Influence of a dammed reservoir on nutrient (N, P, Si) loads and ratios of the Thames River, Ontario

by

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Author’s Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of contribution

Chapter 2

This chapter is a co-authored, manuscript-format paper. I was primarily responsible for data analyses and writing, with feedback from Chris T. Parsons (CTP) and editing support from Heather Townsend (HT), Linden Fairbairn, Tamara Van Staden, and Bhaleka Persaud. This project was conceptualized by CTP and Mohamed Mohamed, with further development and feedback from Ryan Sorichetti, Nandita Basu, and Philippe Van Cappellen (PVC). Fieldwork was conducted by me and Amanda Niederkorn (AN), with the assistance of co-op students Alyssa Graham (AG) and Lisa Kester (LK), and many fieldwork volunteers. Laboratory work was conducted by me, AN, and Marianne Vandergriendt (MVG), with the assistance of AG. I wrote the computer codes with help from John Dony and Meguel Yousif.

Chapter 3

This chapter is also a manuscript-format paper. I was responsible for data analyses and writing, with editing support from Steph Slowinski and HT. Research questions and methodology were developed by CTP and PVC. Fieldwork was conducted by me and AN, with the assistance of co-op students AG and LK, and many fieldwork volunteers. Laboratory work was conducted by me, AN, and MVG, with the assistance of AG.

I am the sole author of all other chapters in this thesis.

Abstract

The increasing frequency and severity of harmful algal blooms (HABs) in Lake Erie have been troubling developments in the past few decades. Excess loads of phosphorus (P) from the watershed are considered to be a primary driver due to the role of P as a limiting nutrient for primary production. Additionally, the roles of nitrogen (N) and silicon (Si) on HABs have generated considerable research interest recently due to the influences of N:P:Si ratios on phytoplankton community composition and algal bloom toxicity. The Thames River, in southwestern Ontario, is a significant tributary source of nutrients to the western basin of Lake Erie from the Canadian side. Evaluation of nutrient sources, loads, and reduction strategies within the Thames River Watershed are therefore critical to guide management strategies to mitigate HABs in Lake Erie. Currently, the majority of nutrient management strategies focus on limiting nutrient loss from the landscape without considering the effects of dammed reservoirs along the river corridor. On a global scale, dammed reservoirs attenuate N, P, and Si fluxes and have also been shown to alter nutrient speciation through physical and biogeochemical processes. However, in-reservoir retention efficiencies are highly variable and may fluctuate between source and sink. The influences of Thames River's largest reservoir, Fanshawe Reservoir, on nutrient loads, speciation, and ratio have not been fully evaluated due to a lack of primary water chemistry data.

In Chapter 2 of this thesis, I evaluated Fanshawe Reservoir's influence on Thames River's P flow on annual and seasonal time scales by 1) quantifying the reservoir's P retention efficiencies using a mass balance approach, and 2) assessing the changes to P speciation using the ratio of dissolved reactive P to total P (DRP:TP) as an indicator of load bioavailability. Annually, Fanshawe Reservoir functioned as a P sink by retaining 28% (41 tonne) and 48% (92 tonne) of TP loads in 2018 and 2019, respectively. Seasonally, the reservoir altered between a sink and a source of P. Net P releases occurred during the summers of 2018 and 2019 and the spring of 2018, driven by internal P loading and increased discharge from the dam. The reservoir did not exert a strong influence on DRP:TP annually, but increases were observed during both summers. The findings of this chapter demonstrate that Fanshawe Reservoir is an important P sink on the Thames River, with further influences on the timing and speciation of P loads.

In Chapter 3, I assessed Fanshawe Reservoir's influence on N:P:Si ratios of nutrient fluxes on the Thames River by 1) calculating the reservoir's dissolved inorganic N (DIN), dissolved inorganic Si (DSi), and DRP retention efficiencies, and 2) comparing DIN:DRP and DSi:DRP ratios between inflow and outflow nutrient loads. Additionally, I identified the general transport behaviors of DIN, DRP, and DSi by analyzing their concentration to discharge (CQ) relationships. From 2018 to 2019, Fanshawe Reservoir retained DRP (28.6%) and DSi (5.6%) but released DIN (-6.2%). The preferential retention of DRP over DIN and DSi increased DIN:DRP and DSi:DRP ratios leaving the reservoir, and potentially increased N availability and P limitation in downstream water bodies. Increases to N availability could intensify algal bloom toxicity, however, P retention by the reservoir may offset the extent of eutrophication. Upstream of the reservoir, DIN and DRP exhibited mobilization transport behaviors, and DSi was chemostatic. Downstream of the reservoir, DRP shifted to chemostatic, likely due to in-reservoir processes of internal P loading during the low flow summer and enhanced retention during high flow events, both of which decreased the long-term variability of DRP concentration with flow. Overall, the findings of this chapter show that Fanshawe Reservoir is decoupling Thames River's nutrient flow by altering both the quantity and ratio of nutrient load.

The combined findings from Chapter 2 and 3 indicate that Fanshawe Reservoir exerts a major influence on Thames River's nutrient flow. To help mitigate excess P loads to Lake Erie, in-reservoir P retention may be enhanced through nutrient management strategies within the reservoir, in supplement to land-based strategies that are currently in place. Changes to N:P:Si ratios through preferential retention of P over N and Si, however, may lead to adverse effects in downstream water bodies, and highlight the need to establish dual nutrient reduction goals addressing both excess P and N within the watershed.

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Dedication

To my parents, who taught me to love the environment and the people around me.

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Chapter 1
Introduction

1.1 Eutrophication of Lake Erie

Anthropogenic nutrient loading is one of the main driving forces behind aquatic eutrophication occurring worldwide, where an elevated quantity of phosphorus (P) is typically found in the eutrophic waters (Carpenter & Bennett, 2011). P is an essential element to life and is often the limiting or co-limiting nutrient for primary production in freshwater ecosystems (Vollenweider, 1968; Schindler, 1977). However, excess P could lead to the formation of harmful algal blooms (HABs), leading to poor water quality and extensive bottom water anoxia, which can severely impair the health of an ecosystem. Lake Erie, the shallowest of the Laurentian Great Lakes with the shortest water residence time of 2.7 years (Quinn, 1992), has experienced periods of severe eutrophication since the 1960s due to intensive point source and non-point source nutrient pollution (Scavia et al., 2014). This led to the signing of the binational Great Lakes Water Quality Agreement (GLWQA) between Canada and the U.S. in 1972, which facilitated domestic action plans to reduce P inputs from the watershed. Significant decreases of P loading into Lake Erie were documented during the 1970s, primarily attributed by reductions of direct point sources and regulation of phosphate concentration in detergents (Dolan, 1993; Scavia et al., 2014). These actions were largely successful during the following decade, which saw a decrease in the prevalence and severity of HABs (De Pinto et al., 1986). However, severe HABs re-emerged in the mid-1990s and have progressively worsened, purportedly due to the combined effects of 1) elevated load of dissolved reactive P (DRP), and 2) internal P loading induced by bottom water anoxia following algal bloom events (Michalak, 2013).

