; Loeb et al. 2008; Buso et al. 2009), could also greatly influence P concentrations and transport via groundwater. It is critical to understand what role groundwater is playing in P input to lake waters as it may be a key to understanding and managing hazardous algal blooms and other consequences of excess nutrient loading to water bodies.

The overall goal of this study was to evaluate groundwater seepage for its role in P loading dynamics at representative sites distributed around the entire shoreline of Oneida Lake, located in Central NY. The lake is a mesotrophic, polymictic, shallow lake, with a surface area of approximately 207 km^2, and a shoreline length of 88 km, which is widely used for tourism, fishing, and recreation (Rudstam et al. 2016). This is one of the few studies that attempts to evaluate the role of groundwater seepage on P dynamics along the entire shoreline of a large lake (greater than 100 km^2) in which tributaries are the primary water source. Oneida Lake is ideal for this evaluation as previous research has demonstrated that subsurface groundwater flow occurs along the entire shoreline of the lake (Schneider et al. 2005). Previous work also documented that there are significant concentrations of P in groundwater seepage entering Oneida Lake along a short stretch of the southern shoreline, and that loadings were related to the adjacent land use, precipitation patterns, and distance from the shoreline (Chapter 1). The specific objectives of this study were to:

1. Estimate the concentrations, flows, and resulting loads of dissolved P transported by groundwater at representative locations around Oneida Lake’s 88 km long shoreline.

2. Analyze the spatial and temporal variability of P loading by groundwater seepage along the Oneida Lake shoreline throughout the summer 2020, and
3. Evaluate potential drivers of groundwater patterns by using statistical models to a) assess the influence of precipitation prior to sampling events, b) compare dynamics among shorelines associated with large drainage basins, and c) compare P loading among shorelines differing in proximate adjacent land use.

2. Methods and Materials

2.1 Study Site

Our study was conducted at Oneida Lake (43°10′N, 75°52′W), located in central New York, 18 km east of the city of Syracuse. The lake is part of the Oswego River Basin which is part of the greater Lake Ontario basin. The lake is of glacial origin, with a consolidated sedimentary bedrock underlying the whole basin (Kantrowitz 1970). The watershed is characterized by a continental climate with warm, dry summers and cold, snowy winters. The lake runs from east to west dividing its 3579 km^2 watershed into two similar sized halves, with long North and South shores associated with the two halves (

Figure 7). The northern and southern sub-watersheds are of similar geological origin, both presenting geological layers with high hydraulic conductivity, but prominent differences in its hydrometeorological conditions, which have significantly influenced its land use and land cover. The southern half underlying geology consists of successive bedrock layers of limestone, shale, dolomite, and sandstone overlain by unconsolidated glacial till. The northern half is dominated by a 76 m thick base layer of sandstone shale, which intercepts and underlies a portion of Oneida Lake, and is overlain successively by layers of dolomite, middle shale, limestone and upper shale (Kantrowitz, 1970). The mean annual precipitation is 965 mm in the southern basin and 1300-1500 mm in the northern basin (USGS, 2010). Much of the precipitation originates as snowfall in the winter and is stored as snowpack. The northern sub-basin received 3-5 m of snowfall annually, which is the highest reported snowfall east of the Rocky Mountains, due to the basin position east and down-wind of Lake Ontario. As a result of the long snowy winters and acidic soils, the northern half is dominated by forest with numerous wetlands, and minimal agriculture; while the southern half is dominated by agriculture, suburban areas around the city of Syracuse, woodlands, and 2100 ha. swamp (Cicero Swamp) (Schneider et al. 2016). Approximately 56 percent of the precipitation that falls in the watershed reaches the lake through surface inflow (Mills et al. 1978). The rest is redistributed through evaporation, transpiration by trees and plants, and groundwater recharge. Seven tributaries, three in the south, four in the north, contribute to the overland surface flow to Oneida Lake. Although surface inflow from the northern watershed represents most of the total water volume entering the lake, the majority of the nutrient inputs are coming from tributaries that drain the farmlands of the southern watershed. Water flows out of Oneida Lake into Oneida River which is located at the western edge of the lake. The combined sedimentary bedrock and glacial deposits result in a high ability to store and transmit water creating an extensive system of aquifers that underly large portions of the watershed. This setting, combined with a steep topographic relief over hundred meters of elevation towards Oneida Lake, facilitates the superficial and groundwater flow from both sub-basins into Oneida Lake (Schneider et al. 2016).

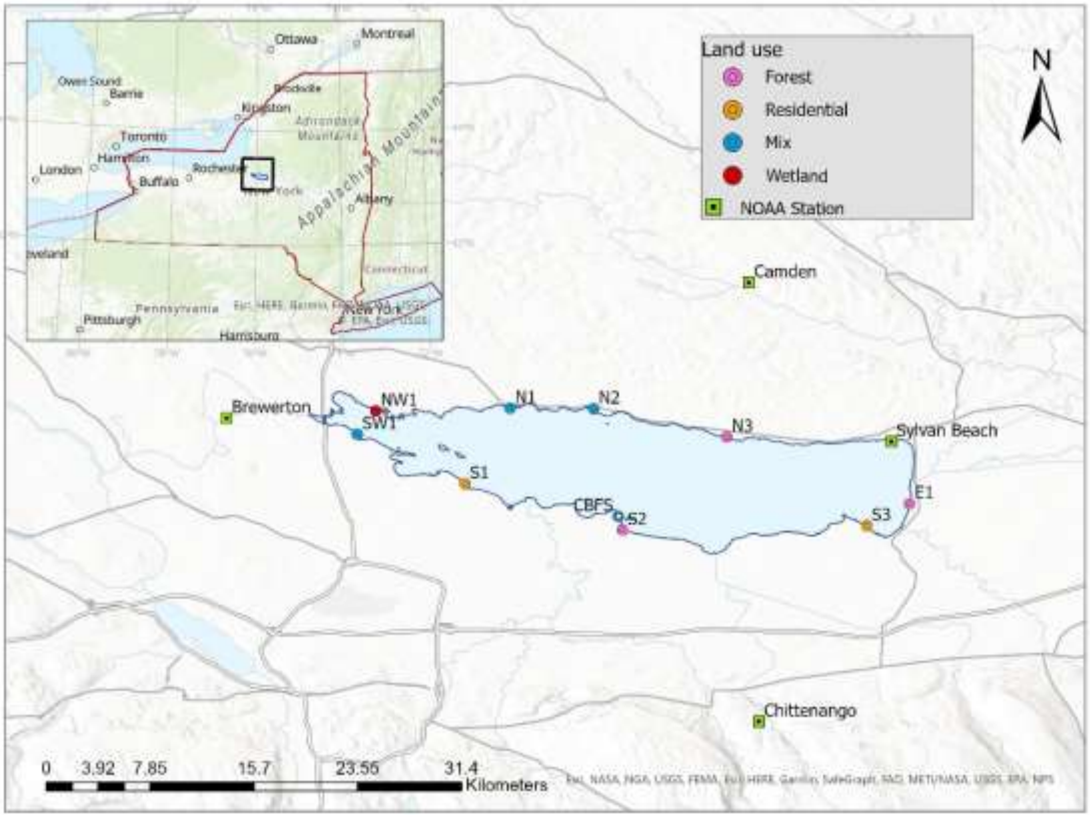

Figure 7. Oneida Lake location within NY State and sampling stations (points) at representative sites around Oneida Lake shoreline. Letters represent the lake shore cardinal point, and colors represent shore adjacent land use to sampling site.

The watershed includes portions of six counties and 69 municipalities, with a human population of approximately 262,164 based on the 2000 US Census, mainly aggregated in Onondaga County. The lake's shoreline extends for 88 km, is mainly used for recreational activities, and is characterized by both permanent and seasonal housing. The majority of the housing units in the Oneida Lake watershed are serviced by a public sewer system, with the remaining housing relying on septic systems for wastewater disposal. By the time of this study, most of the houses located in the lake's shoreline have been connected to sewer system.

2.2 Sampling design, collection, and analyses

For this study we selected ten sites distributed along the entire shoreline of Oneida Lake to install sampling stations for groundwater seepage flow and its P concentrations. Sites were selected for its accessibility from land or by boat and were chosen to get representation of the whole lake shoreline, which result in five sites located along the southern shore, four along the northern shore, and one site on the eastern shore in between the two main tributaries inlets (

Figure 7). The shoreline adjacent land use to each sampling site was identified using Google EarthPro by categorizing the main land cover in a rectangle of 200 m parallel to the shore by 500 m wide in the shore area adjacent to the sampling site. If more than 5 houses were located on the shoreline, the site was characterized as residential despite other land covers. This resulted in four sites located next to forested areas, two in residential areas, four that were a mix of residential, forest and abandoned field, and one site next to a wetland area. Sampling stations consisted of a seepage meter to estimate groundwater seepage flow rates and pore water samples installed ~40cm into the lakebed sediments to collect pore water samples for Total Phosphorus (TP) and Soluble Reactive Phosphorus (SRP) analyses. Please refer to Chapter 1 for further details on sampling stations' setting and sample collection, processing, and laboratory analyses. It is important to note that even though we analyzed the samples for TP and not for Total Dissolved P (TDP), meaning we did not filter the samples in the laboratory before digestion, most of our samples were clear in color. The permeable tips of the pore water samplers (as detailed in Chapter 1) was perforated to ~1mm in diameter, and the flexible plastic tube inside was wrapped in a polyethylene sponge filter, with the purpose of preventing small clay sized sediments from interfering with sampling. As a result, we anticipate that particulate fractions will be mostly absent in our samples; and most of the P measured as TP would be in dissolved form. In this study all stations were located 10 m from the shore. Lake samples were taken in the immediate vicinity of pore samplers with the purpose of comparing pore and lake water chemistry with a focus on P concentrations. Samples were taken once a week for nine weeks during summer 2020 (June to August). Groundwater seepage meters were activated 24 to 72 hrs. before sample collection and reading. Due to accessibility issues and personnel availability restrictions associated with the COVID-19 pandemic, not every site was sampled every week, which resulted in a heterogeneous number of samples at each site (Table 1). Sites located on the southern and eastern shore were more accessible due to the availability of land access. Consequently, samples from these sites were collected more or less on a weekly basis (n = 9 to 14), except for site S3, which was added later in the season. On the other hand, sites located on the northern shore were more challenging to access, resulting in fewer samples from each site, except for site N2, where samples were collected weekly (n=10). However, for the remaining northern sites (n= 5 to 6), we ensured sample collection throughout the entire season, with a minimum of one sample per month at each site. At Site NW1 located next to a big wetland, seepage meters were consistently missing the day after installation for unknown reasons (removed by the public, high water flow, loose soil). As a consequence, there is no seepage reading for this site, and in order to estimate P loadings using P concentrations sampled for that site, we used the weekly average flow rates for sites located on the north shore.

2.3 Data Analysis

A descriptive summary analysis was used to characterize and estimate groundwater flows, P concentrations, and P loads into Oneida Lake shoreline. P loads were calculated by multiplying average hourly groundwater seepage flow by P concentrations at each sampling event.

Linear regression modelling was used to compare flows, concentrations, and loadings between the north and the south shore. The site located on the east shore (E1) was excluded from this analysis. Linear regression models were also used to evaluate the relationship between precipitation and adjacent shore land use, with flows, concentrations, and loads. All response variables were $\log_e$ transformed to meet normality assumptions. In order to account for repeated measurements over time at the same site, we used linear mixed effect models (LMM) fitted by maximum likelihood using site as a random effect for the intercept. In addition, due to the longitudinal structure of the data set, we included time as a fixed effect (Bates 2009). The precipitation analysis was kept separately from the land use analysis to avoid issues with statistical power given the sample size. For the land use analysis, the site located next to the wetland area (NW1) was excluded from the analysis due to lack of replication. Precipitation data was obtained from the closest NOAA weather station to each sampling site (8 to 15 km away), which resulted in more than one precipitation data set involved in the analysis, and in most cases one station was used for more than one site (Table 7). Thus, for precipitation analyses a random effect for weather station was also included in the models. Seven aggregations of the precipitation data were used for the analysis (Precipitation in the previous 24 hrs, 48 hrs, 72 hrs, cumulative precipitation in the previous 48 hrs and 72hrs, and number of days since the last rain event), in order to understand how regional rainfall affects groundwater seepage flows and its P loading at the lake shoreline. Each precipitation aggregation was used separately, resulting in seven different models for each response variable, with the final model selection based on Akaike's information criterion (AIC) (Akaike 1992).

Results were considered significant when p-values <0.05. All statistical analyses were run in R software (R Core Team 2021). Mixed models were run using the lmerTest package (Kuznetsova et al. 2017).

Table 7. Meteorological data used for precipitations analysis. NOAA Stations Name and ID and its association with groundwater sampling sites

NOAA Station ID	NOAA Station Name	Sampling Sites
US1NYMD0016	CHITTENANGO 2.1 ESE, NY US	S1, S2, S3, CBFS
USC00301110	CAMDEN, NY US	N1, N2, N3
US1NYOD0061	SYLVAN BEACH 1.6 NW, NY US	E1
USC00300870	BREWERTON LOCK 23, NY US	NW1, SW1

3. Results

3.1 Groundwater Flows

A total of 87 groundwater seepage flow readings were made during summer 2020 at nine stations in representative sites distributed around the entire 88 km shoreline of Oneida Lake. Due to accessibility issues, sites located on the South shore of the lake were sampled more frequently than sites located on the North shore, resulting in a total of 49 readings and samples collected on the South shore versus 27 on the North shore. Across all sites the mean groundwater flow for 2020 was 0.81 L/m^2-day (SD=1.34 L/m^2-day) (Table 8). Seepage flow rates were highly variable both spatially and temporally. Comparison among sites indicated that the highest average flow (1.92 L/m^2-day) occurred at station E1 located on the East shore between the inlets of the two main tributaries to the lake (

Figure 7). This site also exhibited the greatest range of variation (SD=2.2 L/m^2-day). Individual flow measurements, across all sites, oscillated between -0.93 and 5.12 L/m^2-day. Negative numbers indicate that lake water was recharging the groundwater, a phenomenon that was observed at least once at seven of the sites during the summer. However, the frequency and magnitude of such events were significantly lower than events where groundwater discharged into the lake. Comparisons between the two shores indicated that average flow rate on the South shore was higher and more variable (mean ± SD = 0.8 ± 1.20 L/m^2-day) than on the North shore (0.28 ± 0.56 L/m^2-day) (Table 8). Sites located on the South shore also exhibited higher individual values than sites located on the North shore (Figure 8A).

Spatially, Site S1 deserves a special note as it exhibited the lowest flow rate for the whole lake and seems to be particularly different when compared to other sites along the South shore. Individual flow rates values ranged from -0.88 to 0.4 L/m^2-day (Table 8), presenting positive values for flow rate only three times out of the nine weeks sampled during the season. This resulted in a negative overall average flow rate for the site, where, for most of the summer, groundwater was recharged and not discharged into the lake. Moreover, when groundwater was discharging into the lake, the rates were among the lowest registered in this study.

Groundwater seepage flow rates were also highly variable over time during the study period. On some weeks, flow rates were highly different among sites, with some sites showing low rates and other sites, sometimes nearby, having high rates (Figure 8B). For example, during week 5 (July 16 & 17, 2020) site S2 exhibited flow rates up to 4.08 L/m^2-day while the rates for site S4, which is in close proximity (Figure 7), was 2.16 L/m^2-day. On the other hand, during week 7 (August 6 & 7, 2020), all the sites had flow rates between 0.48 and 0.96 L/m^2-day. Interestingly, weeks 6, 7 and 8 (July 23 to Aug 20, 2020) appeared more homogeneous in terms of flow rates than the initial weeks.

Table 8. Groundwater flow, Pore water Total and Soluble Reactive Phosphorus concentrations (mg/L), and Loads (mg/m^2 day) (mean, standard deviation, minimum and maximum) by sampling site at Oneida Lake during summer 2020.