On the Canadian side, the Thames River represents the largest tributary P load into Lake Erie's western basin (Maccoux et al., 2016). The Thames River watershed is largely dominated by agricultural land use (79.5%), but several major cities such as London and Stratford are also situated within the watershed (Ontario Ministry of Natural Resources and Forestry, 2020). The Thames River discharges into Lake St. Clair, which shortly flows into western Lake Erie. Under the latest GLWQA amendment (2012), Canadian and U.S. federal governments committed to update and review P load reduction targets for priority tributaries that discharge to the western and central basins of Lake Erie, including the Thames River. In 2016, these targets were adopted by both countries and specified a 40 percent reduction of spring total P (TP) load and DRP load by 2025 in comparison to 2008 levels (binational.net, 2016). To help achieve this target on the Canadian side, the federal and provincial (Ontario) governments established the Canada-

Ontario Lake Erie Action Plan (2018) that outlined various P load reduction strategies such as: agricultural land use management change, wastewater treatment plants (WWTP) upgrades, green infrastructure developments, and wetland conservation improvements (Environment and Climate Change Canada & Ontario Ministry of the Environment and Climate Change, 2018). Besides WWTP upgrades, majority of the proposed or currently implemented strategies are land-based approaches that focus on reducing P runoffs. Once P has entered the rivers, various cycling processes occur naturally, transforming P between dissolved and particulate phases, and between organic and inorganic species. The cumulative effect of these process further alters P fluxes along the river corridor, with impacts on P received by downstream water bodies.

1.2 P cycling in rivers

The main transport pathway for P from the continents to the oceans is through rivers. Unlike nitrogen and carbon, P has no stable gaseous phases and therefore atmospheric P cycling is limited to the transport and chemical processing of particulate mineral aerosols (Berner & Berner, 1987; Nenes et al., 2011). Riverine P is typically differentiated between particulate and dissolved phases, with further separation between organic and inorganic molecular compositions (Meybeck, 1982). In natural environments with minimal human perturbation, P within rivers mostly exists in particulate forms (mineral associated P, biomass P), and the more immediate bioavailable dissolved P species are kept at relatively low concentrations due to rapid uptake and recycling within the biosphere (Berner & Berner, 1987). Under anthropogenic pressures however, the dominant P species entering rivers could vary widely depending on the sources of P pollution. Point sources (e.g. sewage discharge, wastewater effluent) are typically concentrated in dissolved P species, and consistently discharge throughout the year. Non-point sources (e.g. agricultural and urban runoffs) on the other hand, are more dependent on high flow events, discharging in episodic or seasonal patterns (Withers & Jarvie, 2008). Furthermore, the dominant P form from non-point sources could vary temporally and spatially depending on the type of land use and management. For example, the conversion from tillage to no-tillage or conservative-tillage practices on farmlands reduces soil erosion and the loss of particulate P, but this often results in elevated runoff of dissolved P due to soil P stratification, where loosely bound phosphate preferentially accumulates in the non-inverted topsoil (Ulén et al., 2010). Once P enters the river, various physical and biogeochemical processes take place, transforming the speciation of P, and potentially changing the bioavailability of the overall P load. The major processes are sorption/desorption, precipitation/dissolution, assimilation/decomposition, and sedimentation/ resuspension.

1.2.1 Sorption/desorption

Both organic and inorganic dissolved P are known to interact with sediments and suspended particles through sorption/desorption processes, particularly with clay particles and iron (Fe) or aluminum (Al) (hydr)oxides due to the combined effect of their suitable surface binding sites and large surface areas (House, 2003; Lijklema, 1980). P sorption removes dissolved P from porewater or directly from the water column, promoting P retention and storage in sediments. P sorption occurs via ligand exchange and electrostatic attraction between positively charged binding surfaces and either orthophosphate (H2PO4- and HPO42-), or the phosphate groups of dissolved organic P species (e.g. DNA-P and RNA-P) (Withers & Jarvie, 2008; Karl & Björkman, 2015). Desorption mobilizes P and can be induced by changes in pH, redox condition, and aqueous anion concentration that result in increased competition for binding sites or decreased electrostatic attraction (Withers & Jarvie, 2008). For example, phosphate sorption becomes less effective with increasing pH, which enhances competition for iron or aluminum ion binding sites from hydroxyl ions (Lijklema, 1980). The same effect can be observed with increasing aqueous anion concentration due to surface binding site competition (Froelich, 1988). Under anoxic conditions, iron (Fe III) (hydr)oxides and phosphates will undergo reductive dissolution, releasing any phosphate within or bound to their structures to the porewater, or to non-redox sensitive solid phases (Mortimer, 1941; Parsons et al., 2017). The sorption and desorption of dissolved P by suspended solids and sediments are important processes in controlling the levels of P available for uptake by biota (Froelich, 1988).

1.2.2 Precipitation/dissolution

Unlike phosphate adsorbed to particulate surfaces, phosphate minerals represent potentially more stable long-term sinks for P in the sediments. Calcium and iron phosphate minerals particularly are commonly observed in aquatic sediments, and the precipitation and dissolution of these minerals can significantly impact the distribution of P between particulate and dissolved phases (Orihel et al., 2017). Various factors control the stability of phosphate minerals such as redox condition, pH, temperature, and pore water chemical composition e.g. sulfate concentration (Katsev et al., 2006). The favorable conditions for precipitation or dissolution will vary depending on the mineral under consideration. For example, precipitation of the iron-phosphate mineral vivianite ($Fe_3(PO_4)_2$) takes place under anoxic conditions with abundant iron (Fe II) ions but can be dissolved by H_2S generated during sulfate reduction (Gächter & Müller, 2003). H_2S then reacts with the Fe^{2+} (aq) mobilized from vivianite, forming iron monosulfide precipitates (FeS) such as mackinawite (Caraco et al., 1989; Gächter & Müller, 2003). In hardwater environments, co-precipitation of phosphates with calcium carbonates is also common (Parsons et al., 2017), where phosphates are retained in calcium phosphate minerals such as apatite (House et al., 1998; Markovic et al., 2019).

1.2.3 Assimilation/decomposition

Assimilation is the incorporation of dissolved P by primary producers and microorganisms into their molecular structures, resulting in the transformation of dissolved P into particulate organic P (Withers & Jarvie, 2008). Dissolved inorganic P in the forms of orthophosphate ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) are most readily available for uptake by biota; however, some forms of dissolved organic P could also be assimilated by freshwater plankton (Bentzen et al., 1992). Assimilation by phytoplankton and bacteria occurs within the water column and also by periphyton at the sediment-water interface (Dodds, 2003). After death, biomass P is re-mobilized during decomposition, producing dissolved organic P, which could be assimilated again by phytoplankton, or further broken down to orthophosphate through mineralization and hydrolytic processes (Orihel et al., 2017).

1.2.4 Sedimentation and resuspension

Suspended particles are deposited under slower flow conditions and may act as a significant source of P to sediments. The composition of deposited particulate P is highly variable and may occur in mineral or organic forms such as dead algal debris (House et al., 1998; Shinohara et al., 2012; Joshi et al., 2015). Deposition of suspended inorganic solids such as clay particles and iron oxides and hydroxides can provide a sink for dissolved P subsequent to sorption processes in the water column. Any P already bound to the depositing particles will be removed from the water column and stored in the bottom sediments, at least temporarily (Keup, 1968). The conditions at the sediment-water interface and diagenetic processes will ultimately determine whether long-term retention (sorption, precipitation, and assimilation) or mobilization (desorption, dissolution, and decomposition) of P will occur. Resuspension of sediments due to increased flow, localized water current, and bioturbation mobilizes fine grained particulate P and dissolved P previously entrapped in pore water, leading to higher P transport to downstream river (Withers & Jarvie, 2008; Matisoff & Wang, 1998). However, physical mixing could also increase the oxygen level at the sediment-water interface and transfer anoxic sediments into the oxygenated water column, promoting P retention processes such as iron phosphate precipitation (Reddy et al., 1999).

1.3 Phosphorous retention by dammed reservoirs

Damming can drastically modify a river's natural flow regime by transforming a portion of the river channel into a reservoir, which exhibits both river-like and lake-like characteristics. Compared to the original river environment, a reservoir has longer water residence time, lower flow velocity and water turbidity, and higher rates of primary production (Friedl and Wüest, 2002). Furthermore, the timing and quantity of riverine nutrient transportation to downstream water bodies are disrupted by damming (Van Cappellen & Maavara, 2016). This includes modifications to P fluxes, speciation, and bioavailability, which is especially important to downstream algal growth due to P's role as a limiting nutrient to primary production (Vollenweider, 1968; Schindler, 1977). Within a reservoir, three compartments could typically be observed: 1) a fluvial environment where the river enters the reservoir with the highest flow velocity and turbidity, 2) a lentic environment closest to the dam wall where the water is the most stagnant and deepest (most favorable for stratification), and 3) a transitional environment in-between the previous two compartments (Soares et al., 2012). After dam construction, the reduced flow velocity and increased water residence time promote assimilation of dissolved P by biota, followed by subsequent burial in the bottom sediments (Friedl and Wüest, 2002). Furthermore, suspended particulate P deposits at higher rates under lower flow conditions, and longer water residence times allow longer duration of contact between dissolved P and sediments, enhancing sorption processes (House et al., 1998; Neal et al., 2006; Froelich, 1988). Damming also alters the natural water volume to bed sediment ratio, with implications for the dominant P processes. P processes at the sediment-water interface typically dominate under lower water volume to bed sediment ratio (e.g. headwater streams), while processes associated with suspended particles and assimilation by biota within the water column are most prominent under higher water volume to bed sediments ratio (Withers & Jarvie, 2008). Thus, the dominant P processes could evolve within a reservoir while transitioning from the shallower fluvial environment with higher flow velocity to the deeper lentic environment with more stagnant water.

While reservoirs are known to attenuate P, the retention efficiency could vary between different P species. For example, reservoirs in Luxembourg have higher TP retention efficiencies compared to DRP, and similar responses were observed in reservoirs in the Lake Winnipeg drainage basin, where retention efficiencies were higher for TP than total dissolved P (Salvia-Castellvi et al., 2001; Donald et al., 2015). Based on data compiled by Maavara et al. (2015) from 155 dammed reservoirs, P retention efficiency generally correlates ($r^2 = 0.14$) with water residence time on a global scale, where higher P is retained in reservoirs with longer residence times (Figure 1.1). This indicates that P retention efficiency of a reservoir could vary temporally between seasons and years depending on hydrological regimes and dam management practices. While the rate of inflowing water is dictated by upstream river's flow, the discharging quantity and location from the reservoir could be controlled by dam operations, with effects on water residence time and total water volume.

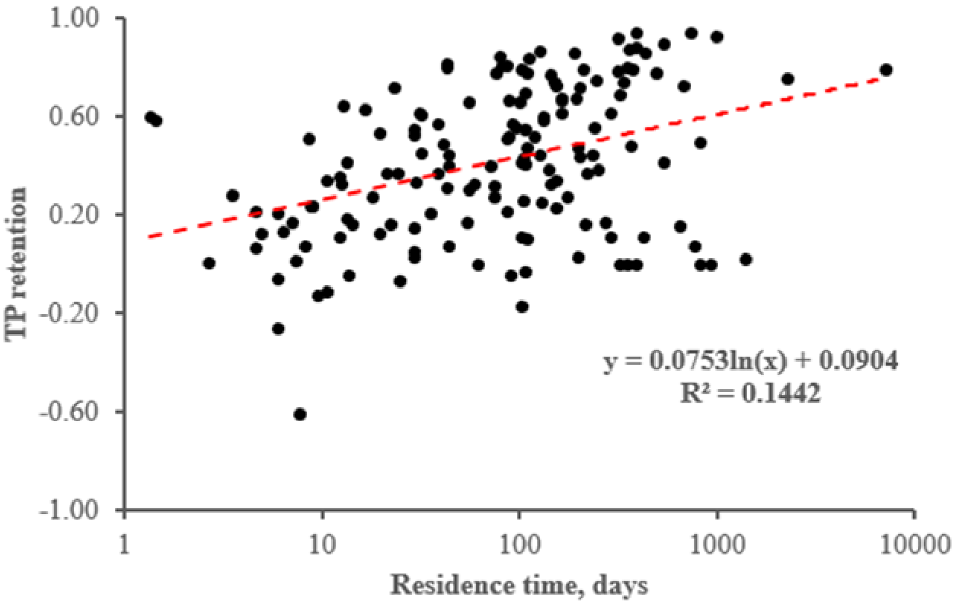

Figure 1.1 Global TP retention efficiency under various water residence time (dataset compiled by Maavara et al., 2015).

Under certain conditions at the sediment-water interface, bottom sediments can act as a P source to the overlying water through internal P loading. This is most commonly observed in lakes and reservoirs with long history of eutrophication and nutrient pollution. Large quantities of legacy P accumulated in the sediments act as an important source of DRP even after decreases to external P loading (Søndergaard et al., 2013). Internal P loading involves various physical and biogeochemical mechanisms that are commonly associated with orthophosphate and organic P such as: 1) desorption of phosphate from clay particles and iron (III) or aluminum oxide and hydroxides, 2) dissolution of minerals containing phosphate in their structures, and 3) hydrolysis and mineralization of organic matter (Orihel et al., 2017). Numerous environmental conditions have important effects on internal P loading such as: pH, ionic strength, water hardness, oxygen content, and nitrate concentration. The most notable and commonly observed condition that favors internal loading is low dissolved oxygen concentration at the sediment-water interface. In surficial sediments, P is often retained by iron (III) (hydr)oxides, which are redox sensitive. During prolonged anoxic events, iron (III) (hydr)oxides will undergo reductive dissolution, releasing any adsorbed P to porewater, where it may remain or become associated with alternative solid phases within the sediments (Mortimer, 1941; Parsons et al., 2017). A positive feedback relationship between algal blooms and reductive dissolution is therefore observed. The degradation of algae necro mass at the sediment-water interface first consumes benthic oxygen, leading to anoxia or hypoxia conditions that facilitate reductive dissolution of iron (III) (hydr)oxides and internal P loading, which mobilizes more bioavailable P for algal growth in surface water. However, high nitrate concentration could prevent or delay iron (III) (hydr)oxide reductive dissolution during short periods of anoxia (Ripl, 1976). After oxygen is depleted, nitrate acts as a terminal electron acceptor during mineralization of organic matter, with more favorable energetic yield than iron (III), thus preventing the reductive dissolution of iron (III) (hydr)oxides and the release of associated P to the aqueous phase (Parsons et al., 2017).

On the Thames River, the extent of P retention or export caused by dammed reservoirs have not been extensively assessed. A couple studies (Vandermeulen & Gemza, 1991; Nürnberg & LaZerte, 2015) were conducted on one of the Thames River's dammed reservoirs (Fanshawe Reservoir), where annual P mass balance was estimated. However, these studies were based on data collected during the summer months (May to October), and the load estimations only provide single season (summer) mass balance, or annual mass balance extrapolated from single season estimations. Further, neither of these studies was subject to peer-review. This lack of comprehensive understanding of reservoir-effects along the Thames River is reflected by the almost entirely land-based P load reduction strategies currently in place or proposed. The potential to integrate dammed reservoirs as points of intervention has not been fully considered yet.

1.4 The role of nutrient ratio on HABs and influences of dammed reservoirs

The reduction of excess P loads has been the focal point of GLWQA since its inception; however, the roles of nitrogen (N) and silicon (Si) as potential controls on HABs have also received considerable attention (e.g. Officer & Ryther, 1980; Conley et al., 1993; Conley et al., 2009; Paerl, 2009; Andersen et al., 2020). Both N and P are essential elements of life and are often the primary limiting nutrients for primary production in aquatic environments (Paerl, 2009). Although Si is not an essential element for all life, it is essential for diatoms, an important phytoplankton group inhabiting freshwater and marine environments (Humborg et al., 2000; Struyf et al., 2009). The ratio at which phytoplankton uptake N, P, and Si is benchmarked against the Redfield-Brzezinski ratio of N:P:Si = 16:1:15 (Redfield, 1934; Brzezinski, 1985). However, Redfield-Brzezinski ratio was determined using the average marine phytoplankton biomass. Thus, the preferred N:P:Si uptake ratios vary between phytoplankton species, and an environment's N:P:Si availability can shape the composition of phytoplankton communities (Hecky & Kilham, 1988; Lagus et al., 2004).