Parameter	**Summary/Site**	**E1**	**N1**	**N2**	**N3**	**NW1**	**S1**	**S2**	**S3**	**S4**	**SW1**	**North Shore**	**South Shore**	**All (including the site E1)**
Flow L/m2 day	**n**	11	6	10	6	ND	9	11	6	14	9	27	49	87
	Mean	1.92	0.47	-0.12	0.76		-0.31	1.54	0.48	1.22	0.57	0.26	0.80	0.77
	SD	2.22	0.40	0.52	0.17		0.44	1.09	0.43	1.55	0.63	0.56	1.20	1.31
	Min	-0.52	0.16	-0.93	0.56		-0.88	0.37	-0.16	-0.09	-0.09	-0.93	-0.88	-0.93
	Max	5.12	1.20	0.51	0.97		0.40	4.16	0.97	4.61	1.41	1.20	4.61	5.12
TP mg/L	**Summary/Site**	**E1**	**N1**	**N2**	**N3**	**NW1**	**S1**	**S2**	**S3**	**S4**	**SW1**	**North Shore**	**South Shore**	**All (including the site E1)**
	n	11	6	10	6	5	9	11	6	14	9	27	49	87
	Mean	34.96	31.67	49.87	11.23	4.47	13.64	23.78	11.53	26.92	21.76	28.73	21.09	25.22
	SD	37.59	34.23	44.96	9.87	3.22	8.62	28.08	13.79	19.88	26.65	36.17	21.50	29.02
	Min	0.88	0.83	0.56	0.24	0.68	0.65	0.17	0.36	9.93	0.69	0.24	0.17	0.17
	Max	88.00	88.43	102.35	24.80	8.67	22.21	72.09	33.78	62.39	64.82	102.35	72.09	102.35
SRP mg/L	**Summary/Site**	**E1**	**N1**	**N2**	**N3**	**NW1**	**S1**	**S2**	**S3**	**S4**	**SW1**	**North Shore**	**South Shore**	**All (including the site E1)**
	n	11	6	10	6	5	9	11	6	14	9	27	49	87
	Mean	0.06	0.07	0.17	0.08	0.18	0.10	0.06	0.12	0.08	0.05	0.13	0.08	0.09
	SD	0.02	0.02	0.25	0.02	0.11	0.05	0.01	0.10	0.05	0.01	0.16	0.05	0.10

Parameter	Summary/Site	E1	N1	N2	N3	NW1	S1	S2	S3	S4	SW1	North Shore	South Shore	All (including the site E1)
	Min	0.04	0.04	0.03	0.06	0.04	0.02	0.02	0.06	0.01	0.04	0.03	0.01	0.01
	Max	0.11	0.11	0.85	0.10	0.29	0.16	0.07	0.30	0.20	0.07	0.85	0.30	0.85
SRP:TP Ratio	Summary/Site	E1	N1	N2	N3	NW1	S1	S2	S3	S4	SW1	North Shore	South Shore	All (including the site E1)
	n	11	6	10	6	5	9	11	6	14	9	27	49	87
	Mean	0.024	0.025	0.039	0.101	0.108	0.012	0.035	0.087	0.005	0.020	0.064	0.026	0.037
	SD	0.035	0.050	0.070	0.164	0.180	0.008	0.078	0.087	0.005	0.023	0.118	0.054	0.079
	Min	0.0005	0.0007	0.0004	0.0039	0.0201	0.0024	0.0007	0.0021	0.0002	0.0006	0.0004	0.0002	0.0002
	Max	0.083	0.115	0.227	0.401	0.430	0.025	0.259	0.200	0.019	0.057	0.430	0.259	0.430
TP mg/m^2 day	Summary/Site	E1	N1	N2	N3	NW1	S1	S2	S3	S4	SW1	North Shore	South Shore	All (including the site E1)
	n	11	6	10	6	5	9	11	6	14	9	27	49	87
	Mean	74.84	6.28	4.88	7.57	1.98	0.84	40.73	5.78	31.11	20.40	5.25	22.64	23.85
	SD	133.25	8.23	11.65	6.27	1.93	2.52	51.59	6.43	46.47	33.90	8.47	39.47	58.29
	Min	-0.06	0.00	-0.05	0.17	-0.01	-0.04	0.19	0.00	-0.01	0.00	-0.05	-0.04	-0.06
	Max	450.91	22.41	36.34	16.29	4.58	7.56	143.62	13.19	175.12	85.25	36.34	175.12	450.91
SRP mg/m^2 day	Summary/Site	E1	N1	N2	N3	NW1	S1	S2	S3	S4	SW1	North Shore	South Shore	All (including the site E1)

Parameter	Summary/Site	E1	N1	N2	N3	NW1	S1	S2	S3	S4	SW1	North Shore	South Shore	All (including the site E1)
	n	11	6	10	6	5	9	11	6	14	9	27	49	87
	Mean	0.086	0.035	-0.002	0.059	0.075	-0.003	0.092	0.078	0.117	0.029	0.03	0.07	0.06
	SD	0.12	0.04	0.02	0.02	0.07	0.01	0.07	0.11	0.24	0.03	0.05	0.14	0.12
	Min	-0.016	0.013	-0.035	0.037	-0.029	-0.016	0.008	-0.003	-0.002	-0.003	-0.03	-0.002	-0.002
	Max	0.35	0.11	0.03	0.08	0.15	0.018	0.257	0.294	0.915	0.078	0.15	0.91	0.91

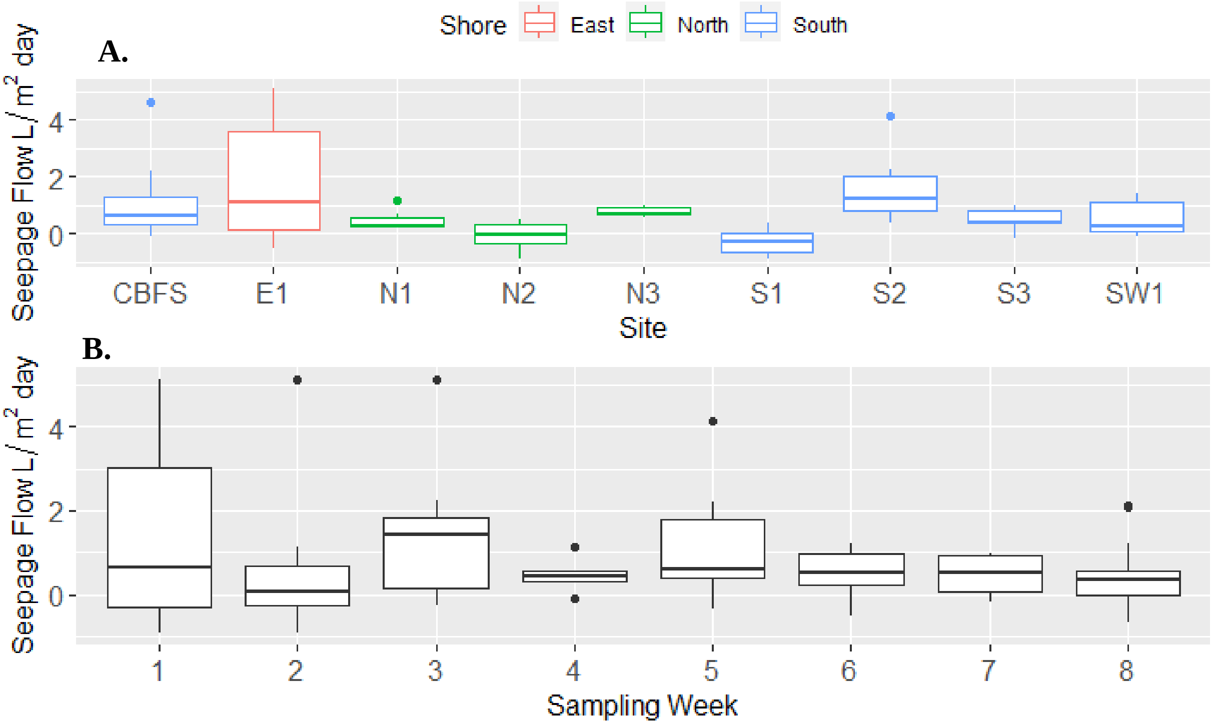

Figure 8. Boxplots showing groundwater flow rates into Oneida by sampling site (A) and sampling week (B) during summer 2020.

3.2 Phosphorus Concentrations

A total of 87 pore water samples were collected during summer 2020 across the ten sites distributed along the entire Oneida Lake shoreline. Mean pore TP concentration across sites was 25.2 mg/L (SD= 29.02 mg/L). Individual values range from 0.17 to 102 mg/L. Mean pore SRP concentrations were considerably lower than pore TP concentrations with a mean of 0.09 mg/L (SD=0.1 mg/L) across all sites (Table 8). Individual values range from 0.07 to 0.85 mg/L. TP concentrations were highly variable both across time and space (Figure 9 and Figure 10). Spatially, means for individual sites range between 4.5 mg/L (site NW1) and 49.8 mg/L (site N2). Similar to groundwater seepage flow rates, concentrations were highly different between sites during some weeks (June 29 to July 1), while on other weeks, such as week 8 (Aug 17 to 20), concentrations were more homogeneous around the lake. Interestingly, both the weekly mean TP and its variability among sites decreased dramatically with summer's progression (Figure 10). Conversely SRP concentrations were more homogeneous both temporally and spatially (Figure 9 and Figure 10). Means for individual sites range from 0.05 to 0.18 mg/L, and most sites exhibited low variability (SD below 0.05 mg/L), except for sites N2 and NW1 (Table 8). Temporally, the variability within weeks was also low, and no temporal longitudinal pattern was observed (Figure 10).

3.3 SRP:TP Ratio

The SRP:TP ratio is highly heterogeneous across sites and along the summer season at Oneida Lake shoreline. The average ratio per site ranges between 0.005 and 0.11, with individual values ranging from 0.0002 to 0.43. Temporally some sites show high variability across time such as N3, and S3 with SD of 0.16 and 0.087 respectively.

While others, such as N1 and S4 show low variability over time (SD=0.05 & 0.005, respectively) (Table 8). Overall, mean SRP:TP ratios seemed to increase as the season progressed, as did variability between sites. Average SRP proportion of TP and variability among sites were higher during weeks 7 and 8, compared to weeks 1 and 2, as well as variability between sites.

In terms of concentrations, site NW1 showed an interesting pattern depicting the lowest concentration and variability for TP, but the highest mean and variability for SRP. This site is located adjcent to a wetland and its sediment characteristics were different than the rest of the sites. Its sediments presented the higher concentration of organic matter (more than 1%, analysis not shown) across all sites, for example.

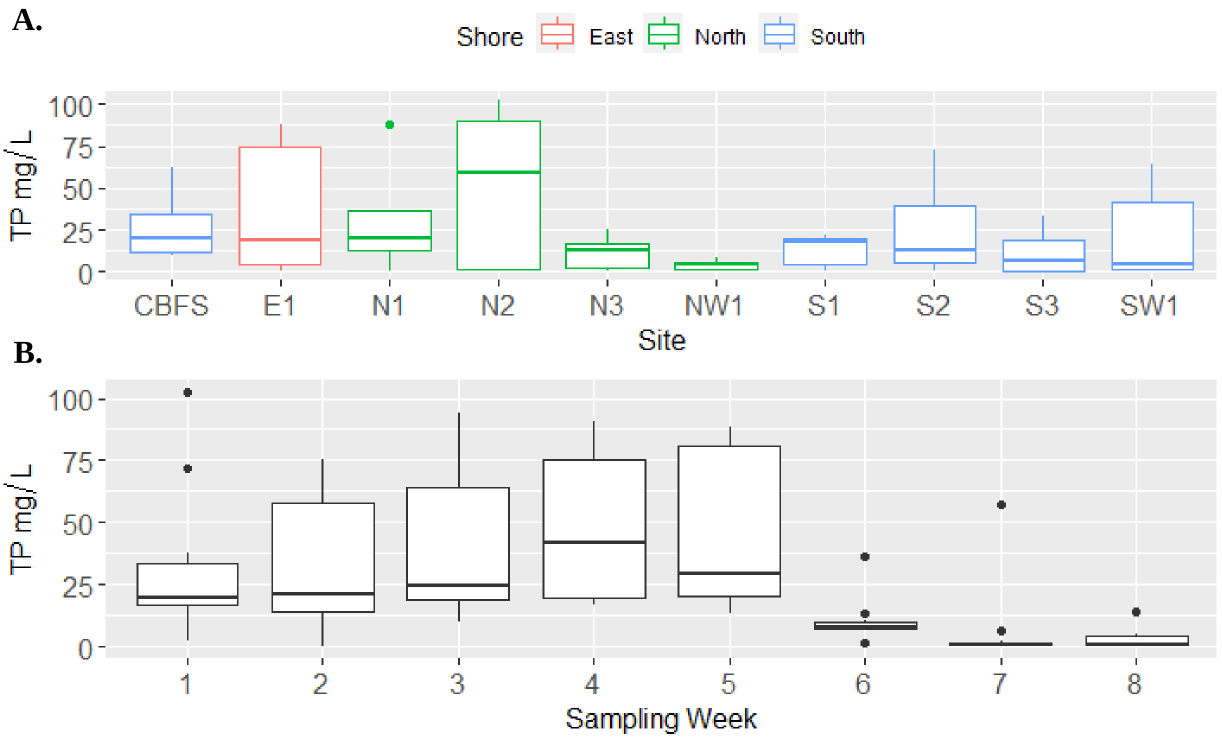

Figure 9. Boxplots show pore water TP concentrations in mg/L by sampling site (A) and sampling week (B).

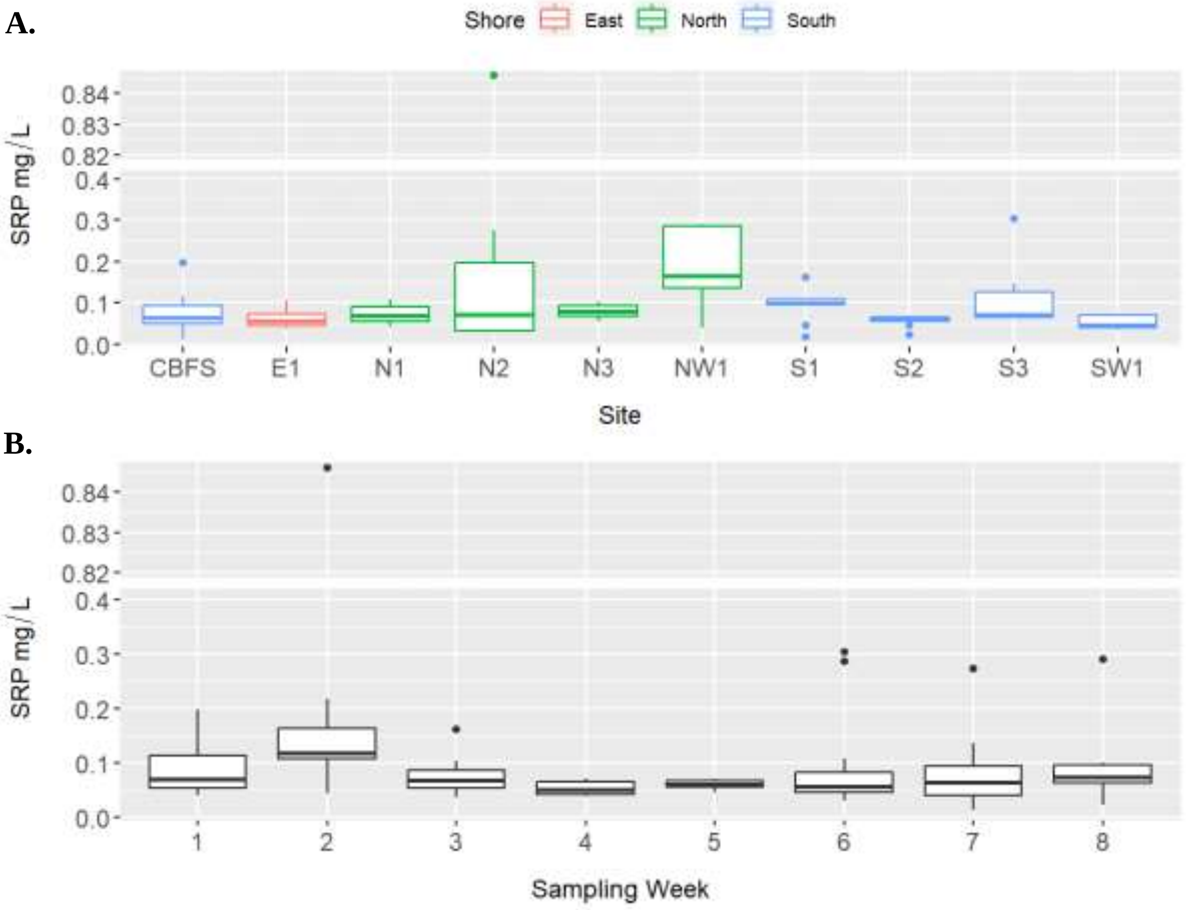

Figure 10. Boxplots show pore water SRP concentrations in mg/L by sampling site (A) and sampling week (B).

3.4 Lake vs. Pore P Concentrations

Pore water P concentrations were significantly higher than the lake water concentrations collected adjacent to the stations along both the North and South shores (Table 9) . Additionally, the concentrations of the lake waters along the shorelines were significantly higher than the P concentrations in the open waters at the center of the lake. Specifically, TP concentrations near the shoreline stations were up to two orders of magnitude higher than waters in the offshore area of the lake, while SRP concentrations were an order of magnitude higher in the littoral water compared to open waters (Table 9).

Table 9. Descriptive summary of Total Phosphorus (TP) and Soluble reactive Phosphorus (SRP) concentrations for pore water samples, and lake samples near shore and off shore.

Parameter	Category	Lake off-shore*	Lake on-shore	Pore
TP mg/L	**n**	13	79	87
	Mean	0.015	0.114	25.22
	SD	0.004	0.160	29.02
	Min	0.009	0.009	0.17
	Max	0.022	1.138	102.35
	Median	0.015	0.073	14.01
SRP mg/L	**n**	13	79	87
	Mean	0.001	0.026	0.092
	SD	0.002	0.016	0.101
	Min	0.001	0.004	0.013
	Max	0.006	0.097	0.846
	Median	0.001	0.026	0.067

3.6 Among Shore Comparison

Oneida Lake divides the watershed into two distinct halves, which have substantial differences in terms of hydrometeorological conditions, land cover and land use. We expected these differences to influence groundwater seepage flow rates and the P dynamics in Oneida Lake. However, the LMM analysis showed no statistically significant differences between the North and South shores for any of the parameters, including groundwater seepage flow rates, P concentrations and P loads ($p>0.05$, analysis not shown).