In Si limited environments, diatoms are out competed by non-siliceous phytoplankton such as flagellates and cyanobacteria, which contain a higher portion of undesirable and harmful species capable of producing toxins (Officer & Ryther, 1980; Conley et al., 1993). In contrast, due to the rapid growth rates of diatoms, waters rich in Si generally favor diatom blooms until dissolved Si is depleted (Conley, 2002; Paerl et al., 2006; Royer, 2019). In temperate water bodies, diatom blooms are common occurrences during late spring or early summer, followed by a period of Si limitation during which non-siliceous phytoplankton dominate (Officer & Ryther, 1980; Conley, 2002).

The effect of N availability on phytoplankton community composition is arguably more complex than Si. Schindler (1977) theorized that cyanobacterial blooms may be favorable under N limited conditions due to diazotrophic cyanobacteria's ability to fix atmospheric N_2 in response to N deficits. To limit occurrences of cyanobacterial blooms, Schindler (1977) recommended against the reduction of external N load to maintain high N:P ratios and identified excess P as the primary driver of HABs. However, N fixation is an energy intensive process, and rates of N fixation are typically lower than rates of denitrification, a process that eliminates bioavailable N (Seitzinger, 1988). A lack of N accumulation in most U.S. lakes was demonstrated by Scott et al. (2019), with results showing N deficit in majority of eutrophic and hypereutrophic lakes, highlighting the need for dual nutrient reduction strategies addressing both P and N pollutions. Moreover, increased N availability, relative to P, can alter the composition of cyanobacterial blooms, with effect on bloom toxicity (Moisander et al., 2003; Kangro et al., 2007). In the Lake Erie's western basin, elevated N concentrations promoted the growth and toxin production of non-diazotrophic cyanobacteria, such as Microcystis, resulting in more toxic cyanobacterial blooms (Gobler et al., 2016). Although excess P loads have historically been considered as the primary driver for freshwater eutrophication and algal bloom formation, excess N loads and the ratios of N:P:Si availability could act as important controls on the composition and harmfulness of algal blooms.

Historically, Si concentrations in rivers were commonly in surplus compared to N and P (Davidson et al., 2012). However, riverine N and P loads have approximately doubled since pre-industrial time, primarily from excess fertilizer runoffs and wastewater discharge (Galloway, 1998; Filippelli, 2008). Riverine Si loads, on the other hand, have remained relatively constant in comparison to N and P, and may fluctuate depending on the type of land use changes within the watershed (Conley, 2002). For example, agricultural activities typically remove biogenic Si from the local terrestrial ecosystem during crop harvesting, thus decreasing riverine Si loads (Struyf et al., 2010). In contrast, urbanization tends to increase riverine Si loads as a result of higher runoffs from impervious surfaces and removal of vegetation covers that act as Si sinks on the landscapes (Carey & Fulweiler, 2012).

The disproportionate increases to N, P, and Si loads driven by anthropogenic forces from the landscape is further modified along the river corridors by dammed reservoirs, which tend to retain N, P, and Si fluxes (Friedl & Wüest, 2002; Humborg et al., 2000). Similar to P retention processes, in-reservoir retention of Si is driven by increased water residence time, which promotes Si uptake by diatoms and subsequent burial in reservoir sediments (Humborg et al., 2000; Conley, 2002). Retention of N occur by a combination of burial and denitrification processes in the sediments; however, in-reservoir N fixation could offset retention by introducing additional N from the atmosphere (Akbarzadeh et al., 2019). On a global scale, dammed reservoirs retain 7% of total N, 12% of total P, and 5% of reactive Si (Maavara et al., 2020a). The preferential retention of P over N and Si by reservoirs, coupled with the disproportionate increase of nutrient exports from the landscape, are altering riverine N:P:Si flow, with potential effects on downstream phytoplankton communities and HAB severity.

1.5 Thesis structure

In this thesis, I address the following research questions:

1. What are Fanshawe Reservoir’s P retention efficiencies on annual and seasonal time scales?

2. What are the changes to Thames River’s P load speciation exerted by Fanshawe Reservoir?

3. What are Fanshawe Reservoir’s N and Si retention efficiencies?

4. What are the changes to Thames River’s N:P:Si ratio exerted by Fanshawe Reservoir?

In Chapter 2, I use a mass balance approach to calculate P retention efficiencies (Research Question 1) and compare DRP:TP ratios between inflow and outflow of the reservoir (Research Question 2). By addressing these two research questions, I hope to identify Fanshawe Reservoir’s influence on Thames River’s P flow to downstream Lake Erie.

In Chapter 3, I expand my mass balance approach to include N and Si (Research Question 3) and compare N:P:Si ratios between inflow and outflow of the reservoir (Research 4). The main objective of this chapter is to assess Fanshawe Reservoir’s influences on Thames River’s nutrient ratio, with implications to downstream phytoplankton community composition.

In Chapter 4, I summarize the main conclusions from Chapter 2 and 3 and discuss potential research directions to be taken after this thesis.

Phosphorus retention and transformation in the Thames River, Ontario: Influence of a dammed reservoir on phosphorus load and speciation

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Chapter 2

Phosphorus retention and transformation in the Thames River, Ontario: Influence of a dammed reservoir on phosphorus load and speciation

2.1 Summary

In response to the re-eutrophication of Lake Erie, extensive efforts are underway to reduce phosphorus (P) export from the watershed. On the Canadian side, the Thames River is the largest tributary source of P to Lake Erie's western basin. However, the role of dammed reservoirs in retaining and modifying riverine P loads from the watershed has not been evaluated comprehensively. We determined via mass balance whether Fanshawe Reservoir, the largest reservoir on the Thames River, was a source or sink of P during 2018 and 2019. Additionally, we evaluated the reservoir's influence on P speciation by comparing the dissolved reactive P to total P ratio (DRP:TP) of upstream and downstream loads. We used four different load estimation models to calculate the range of P loads and retention efficiencies based on year-round discharge and water chemistry data. Annually, Fanshawe Reservoir was a net sink for P, retaining 28% (41 tonnes) and 48% (92 tonnes) of inflowing TP in 2018 and 2019, respectively. Seasonally, the reservoir oscillated between a source and a sink of P. Net P release occurred during the summers of 2018 and 2019 and the spring of 2018, driven by internal P loading and increased discharge from the dam. The reservoir did not exert a strong influence on DRP:TP annually, but increases were observed during both summers, concurrent with internal loading. Our analysis demonstrates that Fanshawe Reservoir is not only an important P sink on the Thames River, but also modulates the timing and speciation of riverine P loads from the watershed.

2.2 Introduction

Beginning in the 1960s, the detrimental effects of eutrophication became apparent in Lake Erie (USA-Canada), such as severe harmful algal blooms (HABs), development of hypoxic zones, and general deterioration of water quality and ecosystem health (Dolan, 1993). This dire situation led to a binational collaborative effort between the U.S. and Canadian governments in the form of the Great Lakes Water Quality Agreement (GLWQA) in 1972. The GLWQA provided a framework for action plans, policies, and by-laws within the Lake Erie watershed that greatly reduced point source P pollution mainly through wastewater treatment plant (WWTP) upgrades and regulation of phosphate concentration in detergents (Dolan, 1993). These measures were largely successful and a decrease in the prevalence and severity of

HABs was observed in the following decade (De Pinto et al., 1986). However, since the late 1990s, HABs have been increasing in frequency and severity in the western basin of Lake Erie (Michalak, 2013). Excess P input from the lake's watershed is recognized as one of the primary drivers behind this re-eutrophication (Watson et al., 2016; Mohamed et al., 2019). While point source P loads have decreased significantly compared to the 1970s and have remained at a relatively steady level since the 1980s, non-point source (NPS) P loads have not seen any significant changes and have emerged as the dominant source of P to Lake Erie (Scavia et al., 2014).