3.7 Precipitation and land use analysis

LMM were used to further investigate the relationship of groundwater seepage flow, and its P concentrations and loads, with precipitation patterns prior to the seepage measurements (previous 24 hrs., 48 hrs, and 72 hrs, total precipitation accumulated in the previous 48hrs and 72hrs, and number of days since the last rain event). Groundwater seepage flow rates were not significantly related to cumulative precipitation amount for any period up to the previous 72 hrs, however it did decrease significantly with the numbers of days since the last rain event ($p< 0.05$). Interestingly, TP concentrations exhibited a strong positive correlation with precipitation amount in the previous 24 hrs ($p<0.05$), while SRP concentrations were not influenced by precipitation or the number of days since the last rain event. SRP:TP ratio, exhibited a similar pattern to that of TP concentration, with significant correlation with the amount of precipitation in the previous 24 hrs ($p<0.001$) (Analysis not shown). LMM results for TP loads also showed a marginal influence of precipitation in the previous 24hs ($p=0.09$), while SRP loads were significantly correlated with numbers of days since last rain event ($p<0.05$). (Table 9,

Figure 11).

Table 10. Estimated fixed effects models for precipitation and land use analysis. P-values estimated via t-test using Satterthwaite approximations to degrees of freedom. Estimates are in natural logarithmic scale. Significant p-values are bolded.

Precipitation Analysis				
Response Variable	**Groundwater Flow (ln Flow (L/m^2 h)**			
Model	Flow ~ #DryDays + Date + (1|Site) + (1|NOAAStation)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	40.83	119	0.34	0.7343
Date	-0.001	0.002	-0.36	0.7181
Dry Days (#)	-0.07	0.03	-2.62	**0.01**
Response Variable	**TP concentration (ln TP (mg/L))**			
Model	TP ~ Precipitation + Date + (1|Site) + (1|NOAAStation)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	1819	229.7	7.91	<0.0001
Date	-0.041	0.005	-7.91	<0.001
Precipitation 24hs (mm)	0.67	0.26	2.51	**0.01**
Response Variable	**TP Load (ln TP (mg/m2 h))**			
Model	TP Load ~ Precipitation + Date + (1|Site) + (1|NOAAStation)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	1462	592	2.47	0.02
Date	-0.03	0.01	-2.47	0.02
Precipitation mm	1.19	0.69	1.74	*0.09*
Response Variable	**SRP Load (ln TP (mg/m2 h))**			
Model	SRP Load ~ #DryDays + Date + (1|Site) + (1|NOAAStation)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	74.35	139	0.53	0.59
Date	-0.001	0.003	-0.57	0.56
Dry Days (#)	-0.063	0.029	-2.13	**0.036**
Land use analysis				
Response Variable	**Groundwater Flow (ln Flow (L/m^2 h)**			
Model	Flow ~ LandUse + Date + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	44.67	123	0.36	0.71
Date	-0.001	0.002	-0.38	0.70
Residential	-0.75	0.26	-2.84	**0.01**
Mix	-0.42	0.21	-1.97	*0.08*
Response Variable	**SRP concentration (ln SRP (mg/L))**			
Model	SRP ~ LandUse + Date + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	317	135	2.33	0.02

Date	-0.007	0.003	-2.35	0.02
Residential	0.42	0.18	2.28	**0.02**
Mix	0.107	0.14	0.74	0.46
Response Variable	**TP Load (ln TP (mg/m2 h))**			
Model	TP Load ~ LandUse + Date + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	1775	542	3.27	0.001
Date	0.04	0.012	-3.27	0.001
Residential	-2.59	1.08	-2.4	**0.03**
Mix	-1.12	0.88	-1.28	0.23
Response Variable	**SRP Load (ln SRP (mg/m2 h))**			
Model	SRP Load ~ LandUse + Date + (1|Site)			
Predictors	*Estimates*	*SE*	*t*	*p*
(Intercept)	110	141	0.78	0.44
Date	-0.002	0.003	-0.82	0.42
Residential	-0.52	0.29	-1.77	0.107
Mix	-0.44	0.24	-1.84	0.09

The effect of land use adjacent to the shoreline on groundwater seepage flow and P dynamics was also assessed using LMM. Land use was shown to have a significant effect on all the assessed parameters, except for TP concentrations (Table 9). Groundwater seepage flow rates were significantly higher in sites located next to Forested areas compared to Residential sites ($p<0.05$). SRP concentrations were significantly higher in Residential sites, than in Forested areas ($p<0.05$). Interestingly, Forested sites were associated with higher TP loads than Residential sites ($p<0.05$), while SRP Loads exhibited no differences between Forested and Residential sites. Sites with land use classified as Mix (which have components of both Forest and Residential areas) were intermediate between residential and forest sites and not statistically different from either of those site classes (Table 9, Figure 12).

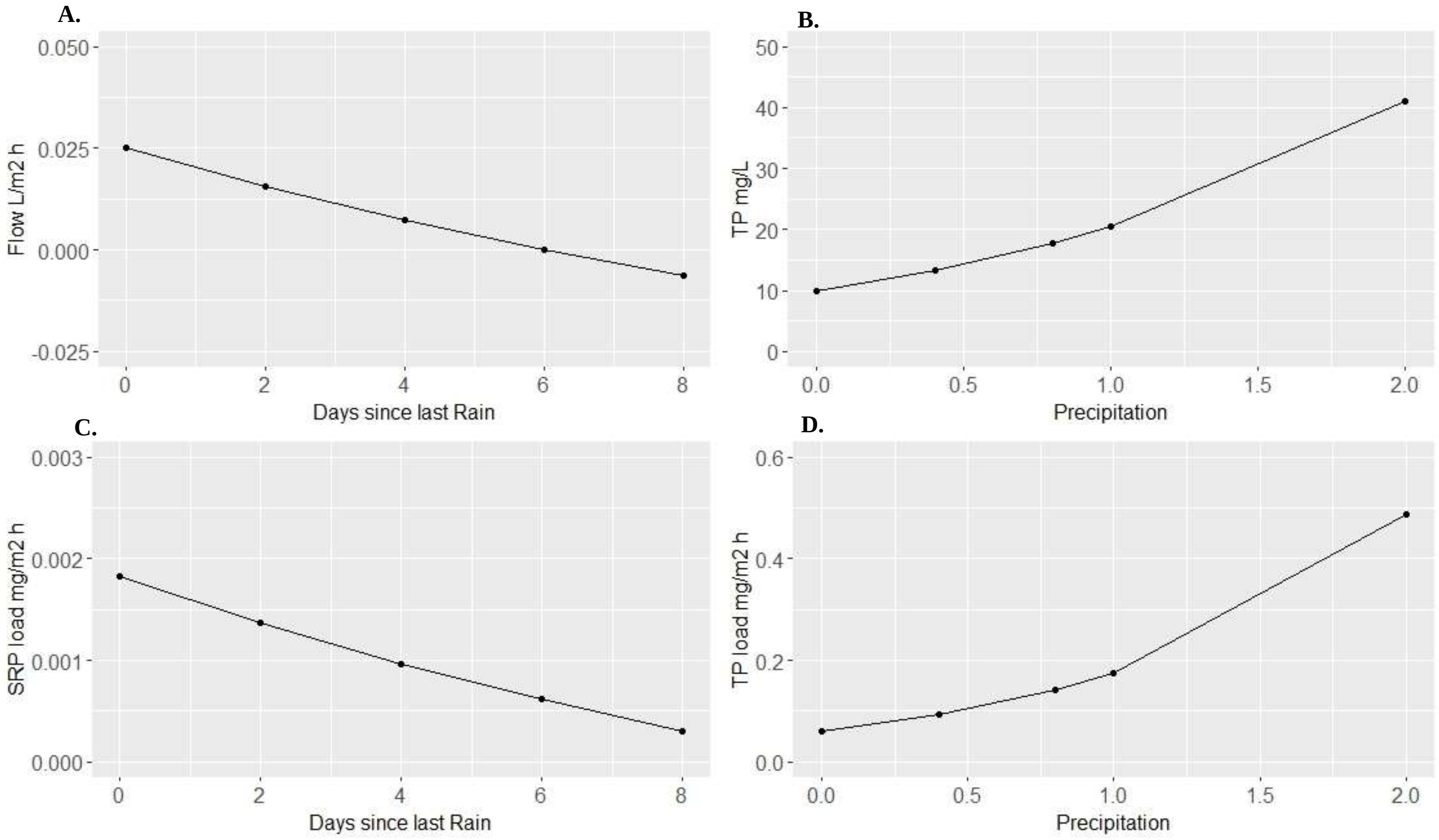

Figure 11. Flow, concentrations, and loads estimates in response to precipitation. A. Groundwater flow rate response to number of days since last rain event. B. TP concentrations response to precipitation (mm) in the previous 24 hrs. C. SRP load response to number of days since the last rain event. D. TP Load response precipitation (mm) in the previous 24 h

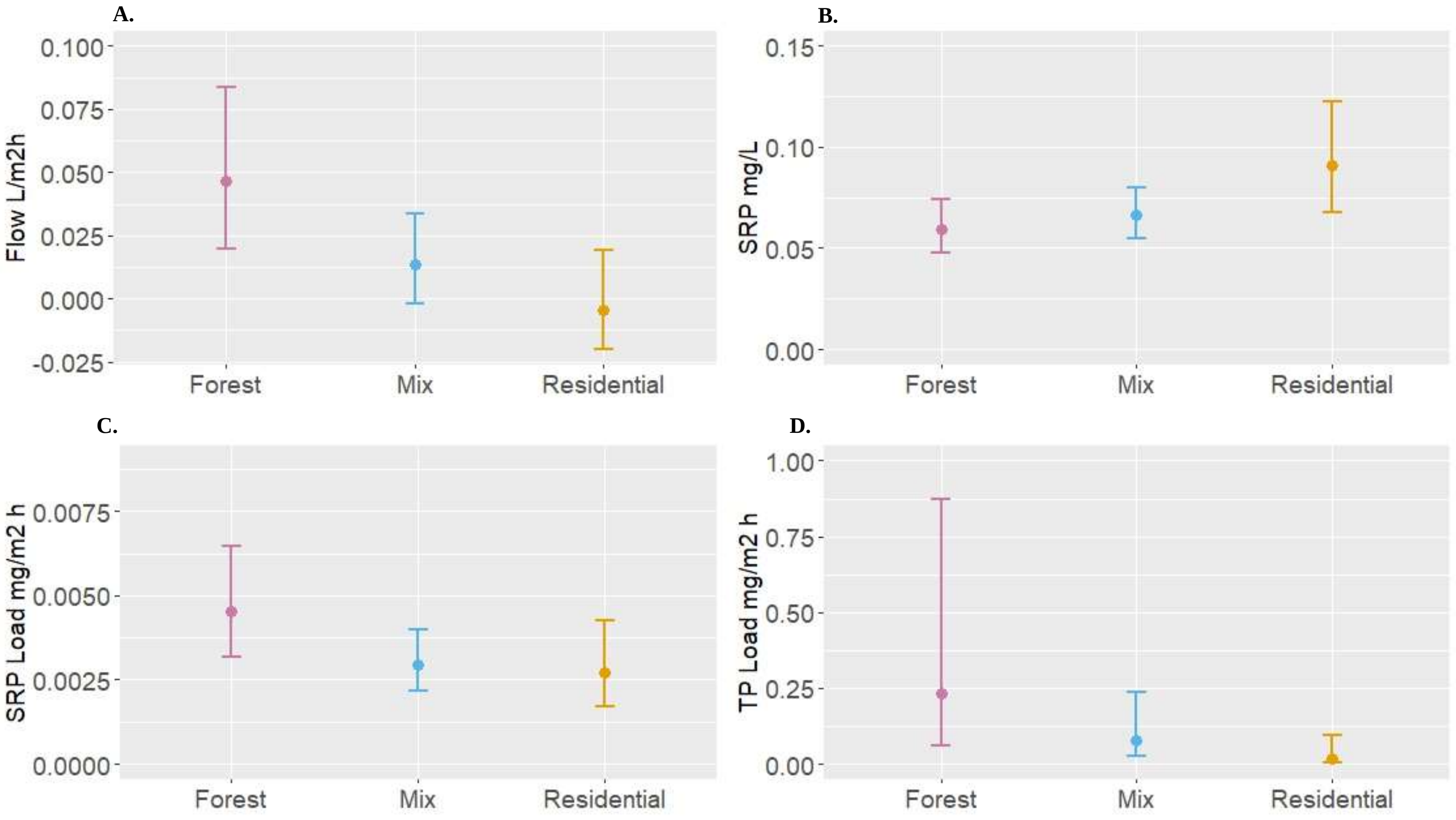

Figure 12. Flow, concentrations, and loads estimates and 95% CI for land use effect. Letters show significant differences between land uses categories ($p<0.05$). A. Land use effect on groundwater flow rates. B. Land use effect on SRP concentrations. C. Land use effect on TP loads. D. Land use effect on SRP loads.

4. Discussion

Results from this research showed groundwater seepage is a constant source of dissolved and likely bioavailable P to the entire shoreline of Oneida Lake. Weather and land use influence water and P fluxes at the sediment-water interface. The amount of precipitation in the previous 72 hrs. and the number of days since the last rain event were significantly correlated with flow rates and P fluxes. Shore adjacent land use was also a significant driver of water fluxes and P concentrations. Sites located next to forested areas exhibited higher water fluxes than sites located adjacent to areas with higher anthropogenic impact, likely due to the effect of increased imperviousness on infiltration rates and subsurface flows. In addition, sites located next to residential areas exhibited higher P concentrations, even though houses in the area of influence were connected to a sewer system, suggesting that septic systems may have a significant impact on P fluxes for years after decommissioning. SRP concentrations and loads were low but constant throughout the season, indicating that groundwater seepage is a constant source of readily available P to the littoral environment. TP concentrations and loads, on the other hand, showed high variability both temporally and spatially. The SRP proportion of TP was very low (less than 4% on average), which was unexpected and opens exciting questions about the type and origin of the main fraction of P entering the lake via groundwater. Given that PP was likely not captured by the instrument used to collect the samples, we hypothesized that dissolved organic P is the main fraction of P entering the lake via groundwater seepage. In the following, we discuss potential links between C and P cycles, and the role of groundwater seepage connecting aquatic and terrestrial processes. In addition, we venture a hypothesis about the possible impact of these P fractions on littoral primary productivity, as algae such as cyanobacteria, possess the mechanism to utilize organic P when inorganic P is scarce, which may confer them with an ecological advantage over other groups. The results of this study suggest that groundwater seepage P loadings may be more significant for lake ecology than traditionally thought, especially in the context of harmful algal blooms and nearshore benthification processes.

An overall mean of 0.81 L/m^2-day of subsurface flow was observed across nine sites located along the entire shoreline of Oneida Lake during summer 2020. The variability between sites was high (SD=1.34 L/m^2-day), with sites located along the south shore showing an overall mean of 0.8 L/m^2-day versus 0.3 L/m^2-day for sites located on the north shore, although flows at the two shores were not significantly different. Schneider et al. (2005) reported an overall average of 1.44 L/m^2 day for 29 sites located around the entire shoreline during summer 1999. They also observed a distinct spatial pattern between the shores, documenting higher flow rates in the north and east shore sites compared to the south shore sites. We found similar flow magnitudes in 2020 and also documented the highest average flow rates in the east shore site but found lower flows in the north shore than the south shore. In general, overall, the northern sub-watershed exhibited higher stream flows compared to the southern, and given the overall higher annual snow and rainfall, we had expected to observe higher subsurface flows rates at the north shore, as was reported by Schneider et al. (2005). However, during summer 2020 both mean and total precipitation in the southern sub-watershed was two times higher than the precipitation in the northern sub-watershed (NOAA, 2020), which is likely the underlying factor influencing this discrepancy. Hydrometeorological conditions, both immediate and past, are known for having a big influence on subsurface flow magnitude and timing (Winter 1983; Rosenberry and Hayashi 2013). In addition, these two studies were conducted 23 years apart and the factors influencing seepage flow dynamics could have changed.

The flow rates documented in this study are within the rates of studies elsewhere (Rosenberry et al. 2015), although not many studies have directly measured groundwater seepage rates on sites representing the entire shoreline of large lakes. Knights et al. (2017), reported higher rates (between 4 to 100 L/m^2-day) during one day in September 2015 at sites located on the Western shore of Lake Erie. Interestingly, in Chapter 1 we reported a more similar range to (Knights et al. 2017) for sites located at Oneida Lake's southern shore for summer 2018 (-1.6 to 23 L/m^2-day). These discrepancies are another example of the high variability that characterizes seepage flow phenomena, and the challenges for understanding its underlying mechanisms and influences.

We also observed changes in direction of seepage in most of the sites at some point during the summer season, however the duration and magnitude of those events were small, similar to what has been reported for many other lakes (Krabbenhoft and Webster 1995; Schuster et al. 2003). One exception of this pattern was observed at site S1 where most of the seepage rates were negative, meaning that groundwater was recharging instead of discharging into the lake. Schneider et al. (2005), reported consistent change in flow direction in sites located in the western shore, near the lake outlet. S1 (Figure 1) was not located near the outlet area of the lake, but in the area of influence of Cicero Swamp, which may be the reason underlying the observed flow pattern. Cicero Swamp is a 2100 ha Wetland, which likely has a strong influence on its sub-basin hydrology. Wetlands have been extensively recognized for their role in altering hydrological pathways (Rosenberry and Winter 1997; Ackerman et al. 2015), and groundwater seepage flows decreasing out of natural and constructed wetlands has been reported (Hunt et al. 1999; Ackerman et al. 2015). At Oneida Lake, seepage flow rates into the lake were significantly lower when wetlands dominate the shore-adjacent landscape compared to other land uses (Chapter 1).

The observed variability in flow rates both across space and time can be in part explained by regional precipitation patterns and shore-adjacent land uses. LMM exhibited a delay effect of precipitation on groundwater seepage rate as flow decreased significantly with number of days since last rain event. Interestingly, in Chapter 1 we reported a more immediate effect of precipitation on seepage flow rates, i.e., the amount of rain in the previous 24 hrs. was positively correlated with flow rates. The discrepancy could be related to the scale of the precipitation data, as the 2018 study focused on sites located at a small stretch of Oneida Lake south shore where rain was monitored daily within 150 m of sampling sites, while in this study the precipitation used for analysis was obtained from the closest NOAA station to each sampling site, which was located within 8 to 15 km away. Evidence suggests that the scale of the precipitation events could affect the length of the flow pathways activated, which will directly influence the time scale of the observed response on seepage flow. Schneider et al. (2005) demonstrated that peaks in groundwater seepage flow were correlated with local rain events at some sites and with regional rain events at others. Rosenberry et al. (2013) reported a variety of time scales, from minutes to days, in the timing and magnitude of groundwater seepage flow rate responses to rain events measured at different scales, in eight lakes located across the United States. It is likely that local precipitation has a rapid effect on shallow local pathways measured in the 2018 study, while regional precipitation has a delayed effect, as in this study, on shoreline flow rates as the pathways activated are longer and deeper (Cherkauer and Nader 1989; Schafran and Driscoll 1993).

LMM indicated that adjacent shore land use was a strong predictor of flow rates at Oneida Lake shoreline. This effect was already documented and reported by Lisboa et al. (unpublished) for a small portion of the lake, and here confirmed at the wide lake scale, in spite of the differences in the sampling design between the two studies. Sampling sites located next to forested areas exhibited significantly higher seepage flow rates compared to sites located adjacent to residential areas. Residential areas are known to decrease the infiltration rate and increase the overland flow rates (Bonneau et al. 2018; Voter and Loheide 2018), thus we expected to observe a decrease in subsurface flows next to residential areas compared to more natural areas like forest, where infiltration capacities are likely higher. Studies that have evaluated the impacts of land use change on infiltration rate and groundwater recharge are consistent with our results (Schiff and Benoit 2007; Siddik et al. 2022).

More novel than seepage flow patterns are the patterns and quantities observed for groundwater seepage P concentrations, and its resulting loads. SRP concentrations range from 0.07 to 0.85 mg/L with a relatively steady trend throughout the season.

SRP concentrations are comparable to those measured for summer 2018 at the southern shore (0.17 ± 0.3 mg/L, Chapter 1), although in that study SRP concentrations were more variable with individual values ranging up to 2.2 mg/L. In 2018, the high values were related to sites located adjacent to a residential area that was not connected into a sewer system and had active septic systems in place. In this study, several sites were located next to residential areas, however concentrations in those sites were lower (max= 0.9 mg/L) compared to the 2018 study, which is likely due to the connection of those houses into a sewer system. Regardless, LLM results for this study indicated significantly higher SRP concentrations in the sites located next to residential areas compared to other sites. There can be several reasons for these as residential areas can alter the flow and nutrients dynamics dramatically due to its associated anthropic impact (Bannerman et al. 1993; Voter and Loheide 2018). Sewer systems have a significant effect on decreasing P loading to adjacent water bodies in comparison with septic systems, however in many places where septics were in place for a long period of time, there could be a lag time in nutrients loading response after septic decommission. (Schellenger and Hellweger 2019) used modelling to understand P loading from onsite wastewater systems (OWS) in a small watershed in Massachusetts and conclude that the loading can persist and even increase for several hundred years after the elimination of all OWS from the watershed, due to groundwater travel time lag and possible temporary incorporation of P into the sediment bed. Moreover, activities like lawn fertilization could have a significant effect on phosphorus loadings (Lehman et al. 2011), especially at lakes shorelines where subsurface fluxes move rapidly into the lake. SRP concentrations did not respond to precipitation quantity or time elapsing from the last rain event.

Combining flow rates and concentrations, SRP loads into the lakeshore ranged from -0.03 to 0.91 mg/m^2- day, which is comparable to the values reported for the south shore in 2018 (0 to 2.4 mg/m^2-day), and within the range for SRP loads reported elsewhere (a more detailed discussion about SRP loads from groundwater seepage can be found in Chapter 1). Similar to concentration patterns, SRP loads remained relatively constant both temporally and spatially, which suggests that groundwater seepage is a constant and steady source of dissolved and readily available P for the littoral environment along the entire shoreline of Oneida Lake. Land use patterns played a significant role in both flow rates and SRP loading. Groundwater seepage flows were significantly higher at Forested sites as compared to Residential, whereas SRP concentrations followed the opposite pattern with significantly higher values at residential sites. As a result, SRP loads exhibited no difference between forest and residential sites, as the effects of flows and concentrations canceled each other out. SRP loads did correlate with the number of days since the last rain event, which is likely due to the effect of precipitation on seepage flow, as SRP concentrations showed no correlation with precipitation.

In contrast to SRP, TP concentrations and loads were much higher and widely variable across time and space. TP concentrations ranged from 0.17 to a maximum of 102 mg/L (x=25.2, SD=29 mg/L), which almost doubled the maximum TP concentration reported in the 2018 study for the south shore. There are no other studies which have measured TP concentrations in groundwater seepage flowing directly into lake shorelines. Studies tend to analyze dissolved P fractions, mainly phosphate, as this is considered the dominant P species in groundwater and also the most relevant from a biological perspective. Total Phosphorus (TP) includes a particulate fraction (PP), that is largely unavailable for immediate uptake by biota (Prestigiacomo et al. 2016), and a dissolved fraction which in general is reported as Total Dissolved P (TDP). TDP includes inorganic P, generally measured as phosphate and reported in the literature as SRP that is immediately bioavailable (Young et al. 1982; Auer et al. 1998), and an organic fraction also known as Soluble Unreactive or unavailable P (SUP). Considering the ratio of SRP to TP indicated that SRP concentrations were in general a small proportion of TP (with averages per sites below 10%) (Table 1), leaving organic dissolved P as the likely predominant fraction entering the lake via groundwater seepage. This is an unexpected result of our study that could have great implications for P and primary productivity dynamics in lake shorelines.

Furthermore, the organic fraction of TDP may be more available for organism consumption than traditionally thought, especially for algae and bacteria. Prestigiacomo et al. (2016), performed bioavailability algae assays on slurries collected from four tributaries to a temperate lake in the northeastern US, and showed that the bioavailable fraction of SUP ranged between 62 to 84% across the four streams. Moreover, studies about cyanobacteria physiology indicate the existence of several physiological strategies to take advantage of Dissolved Organic Phosphorus (DOP), including extracellular enzymes (Xiao et al. 2022). So far, there are three major pathways recognized in the literature to convert organic P into inorganic phosphate for its utilization, including 5’-nucleotidase, C-P pathway, and phosphatase

(Xie et al. 2021; Xiao et al. 2022). Phosphatase is the most studied pathway given its wide occurrence in most phytoplankton species. In addition, its presence has been positively correlated with low concentrations of dissolved inorganic P (Rengefors et al. 2003; Wan et al. 2022), which is indeed the case many times during cyanobacterial blooms (Sommer et al. 2012). Although little is known about whether phosphatase mediated mineralization of DOP meets P demand in cyanobacteria species under inorganic P depletion conditions, it may be a mechanism that conferred ecological advantages to cyanobacteria over other groups of phytoplankton when inorganic P is scarce. Laboratory experiments showed that some cyanobacteria species were able to sustain growth rates solely on organic P sources (Lin et al. 2018; Dong et al. 2019). Xie et al. (2021), for instance, explored the physiological behavior of *Microcystis aureginosa*, one of the leading cyanobacteria species in toxic algal blooms, and showed its ability to utilize a variety of P sources including many forms of organophosphates. Their results suggest that the structure and functions of phytoplankton community may rely not only on P concentrations but also on its composition, highlighting the potential role and importance of other P fractions for lake ecology in addition to SRP.

Evaluation of the relationships between P patterns and land use and precipitation provides some additional insights into the potential biogeochemical processes of TP in lakes. Precipitation in the previous 72 hrs was correlated with increasing TP concentrations, suggesting that the rain events are leaching the TP out of the watershed into the lakes, and a result that supports the idea that TP in our samples is mainly present in dissolved form. Moreover, adjacent shore land use did not show an effect on TP concentrations, which raises the question of the source of this phosphorus. TP may not be directly related to anthropogenic activity, unlike what is generally suggested for SRP. One possible explanation underlying the high concentrations of organic P, could be related to the reported increases of dissolved organic matter (DOM) loading that many lakes in North America and Europe have experienced in recent years (Monteith et al. 2007; Clark et al. 2010). This phenomenon, also known as “browning,” has a significant impact on carbon cycling and affects a range of physical and ecological attributes and processes within lakes. However, studies suggest that it may influence the loading of other nutrients to lakes, as DOC can either contain or complex with N and P (Kortelainen 1993; Dillon and Molot 2005). Studies of leachates from different terrestrial materials showed that DOM contained different amounts of N and P, and in some cases, it can greatly impact N and P fluxes to lakes (Wallace et al. 2008; Berggren et al. 2015). Corman et al. (2018) studied the relationship between DOC loadings, and P & N loadings into seepage lakes in northern Wisconsin and reported significant correlations between DOC, TN, and TP; concluding that nutrients associated with DOM may substantially influence N and P concentrations in lakes. Increasing loading in DOC has been documented in lakes in the northeastern US even where it is not always associated with a change in color (Lapierre et al. 2021), especially in systems with short residence times, like Oneida Lake (average residence time is less than a year and varies seasonally (Mills et al. 1978; Schneider et al. 2016). More research is urgently needed to understand the links between C and P cycles, and the potential role of groundwater seepage connecting terrestrial with aquatic biogeochemical processes.

Porewater P concentrations were significantly higher than those of the adjacent lake water samples (TP: 0.09 to 0.45 mg/L, SRP: 0.05 to 0.1 mg/L). Furthermore, concentrations of P in shoreline surface waters were significantly higher than off-shore open lake concentrations throughout summer 2020. This spatial gradient in P concentrations was previously reported along a small portion of Oneida Lake in the southern shore (Chapter 1), but this study documents that P enrichment is a widespread condition along the entire shoreline of Oneida Lake. As has been previously discussed in Chapter 1, the groundwater-surface water gradients in P concentrations have been reported in many temperate lakes elsewhere and the underlying mechanisms are still under investigation and discussion. Extensive research was conducted in Lake Ontario (Makarewicz and Howell 2012), and other Great Lakes, with intriguing results and postulations about the various role of different factors such as stream discharge, hydrodynamics, and temperature entrapment. Our findings indicate that groundwater seepage is a significant contributor of P to lakes and this source of P is widely overlooked. It identifies special importance for the littoral environment as groundwater seepage interacts with lakes mainly in the shoreline where shallow pathways directly discharge into lakes. Moreover, its relevance increases in the context of shore benthification processes that have been documented in many temperate lakes after dreissenid mussels' invasions (Zhu et al. 2006; Higgins and Vander Zanden 2010; Mayer et al. 2014).

Finally, TP loads around the entire Oneida shoreline exhibited high and widely ranging values (mean=23.85 mg/ m2-day; range = -0.06 to 450 mg/m2-day), which were up to two orders of magnitude higher than the values documented at the south shore in the 2018 study (Chapter 1). These numbers are comparable to TP loads reported for internal loading (i.e: Nürnberg et al. 2013; Orihel et al. 2017) and this loading is occurring at the sediment-water interface throughout the entire lake shoreline. Indeed, it is possible that a portion of groundwater loading may have been included in internal loading estimations for P budgets, as its differentiation is empirically very challenging, and studies keep excluding one from the other, albeit acknowledging the potential relevance of both (i.e: Nürnberg et al. 2013; Orihel et al. 2017). From a management perspective it is crucial to differentiate between the two, as internal loading is related to legacy P, while groundwater seepage is an external P source. Spatial heterogeneity has been previously recognized as one of the major challenges related to the study of chemicals transported by groundwater (Lewandowski et al. 2015, Hupfer et al. 2018). Results from this study exemplify this variability and highlight the need for novel approaches that can better address spatial and temporal heterogeneity. In addition, these results highlight the need for further investigation as groundwater seepage loadings may have significant implications for lake nutrient dynamics and trophic conditions. In our study, TP is dominated by the soluble fraction, with likely little to no PP, which means that most of the P entering the lake via groundwater seepage may be available for algae consumption. As a result, even if groundwater seepage loading represents a small fraction of the total P loading to the lake, it may be highly significant for the trophic status of the lake shore, considering its high relative availability. LMM showed that TP loads were significantly higher at forested areas compared to residential sites, however this result seems to be driven by seepage flow differences, as TP concentrations were not influenced by shore adjacent land use. Similarly, precipitation in the previous 24 hrs. was marginally correlated with TP loads but given that precipitation showed no effect on TP concentrations, it is likely that the effect of flow rates is underlying the effect of precipitation on TP Loads.

5. Conclusion

The results of this research suggest that the role of groundwater seepage on lake's P dynamic may be more significant than traditionally thought. Our findings indicate that it is important to incorporate groundwater P in phosphorus budgets and the discussion of algal bloom drivers, a current water quality issue. In this study we identify several knowledge gaps that may help guide a deeper understanding of the multiple causes underlying current challenges in aquatic ecosystem and its water quality. In addition, our results suggest that there may be strong links between C and P cycling that deserve additional research. Groundwater seepage is a fundamental link between terrestrial and aquatic biogeochemical cycles and needs to be further investigated, including in the context of evaluating effects of management actions to reduce P loading to lakes.

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CHAPTER 3

BEYOND THE SURFACE: COMPARISON OF PHOSPHORUS CONTRIBUTIONS FROM GROUNDWATER AND SURFACE TRIBUTARIES TO ONEIDA LAKE DURING THE SUMMER

1. Introduction

Despite huge efforts to reduce nutrient inputs into lake systems, excess nutrient loading and its resulting consequences for eutrophication are still one of the major threats for aquatic systems worldwide (Conley et al. 2009). Phosphorus (P) as the limiting nutrient in freshwater systems often controls the trophic state of temperate lakes (Schindler 1977; Sondergaard and Jeppesen 2007; Schindler and Hecky 2009). Point sources of phosphorus, particularly those originating from sewage discharges, have been extensively addressed and significantly reduced over time, due to effective regulatory measures and wastewater treatment practices (Orderud and Vogt 2013). Recently, considerable research and management efforts have shifted the focus to identifying and controlling diffuse, non-point sources of pollution. Various land uses have been evaluated for their impact on water quality in rivers and lakes. Agricultural activities, and specifically chronic fertilizer and manure applications interacting with exposed and eroding soils, make this land use a primary source and pathway for P transport into water bodies (Heathwaite et al. 2000; Burt et al. 2008). Using a range of approaches from edge-of-field measurements or monitoring stream concentrations and flows to watershed modeling, researchers have evaluated the factors that control phosphorus loading from agricultural and other land uses into tributary streams (Lisboa et al. 2020, Makarewicz, 2009, Kleinman et al. 2015). The general consensus is that storm events, and the associated runoff, increasingly are dominating the hydrologic flowpaths in most watersheds, and stream phosphorus loads are primarily controlled by the quantity of sediment-bound P transported during storms. Although water containing dissolved P continues flowing in streams between storm events, as baseflow sourcing from groundwater, the levels are significantly lower and have generally been considered negligible.

The role of groundwater transport is emerging as a new, previously under-appreciated source of phosphorus to lakes. Lakes vary in the degree of connection between their surface waters and watershed aquifers. The regional hydrologic flow system, including the pattern of surface water drainage and subsurface groundwater movement, working in conjunction with underlying geology and climatic conditions, determines the relative proportions of water inputs from different sources into each lake (Webster et al. 1996; Kratz et al. 1997). The most comprehensive review of 110 lake evaluations of the groundwater component of a lake hydrologic budget determined that the median percentage was 31% but ranged from 0.01 to 94.4% (Rosenberry et al. 2015). This data set included lakes ranging from 2 ha to 440,000 ha in surface area, although 75% were less than 300 ha in size. There was no relationship between lake surface area and percentage contribution of groundwater to the budget except at the very largest scale, although it was noted that the highest groundwater contributions, i.e., greater than 70%, only occurred in lakes less than 40 ha in surface area. Despite these high contributions, the role of groundwater is generally not evaluated or assumed to be inconsequential. The challenges in quantifying groundwater seepage and its nutrient concentrations are the primary reasons identified by Rosenberry et al. (2015) underlying the disregard of groundwater component in lake budgets. Instead of actual measurements, groundwater fluxes are therefore estimated by solving for residuals in the hydrologic balance equations (Sutula et al. 2001; Ommen et al. 2012). But considering only the net difference between groundwater input and outputs can be misleading and conceal the actual flux processes within the lakes. Moreover, given the small fraction that net groundwater in general represents from a water budget perspective, its nutrient contribution also tends to be underestimated (Lewandowski et al. 2015a).

This situation is even more pronounced for P budgets specifically. Traditionally, natural background concentrations of dissolved P are considered low, and dissolved P assumed to be readily absorbed to soil particles in the vadose zone (Edwards and Withers 2007). However, studies have demonstrated that dissolved P concentrations in groundwater can increase above natural background conditions, and even reach thresholds of ecological significance (Kilroy and Coxon 2005; Griffioen 2006; Holman et al. 2010a; Kidmose et al. 2013). Only a handful of studies have incorporated measurements of groundwater P contributions to an entire lake's nutrient budget and reported the relative contributions of groundwater versus external surface water sources of P to the lake. The majority of this research focused on small groundwater-fed lakes (less than 5 km^2 surface area) (i.e., Shaw et al. 1990; Krabbenhoft and Webster 1995; Ommen et al. 2012; Meinikmann et al. 2015). Comprehensive evaluations of larger lakes are still scarce, although Loeb and Goldman (1979) documented that groundwater represents a substantial proportion of the phosphorus budget in 497 km^2 Lake Tahoe, (Loeb and Goldman 1979). Even when groundwater discharge represents a relatively small contribution to the total lake hydrologic budget, it can significantly influence the state of the lake if the discharging groundwater contains high P concentrations (Shaw et al. 1990; Meinikmann et al. 2015; Nisbeth et al. 2019). These high loadings have been shown to be ecologically significant when they are concentrated within the littoral environment (Roy and Malenica 2013; Knights et al. 2017).