To address this re-eutrophication, more stringent P load reduction targets were adopted by the Canadian and the U.S. governments, which specify a 40 percent reduction of spring TP and DRP loads from priority tributaries that discharge to the western and central basins of Lake Erie (binational.net, 2016). On the Canadian side of the Lake Erie watershed, the Thames River is the largest tributary P source to the western basin (Maccoux et al., 2016) and was identified as a priority tributary for P load reduction (Annex 4 Objectives and Targets Task Team, 2015). Within the Thames River watershed, there have been major and renewed efforts to mitigate NPS P losses from the landscape through implementation of agricultural best management practices (BMPs) and storm water management in urban centers (Agriculture, Food and Rural Affairs, 2015; Environment and Climate Change Canada & Ontario Ministry of the Environment and Climate Change, 2018; Upper Thames River Conservation Authority, 2018). However, a quantitative understanding of the processes influencing P transformation, retention, and remobilization within the Thames River between source areas and the river mouth is still lacking. Particularly, how riverine processes alter the quantity, timing, and speciation of P load delivered to Lake St. Clair.

It has been long recognized that dammed reservoirs modify nutrient fluxes and cycling in rivers (Friedl & Wüest, 2002; Teodoru & Wehrli, 2005; Van Cappellen & Maavara, 2016; Maavara et al., 2020a). On a global scale, reservoirs act as P sinks along river corridors, retaining an estimated 12% of TP load. However, the measured retention efficiencies of individual reservoirs vary widely, ranging from source to sink (Maavara et al., 2015; Némery et al., 2016; Teodoru & Wehrli, 2005). Predicting the influence of any individual reservoir on nutrient retention and transformation can be challenging due to the complex interaction of multiple biogeochemical processes in the water column and sediments (Powers et al., 2015; Donald et al., 2015). Compared to natural riverine environments, reservoirs have longer water residence time, lower flow velocity and turbidity, and deeper light penetration (Friedl & Wüest, 2002). The summation of these lake-like properties enhances in-reservoir primary production and P cycling processes, typically leading to retention of P through sedimentation of both organic and mineral particulate matters

(Van Cappellen & Maavara, 2016). Generally, P retention efficiency correlates with water residence time (Kõiv et al., 2011; Maavara et al., 2015, Donald et al., 2015). However, net release of P can occur in reservoirs with a history of high external P inputs, particularly when external P loads from the watershed decrease, as legacy P in the sediments may be mobilized through internal loading (Søndergaard et al., 2001; Orihel et al., 2017). Furthermore, the speciation and bioavailability of P load may be altered by in-reservoir biogeochemical processes. For example, at the Iron Gate I Reservoir on the Danube River, in-reservoir transformation of particulate P to dissolved P (DP) resulted in a 20% increase to the DP:TP load ratio leaving the reservoir (Teodoru & Wehrli, 2005).

There are three major dammed reservoirs on the Thames River: Pittock, Wildwood, and Fanshawe (Figure 2.1). Of these, Fanshawe Reservoir is the most downstream and has the largest watershed area, surface area, and water storage volume (1430.7 km^2, 2.7 km^2, and 13.1 x 10^6 m^3) (Nürnberg & LaZerte, 2005; Ontario Ministry of Natural Resources and Forestry, 2020). To the best of our knowledge, two previous P mass balance studies have been conducted for Fanshawe Reservoir. The first, conducted by the Ontario Ministry of Environment in 1989 and 1989, was based on relatively high-resolution water chemistry and discharge data, but was limited to the summer season (May to September); the findings of this study concluded that the reservoir was a sink in 1988 but a source of P in 1989 (Vandermeulen & Gemza, 1991). The second and more recent study estimated a long-term P retention efficiency of -28%, indicating that the reservoir has been a net source of TP to the Thames River over several decades (1975 to 2004) (Nürnberg & LaZerte, 2005). However, the P concentration data were sparse (e.g. four data points in 2004) and were, like the first study, confined to the growing season (May to October) which limited the accuracy of loading calculations on which annual P retention estimates were based (Lee et al., 2016).

We hypothesized that in-reservoir P retention and transformation would vary seasonally, due to variations in hydrology as well as physical and biogeochemical processes in the reservoir. By including data spanning all seasons and flow regimes we could improve our conceptual and quantitative understanding of Fanshawe Reservoir's influence on P load and speciation of the Thames River. Specifically, in this study we aimed to 1) determine Fanshawe Reservoir's annual and seasonal retention efficiencies for different P fractions: DRP, dissolved unreactive P (DUP), and particulate P (PP), using a mass balance approach, and 2) assess the changes to P speciation and eutrophication potential using DRP:TP ratio as an indicator. We also discuss the implications of these findings for nutrient management strategies within the watershed.

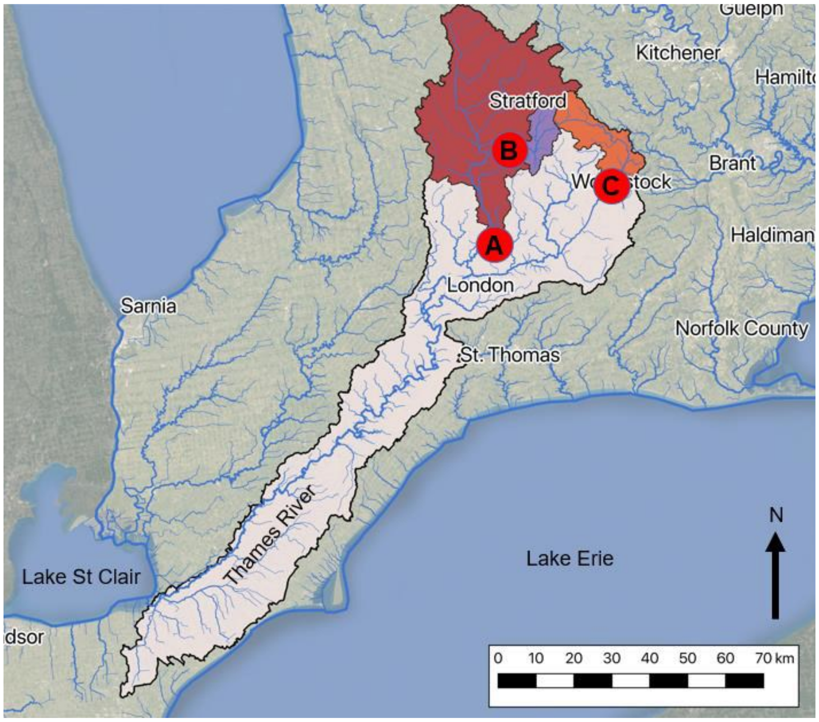


Figure 2.1 Thames River watershed (black outlined area) and locations of reservoirs Fanshawe (A), Wildwood (B), and Pittock (C) with their respective subwatershed colorized in the order of red, purple, and orange. Thames River discharges into Lake St. Clair, which shortly flows into Lake Erie through the Detroit River (not shown).

2.3 Study site and method

2.3.1 Fanshawe Reservoir

Fanshawe dam was constructed in 1953 primarily for flow regulation to avoid flooding in the City of London, which is located approximately 12 km downstream of the dam (Vandermeulen & Gemza, 1991). Currently operated and maintained by the Upper Thames River Conservation Authority (UTRCA), Fanshawe Reservoir also provides hydroelectricity generation (2860 megawatt year^{-1}) and recreational opportunities (UTRCA, n.d.). According to flow data collected between 1981 to 1991 by Water Survey Canada (WSC), Fanshawe Reservoir receives about 97% of its inflow from the Thames River, while the remaining 3% are accounted for by a minor tributary, Wye Creek. Primary outflow from the reservoir is controlled by the dam, which discharges downstream to the Thames River through bottom draw valves 8 to 10 meters below the water surface. The flow is maintained at similar rate to the upstream flow under normal operating conditions. When the water level is high, surface water can also be released through sluice gates at the dam wall.