We hypothesize that the relative importance of groundwater contributions may vary temporally, as well as spatially within a given lake. Sebestyen and Schneider (2001, 2004) documented that groundwater seepage decreased and then reversed direction, with lake water recharging groundwater in a small Adirondack Lake from April through September. During summer dry periods, when streams are dominated by baseflow, groundwater P inputs could help to fuel production in the phytoplankton communities when conditions for primary productivity are at their optimum (Mainstone and Parr 2002). A similar rationale has been proposed for the southern Everglades, where groundwater inputs of P increase in importance during the dry season (Sutula et al. 2001). Within marine ecosystems, nutrient inputs from groundwater are considered equal to or greater than riverine inputs (Taniguchi et al. 2002; Burnett et al. 2003) and Lewandowski et al. (2015b; a) propose that eventually scientists will realize that the role of groundwater in freshwater systems is comparably significant.

Our overarching goal was to evaluate the relative contributions of external sources of P to Oneida Lake, by comparing stream loading to groundwater seepage loading during the summer 2020. Summer is the season where primary productivity increases significantly in temperate climates, and the impact of excessive nutrient loading, such as harmful algal blooms and oxygen depletion, most frequently occur. Moreover, summer is also the season when stream discharges are the lowest, which have led scientists to investigate internal loading as one of the possible drivers underlying summer trophic dynamics in many systems in temperate areas (Nürnberg 2009; Orihel et al. 2017). Here, we explored the hypothesis that groundwater seepage is a significant player in the nutrient dynamic development in temperate lakes during summer months, especially to the littoral environment, where groundwater seepage discharge tends to be the highest (Chapter 1 and Chapter 2). Oneida lake is a mesotrophic, shallow, large lake (>100 km^2) with strong hydrological connections to its watershed trough both surface tributaries and subsurface groundwater flow (Schneider et al. 2016). The watershed is large compared to the lake itself (lake to watershed surface area ratio is 6%), and the large annual volume of precipitation and the lake's shallow bathymetry results in a large amount of water flowing through the lake annually. In addition, previous research has demonstrated that subsurface groundwater flow occurs along the entire shoreline of the lake (Schneider et al. 2005), and my previous research has documented significant concentrations of P in groundwater seepage entering Oneida Lake (Chapter 1 and Chapter 2).

The specific objectives were:

1. to quantify surface water loadings of Total Phosphorus (TP) and Soluble Reactive Phosphorus (SRP) in the five main tributaries draining into Oneida Lake,

2. over the same time period to quantify groundwater discharge rates and loadings of TP and SRP at 10 representative sites distributed around the shoreline of Oneida Lake,

3. to compare the average loadings (in kg/day) between the groundwater and tributaries, by week for each of nine weeks during summer months

4. to compare the loadings in streams with groundwater loadings during baseflow conditions only.

2. Methods

2.1 Study Site

This study was conducted at Oneida Lake (43°10′N, 75°52′W), located in central New York, 18 km east of the city of Syracuse. The lake is part of the Oswego River Basin which is part of the greater Lake Ontario basin. The lake is of glacial origin, with a consolidated sedimentary bedrock underlying the whole basin (Kantrowitz 1970). The lake runs from east to west dividing its 3579 km^2 watershed into similar sized halves. The northern and southern sub-watershed are of similar geological origin, both presenting geological layers with high hydraulic conductivity, but prominent differences in their climatological and land cover patterns. The underlying geology of the southern half consists of successive bedrock layers of limestone, shale, dolomite, and sandstone overlain by unconsolidated glacial till. The northern half is dominated by a 76 m thick base layer of sandstone shale, which intercepts and underlies a portion of Oneida Lake, and is overlain successively by layers of dolomite, middle shale, limestone and upper shale (Kantrowitz, 1970). The combined sedimentary bedrock and glacial deposits result in a high ability to store and transmit water creating an extensive system of aquifers that underly large portions of the watershed. This setting, combined with a steep topographic relief over hundred meters of elevation towards

Oneida Lake, facilitates the superficial and groundwater flow from both sub-basins into Oneida Lake (Schneider et al. 2016).

The watershed is characterized by a continental climate with warm, dry summers and cold, snowy winters. The mean annual precipitation is 965 mm in the southern basin and 1300-1500 mm in the northern basin (NOAA, 2020). Much of the precipitation originates as snowfall in the winter and is stored as snowpack. The northern sub-basin received 3-5 m of snowfall annually, which is the highest reported snowfall east of the Rocky Mountains, due to the basin position east and down-wind of Lake Ontario. The southern basin, on the other hand, receives only one to two meters of annual snowfall (Schneider et al. 2016). Approximately 56 percent of the precipitation that falls in the watershed reaches the lake through surface inflow (Mills et al. 1978). The rest is redistributed through evaporation, transpiration by trees and plants, and groundwater recharge. There are seven major tributaries into the lake, four draining the northern subwatershed (Big Bay Creek, Scriba Creek, Fish Creek, and Wood Creek); and three draining the southern subwatershed (Chittenango Creek, Canaseraga Creek together with Cowaselon Creek, and Oneida Creek). Fish Creek accounts for almost 50 percent of the lake’s total inflow and drains the majority of the northern sub-watershed; followed by Chittenango and Oneida Creeks which together account for 25 percent of the inflow, draining a significant portion of the southern watershed (Figure 13). Water flows out of Oneida Lake into Oneida River, which is the only surface outflow from the lake, located at the western edge and ultimately discharging into Lake Ontario.

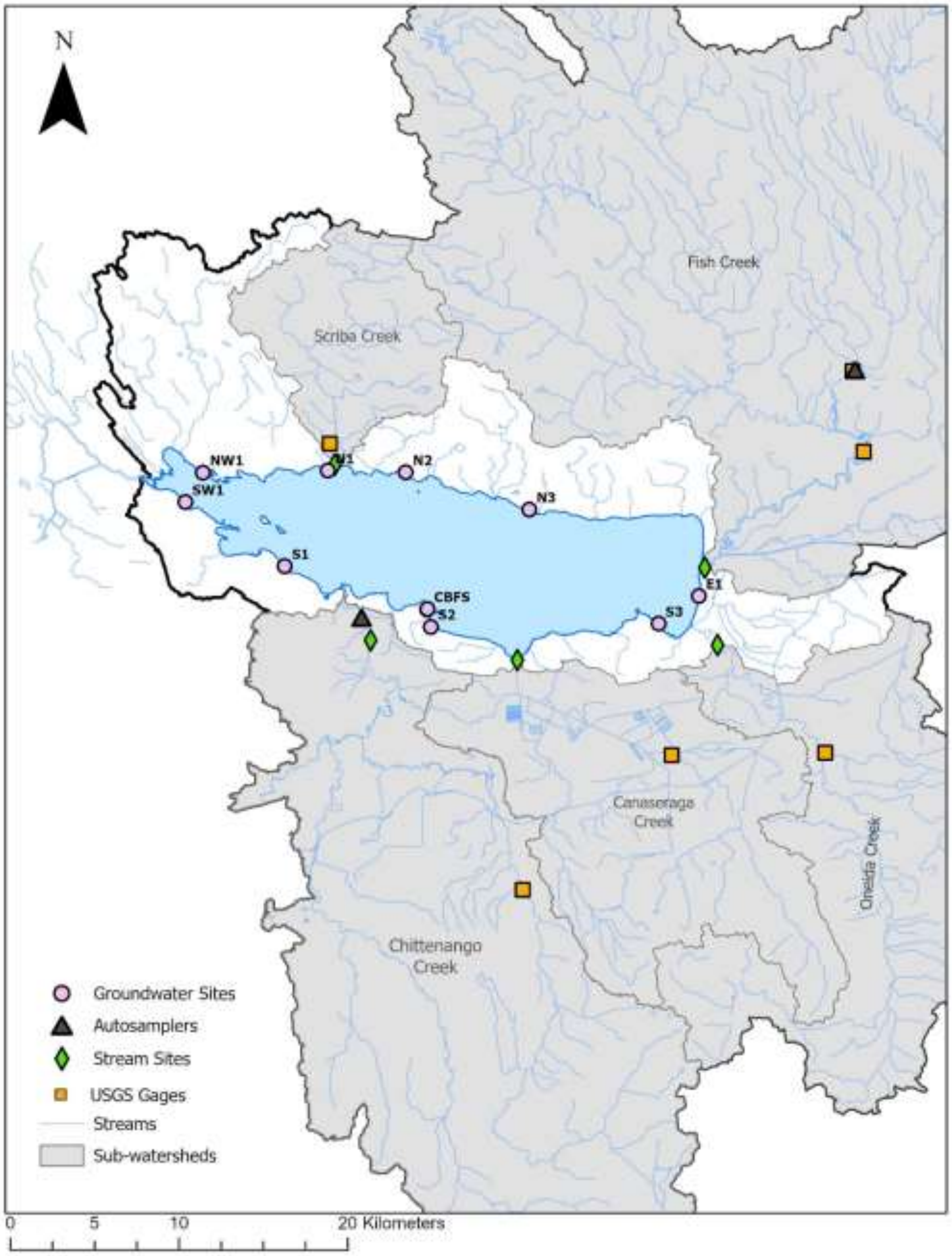


Figure 13. Map displaying Oneida Lake, its main surface tributaries, and its corresponding sub-watersheds. Points indicated sites for groundwater sampling, diamonds sites for stream grab sampling, and triangles sites where autosamplers for high flow events sampling were deployed.

In terms of land use there is a big difference between the southern and northern sub-watersheds as a result of the strong meteorological differences. Soils in the southern half are very fertile resulting in a historical land cover dominated by agriculture. Currently, the land use in the southern basin is almost evenly distributed among agriculture, suburban developments around the city of Syracuse, and forest. Conversely, as a result of the long snowy winters and acidic soils, the northern half is dominated by forest with numerous wetlands, and minimal agriculture (Schneider et al. 2016). Although surface inflow from the northern watershed represents most of the total water volume entering the lake, the majority of the nutrient inputs are coming from tributaries that drain the farmlands of the southern watershed. The lake's shoreline extends for approximately 88 km, and is mainly used for recreational activities, and is characterized by both permanent and seasonal housing.

2.2 Sampling design, collection, and analysis

In order to estimate groundwater seepage P inputs, we selected ten sites distributed along the entire shoreline of Oneida Lake to install sampling stations for groundwater seepage flow and its P concentrations during summer 2020 (Figure 13). Sites were selected for their accessibility from land or by boat and were chosen to get representation of the whole lake shoreline. This resulted in five sites located along the southern shore, four along the northern shore, and one site on the eastern shore in between the inlets of two main tributaries. Samples were taken once a week for 10 weeks during summer 2020 (June to August). Sampling stations consisted of a seepage meter to estimate groundwater seepage flow rates and pore water samples installed ~40cm into the lakebed sediments to collect pore water samples for Total Phosphorus

(TP) and Soluble Reactive Phosphorus (SRP) analyses. Please refer to Chapter 1 for further details on sampling stations setting and samples collection, processing, and laboratory analyses. Due to accessibility issues and personnel availability restrictions associated with the COVID-19 pandemic, not every site was sampled during the same weeks, which resulted in a heterogeneous number of samples at each site (Table 11).

Table 11. Streams and groundwater (GW) pairing of data for loads comparison analysis.

Sampling Week/Event	Data by Shore	Streams Data			GW Data		
		Date	Sampling Method	Rivers	Input Date	Output Date	GW Sites
1	Both	6/17/2020	Grab	All	6/18/2020	6/27/2020	CBFS, S2,N2, S1,NW1
2	Both	6/27/2020	Grab & Auto	All	6/26/2020	7/1/2020	CBFS,S2,N2,S1,N3,NW1
3	Both	6/30/2020	Grab & Auto	All	6/29/2020	7/9/2020	CBFS,S2,N2,S1,N3,N1,SW1
4	South	7/11/2020	Auto	Fish/CH	7/8/2020	7/15/2020	CBFS,S2,E1,SW1
5	Both	7/16/2020	Grab & Auto	All	7/9/2020	7/24/2020	CBFS,S2,E1,N2,SW1,S1,N3,N1
6	South	7/23/2020	Auto	CH	7/22/2020	7/24/2020	CBFS,S1,SW1
7	South	7/29/2020	Grab	All	7/23/3030	8/7/2020	E1,SW1,S1,S3,NW1
8	NA	8/4/2020	Auto	Fish	This data and week are excluded from the analysis, because there is no GW sample to paired with.		
9	Both	8/8/2020	Grab	All	8/6/2020	8/18/2020	CBFS,S2,E1,N2,SW1,S3,NW1,N3
10	Both	8/21/2020	Grab	All	8/17/2022	8/21/2020	CBFS, S2, N2, SW1, S3, S1,NW1, N1

Note: GW refers to groundwater, and auto to autosampler.

Water samples from the five main surface tributaries to the lake (Fish Creek, Scriba Creek, Oneida Creek, Canaseraga Creek, and Chittenango Creek) were collected once a week during the same 10 weeks that groundwater samples were collected (Figure 13). Samples were analyzed for TP and SRP content following the same protocol that was followed for groundwater samples (Chapter 1). In addition to the weekly grab samples that were regularly collected close to the inlet of each tributary to the lake, several storm events were sampled during the summer, using both grab samples and automated samplers. Two ISCO-TM auto-samplers were deployed to capture representative, complete storms events over the summer, one in a northern creek (Fish Creek) and one in a southern creek (Chittenango Creek) (Figure 13). A water level actuator was used to trigger the auto-sampler every time the stream level increased 0.5 cm above baseflow level and was manually adjusted every week to allow for seasonal fluctuations in the overall stream water level. Auto-samplers were programmed to fill a 1L bottle by collecting four 250 ml samples with each sample taken 15-min apart. Each auto-sampler was equipped with 12 bottles that were sequentially over a 12-hour period. The auto-sampler bottles were pre-acidified with 0.5 ml concentrated sulfuric acid to guarantee sample preservation within a week of the storm. The samples collected were analyzed individually for phosphorus concentrations which were incorporated into the final database for analysis. Streams loads were estimated by multiplying the P concentrations by the stream flow at the time of the sample collection. The five streams are gauged by the USGS, thus continuous flow measurements were available to use for loads estimation (Table 12). However, the automated ISCOs were located at varying distances downstream from the USGS gauges, and therefore the USGS flow measurements were adjusted upward within each creek by surface area, to account for the additional sub-watershed area draining into the sampling site in order to get a more accurate estimation for P loading (Hirsch 1979).

Table 12. (A) Precipitation summary (NOAA, 2021) and (B) streams discharge (USGS, 2021) for Oneida Lake watershed during 2020.

A.

Precipitation (mm)				
	North		South	
NOAA Station ID	USC00301110, Camden NY US		US1NYMD0016, CHITTENANGO 2.1 ESE, NY US	
Time/Season	Annual	Summer	Annual	Summer
n	366	92	363	92
mean	2.75	2.37	3.10	4.49
SD	6.00	6.50	7.83	12.43
max	48.51	35.81	76.96	76.96
Total	1006.09	218.44	1125.73	413.51

B.

Discharge L/sec						
USGS Station ID	River	Shore	Period Record	Annual mean (2020)	Annual Historical Average	Mean Summer 2020
4242640	Fish Creek at Becks Grove	North	2014-2020	29,821	34,239	7,890
4242500	Fish Creek East Branch	North	1923-2020*	14,132	15,576	3,160
4245840	Scriba	North	1966-2020*	2,147	2,300	727
4243500	Oneida	South	1949-2020	5,542	4,993	2,311
4243783	Cowaselon/Canaseraga	South	2014-2020	2,022	2,033	1,206
4244000	Chittenango	South	1950-2014*	3,701	3,178	1,424

*Represents non-continuous records.

2.3 P Loading Comparison between Streams and Groundwater Seepage

In order to understand relative contributions of P into Oneida Lake from streams and groundwater during summer 2020, we structured the analysis at different scales, both spatially and temporally. We paired streams and groundwater data which resulted in nine sampling events. We considered both calendar time and hydrometeorological conditions when pairing the data, for example: if samples were taken at the same calendar week but a significant storm event occurred in between the two collections dates, we paired the samples prioritizing flow conditions instead of calendar dates. Table 11 presents a detailed description of the data pairing. For the analysis we first compared loadings from groundwater seepage and streams at each sampling event. Given the strong differences between north and south sub-watersheds, we also separated the comparison by north and south shore. Stream loadings were estimated by multiplying the P concentration by the adjusted river flow at the time of sample collection at each stream sampling site. For shore comparison analysis, weekly stream loading was grouped by subbasin by adding loadings from individual streams, resulting in two streams for the north shore and three for the south shore. For groundwater loading we calculated the average load by sampling events for the sites located on the north and the south shore. Site E1 located on the East shore was used as the division point between the north and the south shores and its respective loading was used as representative for the entire East shore. A 20 m belt around the whole lake was considered as the area of influence of groundwater seepage, resulting in a total area of 1.1 km^2 for the north shore and 1.14 km^2 for the south shore. The shoreline lengths were estimated using ArcGISPro and were longer than the 88km typically reported for Oneida’s shoreline due to higher resolution measurements of small peninsulas and coves (North 55 km^2, South 57 km^2). In addition, we repeated the weekly analysis to develop a cumulative estimate for the entire lake, without separating the calculations by shore. For this calculation we only used the weeks that samples were taken at both shores (Weeks 1, 2, 3, 5, 9, 10) (Table 11). We then used these estimations to calculate a total loading for the entire lake, over the course of these six summer weeks.

2.4 P Loading Comparison between Streams and Groundwater Seepage during baseflow conditions

A big proportion of the loading in the streams is associated with storm events that mobilize big amounts of both dissolved and particulate P from the landscape into the streams. However, the quantity and quality of storm-related runoff is very dependent on the types of land use that occur in a given watershed. Groundwater loading, in contrast, is more constant through time, and even though it does respond to precipitation events (Chapter 1 and Chapter 2), the magnitude of the response is significantly smaller when compared to stream dynamics. In order to really understand the contributions of groundwater versus streams to Oneida Lake, and also to be able to consider the relevance to other lakes with differing land covers, we decided to venture into a third type of analysis in which we compared groundwater loading to stream loading specifically under baseflow conditions only. We identified and selected only those sampling times when the streams were in base flow condition (i.e., no rainfall had occurred for several days), and the stream hydrographs were leveled out. Phosphorus loads were calculated for these sampling dates and compared with those paired dates in the groundwater sites.

3 Results

3.1 Stream flow patterns in the Oneida Lake watershed

Annual mean and total precipitation for 2020 in the north sub-basin were 2.75 mm and 1006 mm respectively, while in the southern sub-basin mean and total precipitation were 3.1 mm and 1125 mm, respectively. During the summer months (June, July, August), the mean and total precipitation registered in the southern basin (4.49 mm and 413.5 mm, respectively) were almost two times greater than the precipitation recorded within the northern basin (218.4 and 2.37, respectively). Precipitation in the northern basin was below the historical average (1300 mm), while precipitation in the southern sub-watershed was above average (965 mm) (Table 12) (NOAA, CDC 2020). Hydrologic processes in the Oneida Lake watershed shift seasonally. Based on historical data from USGS gauge stations at the five main tributaries to the lake, mean monthly discharge at Oneida Lake tributaries increases between March and April, associated with snowmelt. Over the growing season, discharge decreases with the lowest mean monthly discharge observed between July and September, when base-flow is relatively constant. Stream discharges generally increase again in October, after leaf fall and evapo-transpirative losses decline, when temperatures drop, and storms increase (Figure 14).

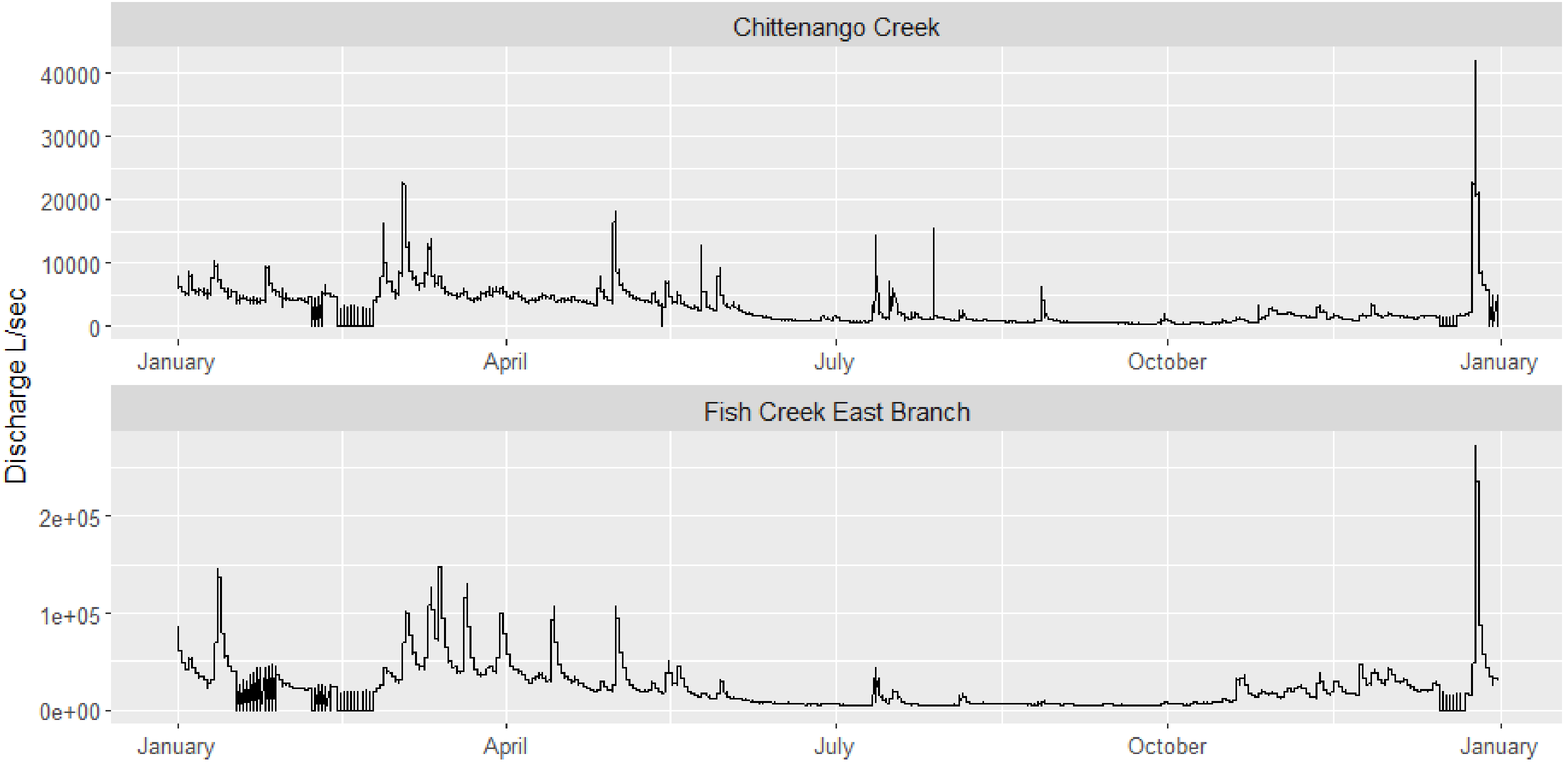


Figure 14. Annual hydrographs for Chittenango Creek located in the southern sub-watershed and the east branch of Fish Creek located in the northern sub-watersheds. The rest of the rivers exhibit a similar annual pattern. Source: USGS, 2020

Patterns of stream flow documented in 2020 reflected the differences in precipitation between the northern and southern halves of the watershed. During year 2020 mean annual discharge for the East branch of Fish Creek, which is the main tributary at the northern shore, was 29,821 L/sec, which was below the annual historical average for the last 5 years (34,238 L/sec) (Table 12). Similar patterns were observed at the West branch of Fish Creek and Scriba Creek, both located in the northern sub-basin (Table 12). Conversely, tributaries located in the southern sub-basin showed mean annual flows above the historical average. Chittenango Creek, for example, showed a mean annual discharge of 3,701 L/sec with a historical average of 3,177 L/sec. The other tributaries draining the southern sub-watershed follow a similar pattern (Table 12) (USGS, 2020).

During the summer of 2020 three significant high flow events were registered at the north and south sub-watershed tributaries. The highest registered flow for summer 2020 at all the creeks occurred on July 12th, associated with a storm event that started on July 11th. In addition, a significant high flow event was observed from July 16 to July 19th in all the creeks. In the southern sub-basin, another significant high flow event was registered between July 27th and July 28th, although no high flow event was observed in the northern sub-basin creeks for that date. Conversely, between Aug 4th and Aug 7th, a significant high flow event was observed at the northern sub-basin creeks, but not at the southern sites (Figure 15).

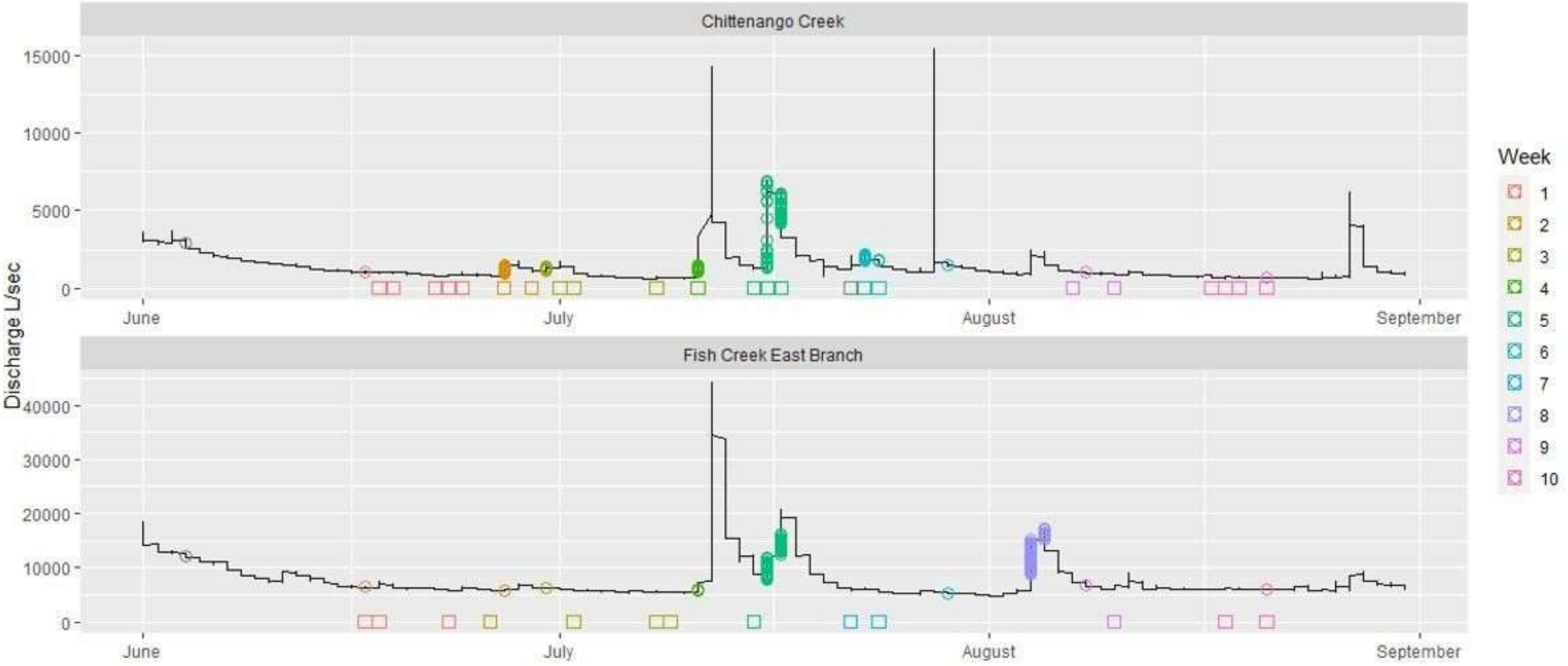


Figure 15. Summer hydrographs, showing times of data collection for streams (circles) and groundwater (squares). Colors indicate data pairing by sampling week.

3.2 Phosphorus in Oneida Lake tributaries

A total of 137 samples were collected from the Oneida Lake tributaries during summer 2020. Summer mean TP concentration for the tributaries ranged from 0.02 to 0.06 mg/L, while mean SRP ranged from 0.01 to 0.04 mg/L. Chittenango Creek, which drained a big portion of the southern sub-basin, exhibited the highest mean and individual concentrations for both TP and SRP across the five tributaries, while Canaseraga and Scriba creek presented the lowest. TP loads ranged from 1.8 kg/day at Scriba Creek to 37 kg/day at Chittenango Creek during summer 2020. Chittenango Creek in the South, and Fish Creek in the north exhibited the highest means for TP loads (37 and 26.2 kg/day, respectively), while Scriba creek presented the lowest (1.8 kg/day). SRP Loads ranged from 0.6 kg/day at Scriba Creek to 23 kg/day at Chittenango Creek. Similar to TP loads, Chittenango and Fish Creek (23 and 13.6 kg/day, respectively) exhibited the highest summer mean, while Scriba Creek the lowest (0.6 kg/day) (Table 13).

3.3 Groundwater Seepage flow and P dynamics at Oneida Lake watershed

A total of 87 pore samples were collected during summer 2020 at Oneida Lake shoreline. Groundwater flows during summer 2020 were highly variable at Oneida lake shoreline, ranging from -0.93 up to 5.12 L/m^2-day. Negative numbers represent moments of groundwater recharge instead of discharge into the lake. Mean seepage flow rates for north shore were 0.26 L/m^2-day, around a third of the mean documented for the south shore (0.8 L/m^2-day) and paralleling the patterns observed in precipitation and stream discharges. TP concentrations ranged from 0.17 to 102 mg/L, while SRP values were between 0.01 and 0.85 mg/L. For both average TP and SRP, the mean along the north shore was higher compared to the south shore. Conversely, loads exhibited the opposite pattern, with the southern shore having higher means than the north shore. Individual values for TP loads ranged from -0.06 to 450 mg/ m^2 -day, while SRP loads ranged from -0.03 to 0.91 (Table 13). Extensive description and analysis of groundwater seepage flows and P dynamics, and its spatial and temporal variability at Oneida Lake during summer 2020 can be found in Chapter 2.

Table 13. Summary for tributaries and groundwater seepage flow, P concentrations and P loads at Oneida lake watershed during summer 2020.

River							**GW**				
Parameter	**Summary/River**	**Canaseraga**	**Chittenango**	**Oneida**	**Fish**	**Scriba**	**Parameter**	**Summary/Site**	**North Shore**	**South Shore**	**Lake**
Flow L/sec*	**n**	8	70	8	43	8	**Flow L/m^2 day**	**n**	27	49	87
	Mean	2981	6187	2397	6885	673		**Mean**	0.26	0.80	0.77
	SD	1294	5051	1060	3607	422		**SD**	0.56	1.20	1.31
	Min	1854	2262	1220	2062	244		**Min**	-0.93	-0.88	-0.93
	Max	5745	23151	4327	14484	1295		**Max**	1.20	4.61	5.12
TP mg/L	**Mean**	0.022	0.064	0.050	0.046	0.027	**TP mg/L**	**Mean**	28.73	21.09	25.22
	SD	0.017	0.023	0.017	0.022	0.006		**SD**	36.17	21.50	29.02
	Min	0.011	0.017	0.031	0.009	0.018		**Min**	0.24	0.17	0.17
	Max	0.062	0.115	0.075	0.102	0.033		**Max**	102.35	72.09	102.35
SRP mg/L	**Mean**	0.005	0.039	0.018	0.023	0.013	**SRP mg/L**	**Mean**	0.13	0.08	0.09
	SD	0.004	0.018	0.014	0.015	0.008		**SD**	0.16	0.05	0.10
	Min	0.001	0.003	0.002	0.001	0.001		**Min**	0.03	0.01	0.01
	Max	0.011	0.079	0.033	0.060	0.024		**Max**	0.85	0.30	0.85
TP Loads kg/day	**Mean**	7.1	37.0	10.8	26.2	1.8	**TP Loads mg/m^2 day**	**Mean**	5.25	22.64	23.85
	SD	9.6	39.0	7.8	20.3	1.3		**SD**	8.47	39.47	58.29
	Min	1.8	3.7	3.4	5.4	0.5		**Min**	-0.05	-0.04	-0.06
	Max	30.7	163.1	28.1	88.8	3.6		**Max**	36.34	175.12	450.91
SRP Loads kg/day	**Mean**	1.4	23.0	4.1	13.6	0.6	**SRP Loads mg/m^2 day**	**Mean**	0.03	0.07	0.06
	SD	1.2	26.1	4.1	12.9	0.8		**SD**	0.05	0.14	0.12
	Min	0.2	0.9	0.2	0.3	0.1		**Min**	-0.03	-0.02	-0.03
	Max	2.9	130.8	12.2	48.4	2.4		**Max**	0.15	0.91	0.91

*Note: Flow values presented in this table are the flow estimation at the sampling site for the sampling dates based on USGS reports.

3.4 P loading Comparison: Streams vs. Groundwater seepage

P loading estimations from groundwater seepage at Oneida lake shoreline and from the five main tributaries to the lake during summer 2020 were integrated into a comparative analysis of P loading from all external sources into Oneida Lake. The analysis was first structured by north vs. shore sub-basin on a weekly basis during summer 2020. Along the north shore, weekly mean TP loads from streams ranged from 8.8 to 71 kg/day, while groundwater TP loads oscillated between 0.8 to 96.9 kg/day. The proportion of total TP load contributed by groundwater varied widely between weeks, ranging from only 5% during week 10 to 92% during week 3 (Table 14, Figure 16A). SRP loading, on the other hand, was consistently dominated by the streams, with the weekly contribution of groundwater to the total SRP loading ranging between 0.04 to 6.7% (Table 14, Figure 16B). Weekly averages for SRP in groundwater ranged from 0.01 to 0.1 kg/day, while for streams values ranged 0.7 to 35 kg/day. Similarly, on the lake's south shore weekly means for TP loads ranged from 8 to 285 kg/day for streams, and from 1 to 146 kg/day for groundwater. The weekly proportion of TP loading transported in groundwater ranged between 7 to 77 % of the total loading along the south shore (Figure 16C). Conversely, groundwater SRP loading proportion was significantly smaller, ranging from 0.06 to 10 % of the total weekly loading (Figure 16D). Mean SRP loads from streams ranged between 1.3 to 181 kg/day compared to 0.03 to 0.15 kg/day from groundwater (Table 14).