Generally, three zones can be identified in run-of-the-river reservoirs based on hydrological behaviors: 1) fluvial zone where the river first discharges into the reservoir, 2) lentic zone closest to the dam wall where water is the deepest and most stagnant, and 3) transitional zone in-between fluvial and lentic zones (Soares et al., 2012). The morphology of Fanshawe Reservoir follows this model quite closely, with a mean water depth of 4.82 m and a maximum depth of 12.1 m close to the dam wall (Nürnberg & Lazerte, 2005). Based on historical data collected between 1954 and 2004, water residence time at Fanshawe Reservoir is approximately 10 days (Nürnberg & Lazerte, 2005). On a seasonal timescale, however, water residence time ranged from 43 days (summer 2018), to 6.5 days (spring 2019) during the study period (UTRCA, personal communication, June 4, 2019).

2.3.2 Mass balance approach

To determine retention efficiency (Eq. (**2.1**), a mass balance approach was used accounting for the major riverine inflow and outflow P loads (Figure 2.2). For inflowing loads, the Thames River upstream of the reservoir is the dominant source, with additional inflow from Wye Creek. TP loads from a local wastewater treatment plant (Thorndale WWTP), which discharges into the Thames River between the upstream sampling site and the reservoir was also accounted for. The only discharge location of the reservoir is at the dam wall, which represents the outflow load.

$$Retention\ (\%) = \left(\frac{Load_{in} - Load_{out}}{Load_{in}}\right) \times 100 \tag{2.1}$$

Expressed as a percentage here, retention efficiencies of positive values indicate net retention of P (sink), and negative values indicate net release of P (source) from the reservoir. In comparison to riverine loads, P inputs via precipitation and groundwater are estimated to be negligible and so were excluded (Keup, 1968; Nürnberg & Lazerte, 2005).

Mass balance calculations were conducted for both annual and seasonal timescales, which were defined based on meteorological definition: winter (December 1 – February 28), spring (March 1 – May 31), summer (June 1 – August 31), and fall (September 1 – November 30) (Kutta & Hubbart, 2016).

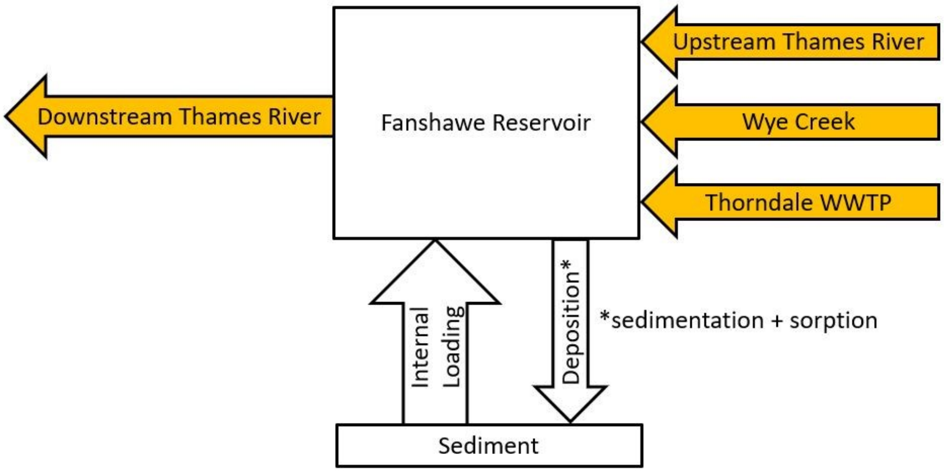


Figure 2.2 Mass balance box model showing inflow and outflow phosphorus loads (yellow arrows) and in-reservoir processes (white arrows).

2.3.3 Streamflow data

Daily discharge data of the Thames River at upstream (station ID: 02GD015) and downstream (station ID: 02GD003) of Fanshawe Reservoir were calculated based on water level (stage) measurements recorded at a 5 minute interval and a corresponding stage-discharge curve. These data were obtained from WSC between December 1, 2017 and November 30, 2019. Unfortunately, similar data collection at a hydrometric station on Wye Creek (station ID: 02GD013) ended in 1991. Therefore, we estimated daily discharge of Wye Creek using a regression relationship between the upstream and Wye Creek WSC stations based on data collected between 1981 and 1991 ($r^2 = 0.759$, RMSE = 0.39) (Appendix A, Figure A.1 and Eq. A1).

2.3.4 River water sample collection

Between March of 2018 and December of 2019, water grab samples were collected by hand at the upstream, downstream, and Wye Creek sites (Figure 2.3) at biweekly intervals (once every two weeks) with supplementary sampling during high flow events. Water grab samples were also collected at the upstream and downstream sites by Environment and Climate Change Canada (ECCC) under the Great Lakes Nutrient Initiative during the time frame of the study (December 2017 to October 2018) and the resultant data were incorporated into load calculations herein. The combined dataset included 72 samples at each of the upstream and downstream sites, and 51 samples at the Wye Creek site.

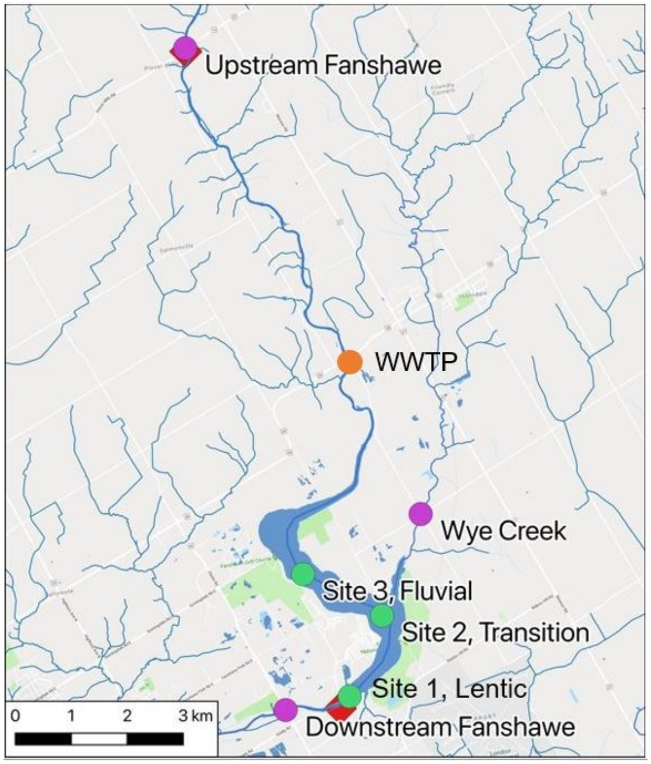


Figure 2.3 Sampling sites at Fanshawe Reservoir and the Thames River. River water sample site, reservoir water sample site, and Water Survey Canada stations are colorized in purple, green, and red, respectively. Location of Thorndale WWTP is colorized in yellow.

2.3.5 In-reservoir water sample collection

Sampling was also conducted at three sites within the reservoir (Figure 2.3). Site locations were selected to represent lentic (site 1), transitional (site 2), and fluvial (site 3) environments. Sites 1 and 2 were further separated into two sampling depths to represent epilimnion (surface water) and hypolimnion (bottom water) lake conditions. Water samples within the reservoir were collected using a peristaltic pump (Pegasus Alexis). Epilimnion samples were collected 1 m below the water surface, and hypolimnion samples were collected 1 m above the bottom sediments. In-reservoir samples were collected on river sampling days excluding high-flow events. Reservoir data were not used in loading model calculations but provided insights on P-cycling processes occurring within the reservoir, with implications for seasonal patterns in retention efficiency and speciation changes.

Water column profiles were taken using a profiler (RBR XR-620) at the three reservoir sites prior to collection of water chemistry samples. Water column profiles include temperature, depth, and dissolved oxygen content.

2.3.6 Analytical methods

The concentrations of three operationally defined P fractions were determined from the river and reservoir water samples: TP, DRP, and total dissolved P (TDP). With the exception of TP analysis, all samples were filtered (< 0.45 μm nylon membrane) upon collection and stored in the dark at ~4°C in glass or polyethylene bottles during transport and prior to analysis. Samples collected by researchers at the University of Waterloo (UW) and ECCC were analyzed in the UW Ecohydrology Laboratory and the Burlington National Laboratory for Environmental Testing (NLET), respectively. In both laboratories, DRP was measured colorimetrically using the molybdate blue method first described by Murphy and Riley (1962). (UW MDL 0.05 μmol L^{-1}, NLET MDL 0.006 μmol L^{-1}). TDP was analyzed by ICP-OES (Thermo Scientific iCAP 6300) at UW (MDL 0.3 μmol L^{-1}) and colorimetrically, after acid persulfate autoclave digestion at NLET (MDL 0.016 μmol L^{-1}). In both laboratories, TP samples were subjected to acid persulfate autoclave digestion prior to analysis (Ontario Ministry of the Environment, 2015; Dayton et al., 2017). The resulting digestate was analyzed by ICP-OES (Thermo Scientific iCAP 6300) at UW (MDL 0.5 μmol L^{-1}) and colorimetrically at NLET (MDL 0.016 μmol L^{-1}). The precision and accuracy for all analyses at UW was <10% RSD based on triplicate measurements of the samples, and ±10% with respect to certified reference materials. Matrix based standards were used for all calibrations. All reagents used during analyses at UW were of ACS reagent grade purchased from Acros Organics, Fischer Chemical, EMD Millipore or Sigma-Aldrich and prepared using 18.2 MΩ.cm^{-1} water (Millipore).

2.3.7 Weather and streamflow regime

To assess whether the weather regime during our study period was representative of typical conditions, we obtained daily records of precipitation and temperature data between 2003 and 2019 from Meteorological Service of Canada’s London CS station (Climate ID: 6144478), which is located approximately 2.5 km from Fanshawe Reservoir. Using the definition from Knapp et al. (2015), we classified wet and dry years based on percentiles of historical distribution of total annual precipitation (TAP). Dry years have TAP <45th percentile, wet years have TAP >55th percentile, and normal years have TAP between 45th and 55th percentile. Furthermore, extreme dry years have TAP <10th percentile, and extreme wet years have TAP >90th percentile (Knapp et al., 2015). The same classification method was applied to flow data from WSC upstream station (ID: 02GD015) to determine the natural variation in the flow regime of the Thames River (e.g. conditions corresponding to low flow and high flow). We further compared the relative difference between upstream and downstream flows on annual and seasonal bases.

Under normal operating conditions, the dam's discharge is typically controlled to mimic upstream flow (UTRCA, n.d.).

2.3.8 Load and retention efficiency

Riverine nutrient loads are usually quantified by load estimation models, and although there are many different models available, no study has conclusively shown the superiority of any one model (Lee at al., 2016; Preston et al., 1989). As such, the method of choice depends on one's judgment based on a wide variety of factors such as: sample frequency and distribution, flow variability, and the strength of correlation between concentration and discharge (Richards & Holloway, 1987; Quilbe et al., 2006). Due to the intrinsic uncertainty of load estimation methods, we took an ensemble approach to establish a range of seasonal and annual loads using four commonly used load estimation models. The models used are flow-weighted averaging estimator (Walling & Webb, 1981), Beale ratio estimator (Beale, 1962), Ferguson regression (Ferguson, 1986), and Weighted Regression on Time, Discharge, and Season (WRTDS) under a modified setting (Hirsh et al., 2010). The "Time" component of WRTDS, which accounts for multi-year variations, was muted to accommodate our shorter sampling timeframe. Therefore, "WRDS" is a more accurate description of the modified model and will be used herein. All model calculations were performed in the R statistical computing environment (R Core Team, 2020); WRDS was calculated using the Exploration and Graphics for RivEr Trends (EGRET) package. For the equations and detailed descriptions of the load estimation models used, see Appendix B.

We further classified and separated TP loads into three fractions: 1) DRP, the most bioavailability form of P, 2) particulate P (PP), which is the difference between TP and TDP, and 3) dissolved unreactive P (DUP), which is the difference between TDP and DRP (Effler et al., 2009; Worsfold et al., 2016). To assess Fanshawe Reservoir's effect on P load speciation and bioavailability, we used DRP:TP ratio as a simple evaluative factor to compare between upstream and downstream loads (Baker et al., 2014).

2.4 Results

2.4.1 Weather and water flow regime

The average annual TAP from 2003 to 2019 was 954mm. Comparatively, 2018 was a wet year (TAP: 969mm) and 2019 was an extreme wet year (TAP: 1057mm). The heavier than average precipitation in 2018 and 2019 was reflected in the flow measured on the Thames River upstream of the reservoir: 2018 and 2019 were both high flow years averaging 21.2 cubic meters per second (cms) and 20.8 cms, respectively. When flow was further separated into seasons, differences were observed between the two years. In 2018, the mean flow was highest in the winter (41.4 cms), followed by spring (22.6 cms), fall (16.6 cms), and summer (4.6 cms). In 2019, the highest mean flow occurred in the spring (39.3 cms), followed by winter (26.6 cms), fall (13.0 cms), and summer (4.2 cms). On an annual basis, downstream flows were slightly higher than upstream in 2018 and 2019, at 1.4% and 5.9%, respectively. Seasonally, downstream and upstream flows generally balanced reasonably well (<10% difference), except three seasons in which downstream flows were greater (>10%) than upstream flows: 2018 spring (11%), 2018 summer (23.6%), and 2019 summer (13.5%).

2.4.2 Annual load, retention, and speciation change

In 2018, the four models provided similar estimates of annual TP loads (Figure 2.4). Upstream TP loads ranged from 156.3 to 130.9 metric tons (MT) (6.9% RSD between model outputs), while downstream TP loads ranged from 124.7 to 88.5 MT (14.6% RSD) (Table 2.1). In 2019, model estimates showed more variability, especially between the interpolation methods (flow-weighted averaging and Beale Ratio) and the regression methods (Ferguson regression and WRDS). Upstream TP loads ranged from 118.6 to 277.7 MT (37.4% RSD), while downstream TP loads ranged from 84.7 to 115.4 MT (12.9% RSD). In both years, annual DRP and PP loads were approximately equal, indicating at least half of the P load was highly bioavailable. DUP loads were substantially smaller, representing the smallest fraction of TP loads (mean of 10% at upstream site and 13.3% at downstream site between models across 2018 and 2019).

All models showed that Fanshawe Reservoir functioned as a net P sink in both 2018 and 2019 (**Figure A.2**). On an annual basis, 20% to 39% of total incoming TP was retained in 2018, and 27% to 58% was retained in 2019. Larger retention efficiency variability between models in 2019 is a result of greater variability in the 2019 load estimates. Retention of DRP was on average lower (29%, 27%) in comparison to PP (31%, 56%) when both 2018 and 2019 are considered together (2018, 2019 retention efficiencies in parentheses). However, this was driven by higher retention of PP compared to DRP in 2019.