Table 14. TP and SRP loads and relative contributions by surface tributaries and groundwater to Oneida Lake (North vs. South) on a weekly basis in summer 2020.

Shore	Source	Week	Mean TP Load (kg/day)	TP Load (%)	Mean SRP Load (kg/day)	SRP Load (%)
North	Stream	1	9.95	20.81	2.66	98.11
		2	10.51	84.83	1.12	97.45
		3	8.81	8.33	0.90	93.31
		5	71.12	72.97	35.00	99.96
		7	10.69	73.10	2.81	98.51
		9	10.57	93.11	0.73	95.06
		10	16.17	95.00	2.92	96.80
	GW	1	37.89	79.19	0.05	1.89
		2	1.88	15.17	0.03	2.55
		3	96.90	91.67	0.06	6.69
		5	26.34	27.03	0.01	0.04
		7	3.93	26.90	0.04	1.49
		9	0.78	6.89	0.04	4.94
		10	0.85	5.00	0.10	3.20
South	Stream	1	14.40	23.49	1.32	90.00
		2	61.33	52.53	47.16	99.85
		3	63.33	30.31	46.87	99.79
		4	88.09	73.55	41.94	99.94
		5	285.34	88.44	181.24	99.94
		6	76.48	93.10	48.21	99.94
		9	25.69	74.72	4.51	98.79
		10	8.85	87.75	2.37	98.19
	GW	1	46.90	76.51	0.15	10.00
		2	55.41	47.47	0.07	0.15
		3	145.58	69.69	0.10	0.21
		4	31.67	26.45	0.03	0.06
		5	37.29	11.56	0.10	0.06
		6	5.67	6.90	0.03	0.06
		9	8.69	25.28	0.06	1.21
		10	1.23	12.25	0.04	1.81

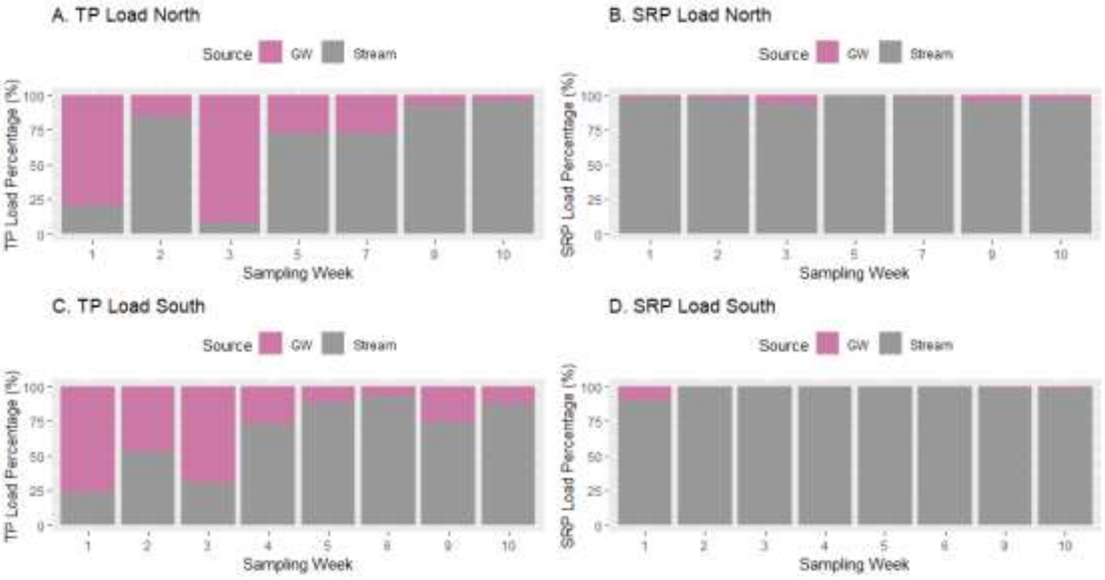


Figure 16. TP (A, C) and SRP (B, D) loading proportions from groundwater (pink) vs. streams (grey) on a weekly basis at Oneida Lake North (A, B) and South (C, D) shores in summer 2020.

When both shores were integrated to gain the entire lake perspective, weekly groundwater TP loading was between 4 to 72 % of the total loading, while SRP was significantly smaller ranging from 0.1 to 2% (Table 15, Figure 17A & B). We integrated the loads for the 6 weeks when data was available for both the north and the south shore and obtained a total P loading for the entire lake from both sources. For TP groundwater contributing added up to 3,335 kg, versus 4,744 kg from streams (Table 15, Figure 18A). For SRP, streams dominated the loading with a total of 2534 kg compared to 6 kg from groundwater (Table 15).

Table 15. TP and SRP loads and relative contributions (percentages) by surface tributaries and groundwater to Oneida Lake on a weekly basis during summer 2020.

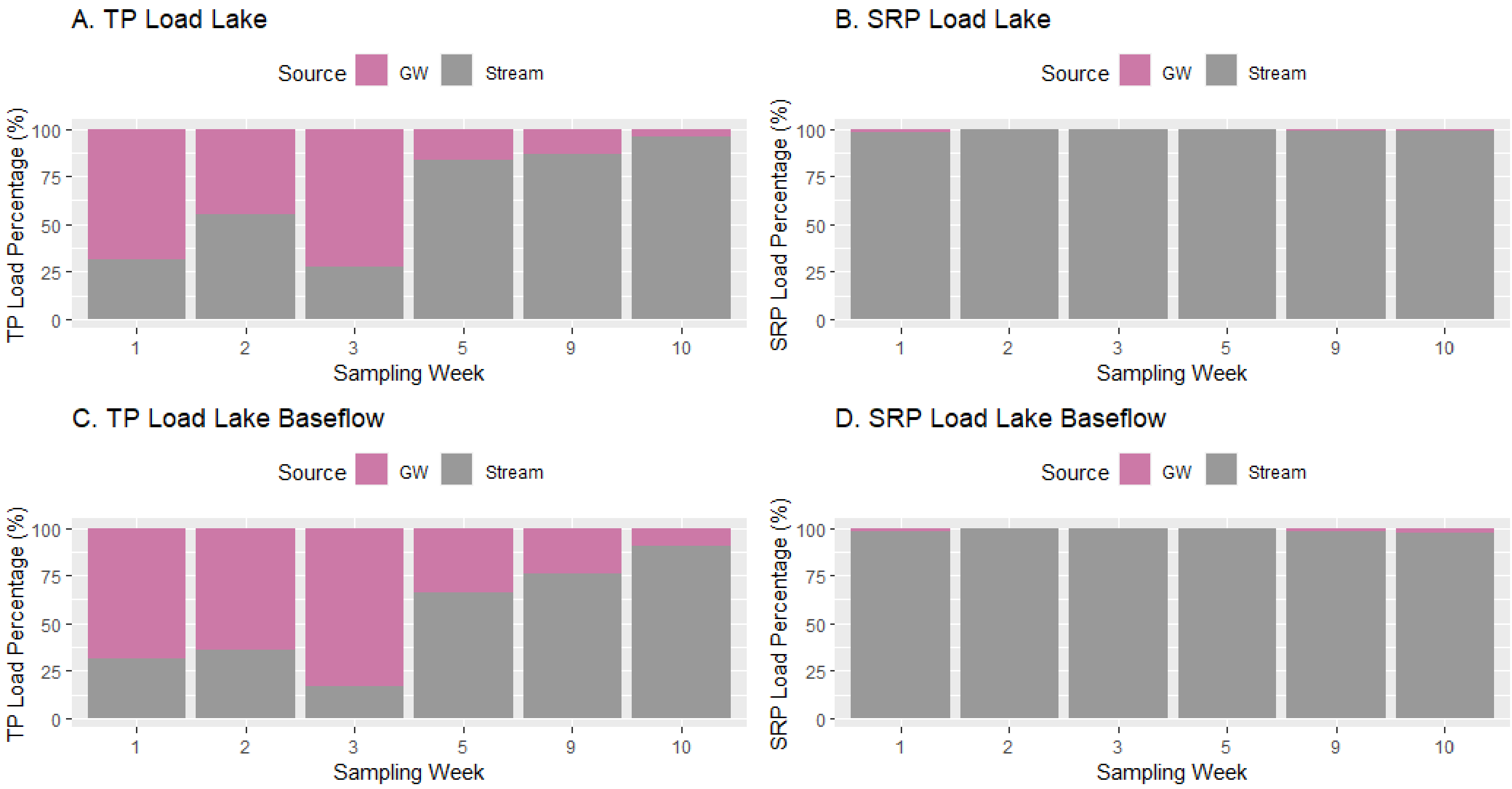
Shore	Source	Week	Mean TP Load (kg/day)	TP Load (%)	Mean SRP Load (kg/day)	SRP Load (%)
Both	Stream	1	40.3	31.6	11.1	98.0
		2	90.3	55.0	67.4	99.8
		3	89.7	27.7	62.0	99.7
		5	337.2	83.3	196.3	99.9
		9	74.0	86.5	8.2	98.8
		10	46.1	95.6	17.0	99.2
	GW	1	87.2	68.4	0.23	2.01
		2	73.9	45.0	0.11	0.17
		3	234.3	72.3	0.16	0.25
		5	67.4	16.7	0.15	0.08
		9	11.5	13.5	0.10	1.17
		10	2.1	4.4	0.13	0.77

Total Load over 6 weeks during the summer

Shore	Source	Week	Mean TP Load (kg)	TP Load (%)	Mean SRP Load (kg)	SRP Load (%)
Both	Stream	All	4744	58.7	2534	99.76
	GW	All	3335	41.3	6.14	0.24

3.5 Comparison of P Loadings under Baseflow Conditions:

Considering baseflow conditions only, the weekly proportion of TP total loading attributed to groundwater ranged between 9 and 83%, while the contribution to SRP oscillated between 0.3 and 2.4% (Table 16, Figure 17C & D). Mean weekly TP loads from streams ranged between 21 and 130 kg/day, while from groundwater means ranged between 2 and 234 kg/day. Mean weekly SRP loads ranged between 5 and 43 kg/day for streams, and between 0.1 to 0.2 kg/day for groundwater (Table 16). Cumulative contributions from groundwater were 60% compared to 40% from stream, when total loading over the 6 summer weeks was calculated (Table 16, Figure 18B).


A. TP Load Lake

B. SRP Load Lake

C. TP Load Lake Baseflow

D. SRP Load Lake Baseflow

Figure 17. TP (A, C) and SRP (B, D) loading proportions from groundwater (pink) vs streams (grey) on a weekly basis at Oneida Lake during summer 2020. Bottom figures (C, D) represent the load during baseflow conditions only.

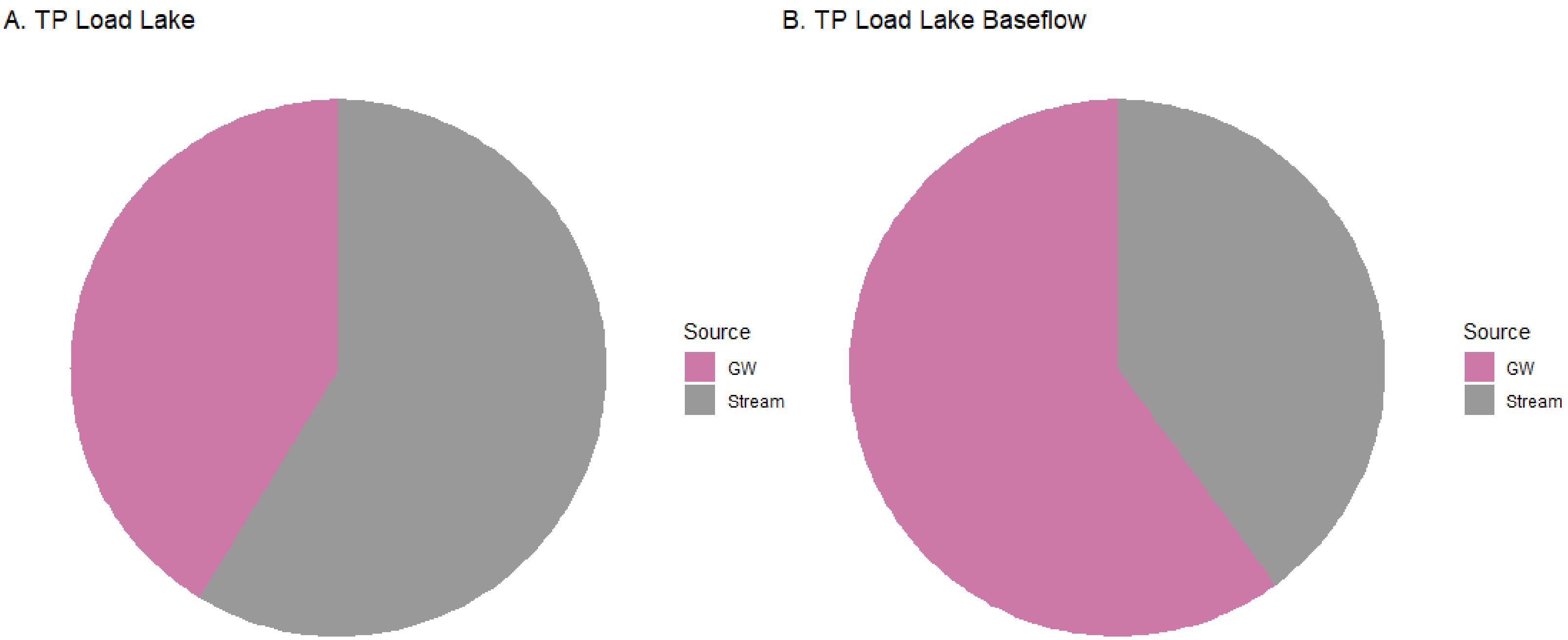


Figure 18. (A) Streams vs. groundwater proportion of cumulative TP loading into Onieda Lake over 6 weeks during summer 2020. Loads during baseflow conditions only are shown in B.

Table 16. TP and SRP loads in kg/day and relative contributions (percentages) by surface tributaries and groundwater, under baseflow conditions only, to Oneida Lake on weekly basis during summer 2020.

Shore	**Source**	**Week**	**Mean TP Load (kg/day)**	**TP Load (%)**	**Mean SRP Load (kg/day)**	**SRP Load (%)**
Both	Stream	1	40.3	31.6	11.1	98.0
		2	41.3	35.9	24.1	99.5
		3	47.9	17.0	23.2	99.3
		5	130.1	65.9	42.8	99.6
		9	36.3	75.9	4.7	98.0
		10	21.2	90.8	5.3	97.6
	GW	1	87.2	68.4	0.23	2.01
		2	73.9	64.1	0.11	0.47
		3	234.3	83.0	0.16	0.67
		5	67.4	34.1	0.15	0.35
		9	11.5	24.1	0.10	2.05
		10	2.1	9.2	0.13	2.43
Total Load over 6 weeks during the summer baseflow Only						
Shore	**Source**	**Week**	**Mean TP Load (kg)**	**TP Load (%)**	**Mean SRP Load (kg)**	**SRP Load (%)**
Both	Stream	All	2219	40	778	99.2
	GW	All	3335	60	6.14	0.78

4. Discussion

The results of this research offer valuable perspectives and insights into the relative contributions of groundwater versus streams to phosphorus loadings and biogeochemical processes within Oneida Lake. These findings have broader relevance and implications for other lakes dealing with water quality concerns related to nutrient loading. Lake eutrophication has traditionally been associated with P inputs from overland and surface flow, highlighting the importance of tributary water sources for nutrient loading. This study provides evidence that groundwater can also carry substantial loads of dissolved P, even in lakes where groundwater represents a relatively small fraction of the total water input. Quantifying tributary loadings during summer 2020 indicated that the five largest tributaries play a key role in loads of SRP and TP to the lake. These loading values are comparable to what has been previously documented for Oneida Lake (Table 17). Significantly greater amounts of total precipitation, and also average precipitation per storm event, occurred in the southern compared to northern sub-watersheds in summer 2020, which influenced the relative contributions of P coming from the different tributaries. In line with the prevailing focus on managing watershed-based nutrient runoff, storms were a major driver of runoff-related sediment-bound TP. Delivery via tributary streams means that the P is entering almost as a set of point sources distributed around the lake. However, during the same time period, groundwater was also inputting phosphorus as near continuous flow diffusely through the entire shoreline littoral zone, estimated as 224 ha in surface area. Relative contributions of SRP from groundwater were minor, but total dissolved P loads in groundwater represented up to 70% of the TP loading by

Table 17. Descriptive analysis for streams P concentrations and loads for three surface tributaries to Oneida lake during summer since 2013 to 2019. (SOURCE: CBFS database, Rudstam 2021)

		Chittenango Creek		**Fish Creek**		**Oneida Creek**	
		CBFS Database	**This Study**	**CBFS Database**	**This Study**	**CBFS Database**	**This Study**
		2013-2019	**2020**	**2013-2019**	**2020**	**2013-2019**	**2020**
TP mg/L	**Annual summer means**	0.03 to 0.07	0.06	0.01 to 0.02	0.05	0.03 to 0.08	0.05
	range ind values	0.005 to 0.60	0.02 to 0.11	0.001 to 0.07	0.009 to 0.1	0.004 to 0.2	0.03 to 0.08
SRP mg/L	**Annual summer means**	0.003 to 0.04	0.04	0.003 to 0.006	0.02	0.004 to0.03	0.02
	range ind values	0.001 to 0.05	0.003 to 0.08	0.002 to 0.01	0.001 to0.06	0.001 to 0.1	0.002 to 0.03
TPL kg/day	**Annual summer means**	20 to 112	37	9 to 48	26	4 to 89	11
	range ind values	1 to 907	4 to 163	0.3 to 281	5 to 89	1 to 732	3 to 28
SRPL kg/day	**Annual summer means**	3 to 48	23	2 to 13	14	0.5 to 15	4
	range ind values	0.3 to 302	1 to 130	0.07 to 83	0.3 to 48	0.1 to 219	0.2 to 12

groundwater and streams each week combined. These inputs were highest in earlier weeks and diminished over the summer. This indicates that groundwater is a major contributing source, providing constant high inputs in early months when waters are warming, and algal development is initiating. Given that stream loading during high flow events is highly variable depending on land use and anthropogenic activities within a given watershed, a comparison of groundwater inputs with tributary loadings solely during baseflow was insightful. Baseflows in streams are dominated by groundwater and this comparison confirmed that groundwater is a significant and comparable source of dissolved TP into streams when storms are not occurring. Such high loads have the potential to change N:P ratios that drive phytoplankton development, including HABs. This study offers a new valuable contribution as it belongs to the limited number of studies that have quantitatively measured and compared nutrient loading from both streams and groundwater into lakes, especially large lakes. It also enhances the perspective of the role of total dissolved P entering lakes by both groundwater and streams; and raises questions about its sources, the factors driving it including climate change, and the meaning for lake and watershed dynamics in the coming years.

Loading estimates from the five main tributaries discharging into Oneida Lake indicated that tributaries are of high importance for TP and SRP loading into the lake during the summer, even though water flows decrease following hydrometeorological conditions typical of northern temperate climates. Total precipitation, and average precipitation per storm event, during summer 2020 were significantly higher on the southern compared to the northern sub-watershed at Oneida Lake, which influenced relative contributions from the different tributaries. Chittenango and Oneida Creek exhibited similar loadings to Fish Creek during the summer, although Fish Creek flows were three times higher, while mean concentrations were only slightly higher in the southern tributaries compared to Fish Creek (Table 12 and Table 13). The P concentrations and loads reported in this study fall neatly within the range of the concentrations and estimated loads that have been reported by CBFS regular monitoring for three of the main tributaries to Oneida Lake (Chittenango, Oneida, Fish Creek) for summers between 2013 and 2019 (Table 17) (Rudstam 2021). Additionally, TP concentrations and loads are also comparable to the values reported by Makarewicz and Lewis (2003), on a report on nutrients and suspended sediments from Oneida Lake tributaries. The five main tributaries were sampled on 12 dates (6 dates on high flow events, 6 dates on baseflow conditions) during the growing season (March to October) of 2002 and 2003. We used Makarewicz and Lewis (2003) mean TP loads for baseflow conditions and calculated the total TP load coming into Oneida Lake from the five streams over 6 weeks (as we did for this study), which resulted in a total load of 6216 kg of TP, which is comparable to our result of cumulative TP loading which rangde between 2219 to 4744 kg of TP (Table 15 and Table 16), depending on baseflow conditions or both baseflow and high flows, respectively. Differences are expected as our calculation is based only on summer months (June, July, August), while their dataset includes months of likely higher flows such as April, May and October.

Our results also showed that high concentrations of phosphorus are carried by groundwater seepage, which is constantly moving through the water-sediment interface along the entire littoral zone of the lake shoreline, which in this study we conservatively estimated as a belt of 224 ha in surface area. A detailed discussion of seepage flow rates, and its P concentrations and loads can be found in Chapter 2. In this study we focus on integrating the individual point measurements into an overall loading estimation for the analysis of relative contributions by external sources. However, the spatial and temporal variability in seepage flow rates and P concentration is shown to be highly challenging for overall loading estimations. While we are reasonably confident of the nutrient concentrations and flow rates used to estimate stream inflows, the groundwater load estimations carry a certain level of uncertainty. This challenge has been recognized by many (Lewandowski et al. 2015b; a; Rosenberry et al. 2015; Hupfer et al. 2018) as one of the main reasons for the disregard of groundwater as a significant component in nutrient budgets. Currently the gap between detailed basic research at a small scale in lacustrine water-sediment interfaces, and the use of those findings to understand the impact or the importance of these processes at a broader scale remains a challenge (Hupfer et al. 2018). We recognize that our approach to estimate overall groundwater loadings is rather simplistic, but it offers a starting point for the integration of lacustrine groundwater discharge into the lake nutrient management conversation.

The relative contribution of SRP by groundwater was small compared to riverine inputs, even when the comparison was performed considering baseflow conditions only. On the other hand, the relative contribution of groundwater TP loads were comparable with surface water contributions both in terms of cumulative inputs and on a weekly basis. However, TP transported in streams is fundamentally different than TP coming in groundwater seepage. Storms are a major driver of sediment bound P loading from streams (Mainstone and Parr 2002) which is highly influenced by land use and anthropogenic activities within the watershed. When runoff related events were excluded from the analysis, focusing only on baseflow conditions, the TP loadings from both sources were even more comparable. In both cases, it is assumed that TP is dominated by the dissolved fraction (See discussion Chapter 2). During baseflow conditions, the relative contributions of TP in groundwater on a weekly basis range between 9 and 83% of total P loading. The proportion of external total dissolved phosphorus contributed by groundwater in other lakes ranges between 3 and 85% (Table 18), however most of these studies are focused on lakes that are primarily groundwater-fed. When looking at lakes that are not primarily fed by groundwater, the maximum proportion of P loading contributed by groundwater decreases to 58%. Although, this represents a significant proportion, it is important to note that most of these lakes are considerably smaller (less than 5 km^2 in surface area) compared to Oneida Lake. This difference in size will likely influence linkage dynamics between the lake and its watershed. Studies that estimate relative P contributions from groundwater and compared them to other external sources of P in large lakes are scarce. Loeb and Goldman (1979), estimated that TDP loading by groundwater from one subbasin (Ward Valley) to Lake Tahoe was 44%, compared to 16% as a proportion of water inputs. Our study is one of the few studies comparing groundwater and river nutrient loading for large lakes.

Table 18. Relative contributions of groundwater to surface water phosphorus inputs at different lakes in the Northern Hemisphere.

Reference	Lake	GW proportion of P inputs (%)	GW proportion of water inputs (%)	Lake Surface area (Km2)	Groundwater Fed lake	Type of P
Meinikmann et al.2015	Lake Andresee, Germany	53	ND	5.14	Yes	SRP
Ommen et al. 2012	Lake Hampen, Denmark	85	70	0.80	Yes	SRP
Juckem and Robertson 2013	Shell Lake, Wisconsin	3	5	10.00	No, no outlet	DP
Robertson et al. 2009	Bardon lake, Wisconsin	27	ND	3.30	Yes	TP
Krabbenhoft et al. 1990	Sparkling Lake, Wisconsin	50	ND	1.00	yes	SRP
Brock et al. 1982	Lake Mendota, Wisconsin	12	30	39.40	No	TDP
Shaw and Prepas 1990	Narrow Lake, Alberta	58	30	1.10	No	TDP
Loeb and Goldman 1979	Lake Tahoe, California (Ward Valley subbasin)	44	16	499 (31)	No	TDP
Labaugh et al. 2009	Miror Lake, New Hamphshire	7	8	0.15	No	SRP
Jarosiewicz and Witek 2014	Maly Borek Lake, Poland	80 (SRP), 76(TP)	46	0.08	Yes	TP and SRP

Note: ND: No data available in the publication. DP: Dissolved Phosphorus, TDP: Total Dissolved Phosphorus.

Overall calculations and comparisons like the ones presented in this study are valuable for summarizing information and enhancing our general understanding of key processes. However, it is important to recognize that riverine inputs and groundwater inputs are fundamentally different in nature. Oneida lake has strong hydrological connections to its watershed and is highly influenced by tributary streams. Quantitatively, on an annual basis, the lake inputs of TP and SRP from external sources will be dominated by streams, however, the spatiotemporal component of these inputs is also highly relevant when analyzing the loading effect onto lake's food web and its ultimate trophic status. The timing and magnitude of nutrient inputs can influence primary productivity, phytoplankton dynamics, and subsequent trophic interactions within the lake (Withers and Lord 2002; Holman et al. 2010b). Inputs from surface tributaries exhibit higher temporal variability compared to groundwater seepage. Big pulses of both dissolved and bound P enter the lake via streams after storms events. During the three months that this study lasted, three significant storm events were registered that resulted in the highest P loadings from streams into the lake during the summer. In those moments, the relative importance of groundwater compared to rivers was tiny. However, during baseflow conditions, which in northern temperate lakes dominate during the summer, the importance of groundwater as a source for dissolved P loads increases up to a similar level as riverine inputs. Moreover, groundwater relative contributions were larger during the first weeks of the summer season and diminished as the season progressed. This temporal pattern suggests that groundwater may play a substantial and consistent role in contributing phosphorus to the lake, particularly during the initial months when water temperatures are rising, and algal development is beginning; as P concentrations have been correlated with chlorophyll-a concentrations in many lakes worldwide (Quinlan et al. 2021). In addition, the spatial component is also important; groundwater seepage occurs around the entire lake shoreline (Chapter 2 and Schneider et al. 2005), providing a constant source of dissolved P to the benthic littoral environment. Many studies have related groundwater seepage flow and its nutrient loading with benthic phytoplankton and macrophytes presence, abundance, composition, and distribution in the littoral environment (Lillie and Barko 1990; Sebestyen and Schneider 2004; Hagerthey and Kerfoot 2005; Naranjo et al. 2019). Rivers, in contrast, enter the lake at specific locations, which can be compared to point sources discharge. Riverine inputs become a concentrated source of nutrients at the initial point of entry (Makarewicz et al. 2012), but for these nutrients to become available for the organisms within the lake, they need to mix and disperse throughout the water column. Moreover, the constant high loads of dissolved P at the water-sediment interface may potentially shift the N:P ratios that drive phytoplankton developments, including HABs, in the nearshore areas. In Chapter 2, we hypothesized that Dissolved Organic Phosphorus (DOP) is likely the main fraction coming in with groundwater, which may be especially important in the context of cyanobacterial blooms, as they possess the physiological mechanisms to use DOP when inorganic fractions are absent or limited (Xie et al. 2021; Xiao et al. 2022).

Lakes are an integral part of their surrounding watershed, and the level of connections between the surface water and its aquifers can vary. If we classify lakes based on the degree of connection they have with their aquifers, we observed a continuum that ranges from mounded lakes, which primarily received water from precipitation, to terminal groundwater-fed lakes, that rely heavily on groundwater sources. Between these two extremes, there are lakes that exhibit varying degrees of connection with their aquifers. In these lakes, groundwater fluxes can be highly variable both temporally and spatially (Shaw et al. 1990; Hagerthey and Kerfoot 2005; Rosenberry and Winter 2009) creating a large heterogeneity in the resources supply. We hope that our findings will encourage scientists and managers to include groundwater analysis when addressing issues related to excess nutrient loading and water quality. Additionally, it is important to broaden the analysis by considering other phosphorus fractions beyond SRP. Future research should also include analysis of TP and TDP, along with N and C to gain a deeper understanding of nutrient ratios and its potential impact on primary productivity. Furthermore, it is necessary to broaden the focus beyond agricultural impacts when studying nutrient loading and availability in water bodies. Many other biogeochemical processes can play important roles in nutrient loading dynamics, as we include groundwater resources in the analysis. For example, carbon dynamics, which have been heavily impacted by global warming may be a key factor when analyzing for nutrients transport trough the vadose and saturated zone (Corman et al. 2018)

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CONCLUDING REMARKS

The overall goal of this research was to investigate the potential of groundwater seepage as a significant phosphorus (P) source to Oneida Lake, a large mesotrophic, temperate lake in central New York. The results indicate that groundwater seepage is a continuous source of dissolved P throughout the sediment-water interface of the entire Oneida Lake shoreline. Although Soluble Reactive Phosphorus amounts were small, Total Phosphorus concentrations and loadings were extremely high, frequently comparable in scale to loadings from of all the tributaries combined. Total phosphorus has traditionally been considered to dominate in association with stream sediment loads during storms. However, in my research, the total phosphorus is dissolved and appears to be associated with other organic compounds, sourced from the watershed itself. This has important implications for the dynamics of P in other lakes. In particular, recent research is demonstrating the role of dissolved organic compounds for their carbon, nitrogen and phosphorus content as potential drivers of the browning phenomenon and shifts in phytoplankton communities, including HABs (Corman et al. 2018; Xie et al. 2021; Xiao et al. 2022). My research adds new information on the key role of groundwater seepage as a potential mechanism for P transport into lakes.

Groundwater seepage flow rates, its P concentrations and the resulting P loadings varied widely, both spatially and temporally across the summer season at Oneida Lake's shoreline. P loadings ranged from negative values, where water recharges into the aquifer instead of discharging into the lake, to moments of little flow (close to zero), to large flows, even comparable to those from surface tributaries. Temporally, patterns of precipitation were significant influential drivers of this heterogeneity at several different time scales. Overall, there was higher than average total rainfall in the southern half of Oneida's watershed during 2020 and lower than average total rainfall in the northern half of the watershed. This process likely explains the lower seepage flow rates documented at the northern groundwater stations, and also the finding in Chapter 1 that flow rates were greater than observed by Schneider et al. (2005) two decades earlier. Over the course of the summer, groundwater TP loadings were higher in the early weeks of summer, and then decreased later in the season. Similarly, research in several Adirondack lakes indicated a seasonal effect such that groundwater seepage and loadings were highest in late spring and early summer when the influence of snowmelt was strongest (Sebestyen and Schneider 2001, 2004). On the shortest time scale, groundwater flow rates decreased significantly with the number of days since the last rain event (up to one week), verifying a process that has been reported for other lakes (Winter 1983; Rosenberry et al. 2013). Spatially, patterns in adjacent land use were also statistically significant drivers of flow rates and P concentrations. Forests were associated with the highest groundwater flow rates and wetlands with the lowest flow rates, both within the 700 m shoreline studied in Chapter 1, and throughout the entire Oneida Lake shoreline (Chapter 2). Residential land uses were associated with higher concentrations of dissolved phosphorus compared to other land use types. The higher P may result from active septic systems, lawn fertilizers, or historical phosphorus use. The importance of groundwater's role in Oneida Lake gets clearer in Chapter 3 when analyzed in comparison to the tributary loadings. The five main streams discharging into the lake were monitored throughout the 2020 summer and transported P loads was very similar to those previously reported for this lake

(Makarewicz and Lewis 2003; Rudstam 2021). However, TP loads by groundwater represented up to 90% of the total phosphorus loading into the lake, depending on week of the summer, making it comparable or greater than the tributary contributions. Moreover, these two sources are very different in terms of how they function to the lake as a whole. Tributary loading enters effectively as series of point sources distributed around the lake. Much of the P is bound tightly to sediment, carried there during storm events, which is strongly dependent on the extent of agriculture and other eroding land uses within each tributary's basin. The sediment-bound P must settle out and overcome a series of biogeochemical transformations before it disassociates and becomes available to organism to consume. The remaining dissolved P takes time to disperse throughout the 207 km^2 expanse of the lake. In contrast, groundwater is a consistent and constant input throughout the littoral zone of the entire lake, discharging dissolved phosphorus directly at the sediment-water interface. My research, similar to others (Makarewicz et al. 2012; Howell et al. 2014; Pothoven and Vanderploeg 2020), documented that these inputs are increasing the concentrations of dissolved P in the overlying lake waters along the shoreline, much above the P concentrations deeper in the pelagic waters of the lake. These conditions are ideal for the development of certain forms of algae whose life cycles incorporate resting stages in the sediment and are poised to take advantage of the discharging P (Barbiero and Welch 1992; Carey et al. 2009, 2014). Additionally, groundwater emerges as a comparable contributor of dissolved phosphorus to the lake shoreline, particularly during baseflow conditions. This finding holds significance in temperate climates, where baseflow conditions prevail during the summer, coinciding with optimal conditions for primary productivity. Groundwater seepage may be a crucial factor aiding to maintain summer primary productivity, and algal blooms in these types of systems.

The heterogeneity in flow rates and P loadings documented here is one of the main reasons (and part of the ongoing challenges) underlying the lack of integration of groundwater seepage as a significant factor in lake's water and nutrient budgets. However, results from this research present strong evidence of the substantial quantities of P that groundwater seepage may be carrying into lakes. Moreover, the inherent variability of this phenomenon will likely have significant implications for the composition and distribution of lake biota, including primary producers and cyanobacteria, especially in the littoral environment. A few other studies have shown that macrophyte and periphyton communities' abundance and composition can be controlled by groundwater flows and its nutrient loading (Hagerthey and Kerfoot 2005; Frandsen et al. 2012; Naranjo et al. 2019). More research is urgently needed to expand our knowledge and understanding of this overlooked factor in lakes' nutrient dynamics.

In this research, I have identified answers to several knowledge gaps that will contribute to a deeper understanding of the multiple causes underlying current challenges in aquatic ecosystem and its water quality. Many of these gaps pertain to the fields of hydrology and biogeochemistry, aiming to improve our understanding of groundwater seepage and the dynamics of water and nutrient exchange at the sediment-water interface. Equally important is the need for interdisciplinary collaboration, as it plays a crucial role in improving our understanding of the links and interactions between lakes and their surrounding environment. I hope that these findings will encourage scientists and managers to include groundwater seepage analysis when addressing issues related to excess nutrient loading and water quality. We have long surpassed the days when limnological research regarded a laks as an isolated microcosm. We now face the challenge of promoting interdisciplinary collaboration to improve our understanding of lake ecosystems that are strongly coupled to their surrounding watershed.

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