Changes to DRP:TP of the annual loads between upstream and downstream sites are shown in Figure 2.5. In 2018, there was no clear trend in DRP:TP shown by the ensemble of loading models. Interpolation and regression methods produced conflicting model estimates. Slight decreases in DRP:TP (-0.03) are shown by interpolation methods, while the Ferguson regression method produced no change and WRDS showed a slight increase (+0.04). In 2019, however, all models showed minor increases to DRP:TP in downstream loads, ranging from +0.07 to +0.16 relative to upstream loads.

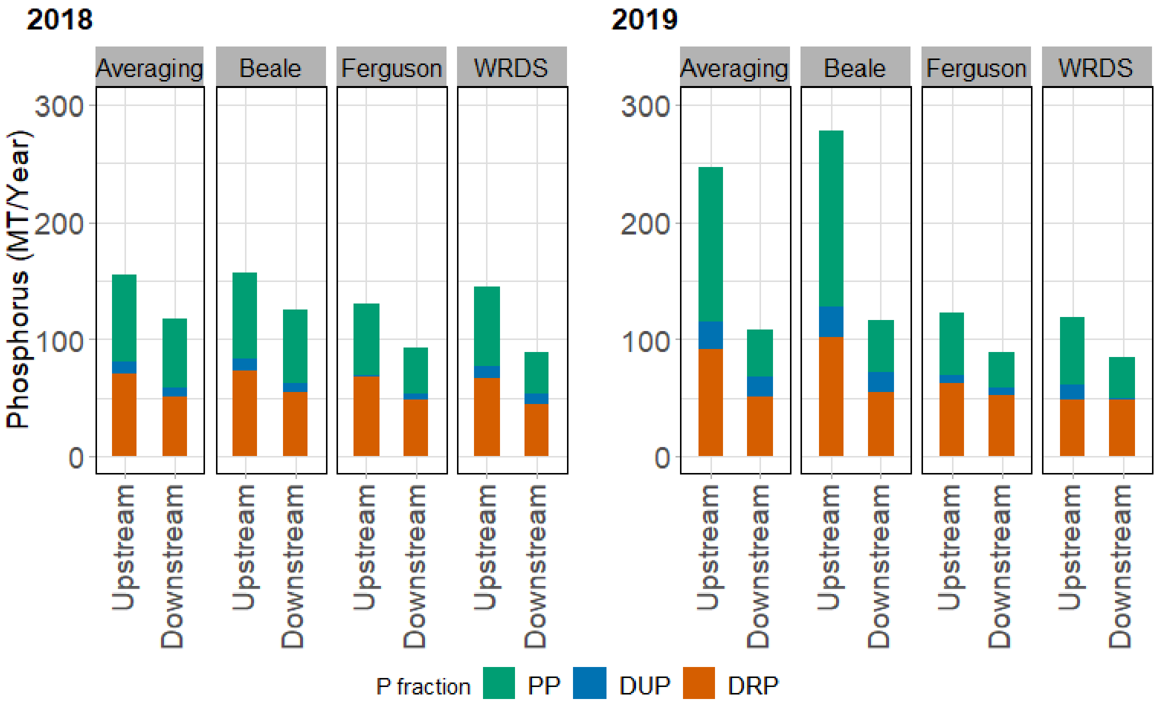


Figure 2.4 Model estimates of 2018 and 2019 annual total phosphorus (TP) loads in metric tons (MT). TP was further separated into particulate phosphorus (PP), dissolved unreactive phosphorus (DUP), and dissolved reactive phosphorus (DRP) fractions. “Averaging”, “Beale”, “Ferguson”, and “WRDS” correspond to the four models used: flow-weighted averaging estimator, Beale ratio estimator, Ferguson regression, and modified version of WRTDS, respectively.

Table 2.1 Model estimates of 2018 and 2019 annual total phosphorus (TP) loads in metric ton (MT) per year. “Averaging”, “Beale”, “Ferguson”, and “WRDS” correspond to the four models used: flow-weighted averaging estimator, Beale ratio estimator, Ferguson regression, and modified version of WRTDS, respectively.

TP load estimates (MT/year)

Model	2018 Upstream	2018 Downstream	2018 Retained	2019 Upstream	2019 Downstream	2019 Retained
Averaging	155.1	117	38.1	245.8	108.5	137.3
Beale	156.3	124.7	31.6	277.7	115.4	162.3
Ferguson	130.9	92.9	43.8	122.5	89.2	33.3
WRDS	144.7	88.5	56.2	118.6	84.7	33.9
Mean	146.8	105.8	41.0	191.2	99.5	91.7

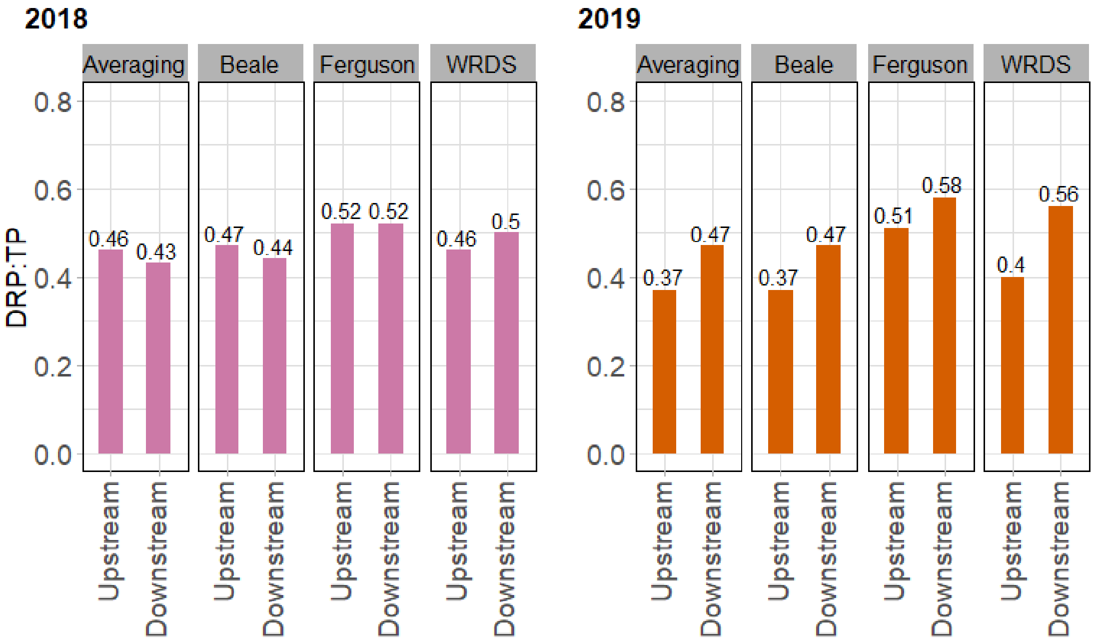


Figure 2.5 Annual phosphorus load speciation changes in 2018 (pink) and 2019 (orange) between upstream and downstream loads using ratio of dissolved reactive phosphorus to total phosphorus (DRP:TP) as bioavailability indicator.

2.4.3 Seasonal load, retention, and speciation change

Between 2018 and 2019, the mean upstream TP loads from the four load estimation models ranged widely between seasons from 1.8 MT (summer 2019) to 106.9 MT (spring 2019). Downstream TP loads followed a similar seasonal pattern, ranging from 3.8 MT (summer 2019) to 72.8 MT (winter 2018) (Figure 2.6). In 2018, at both upstream and downstream locations, the largest TP load occurred during the winter, while in 2019, the largest load occurred in spring. The smallest loads were during the summers for both years. All models produced relatively similar seasonal estimates of loading for all P fractions, except during winter and spring of 2019 at the upstream location. There was a discrepancy between interpolation and regression methods, where regression methods produced smaller TP load estimates in both seasons. For the model results of all seasonal TP loads, see Appendix A (Table A.1 and Table A.2).

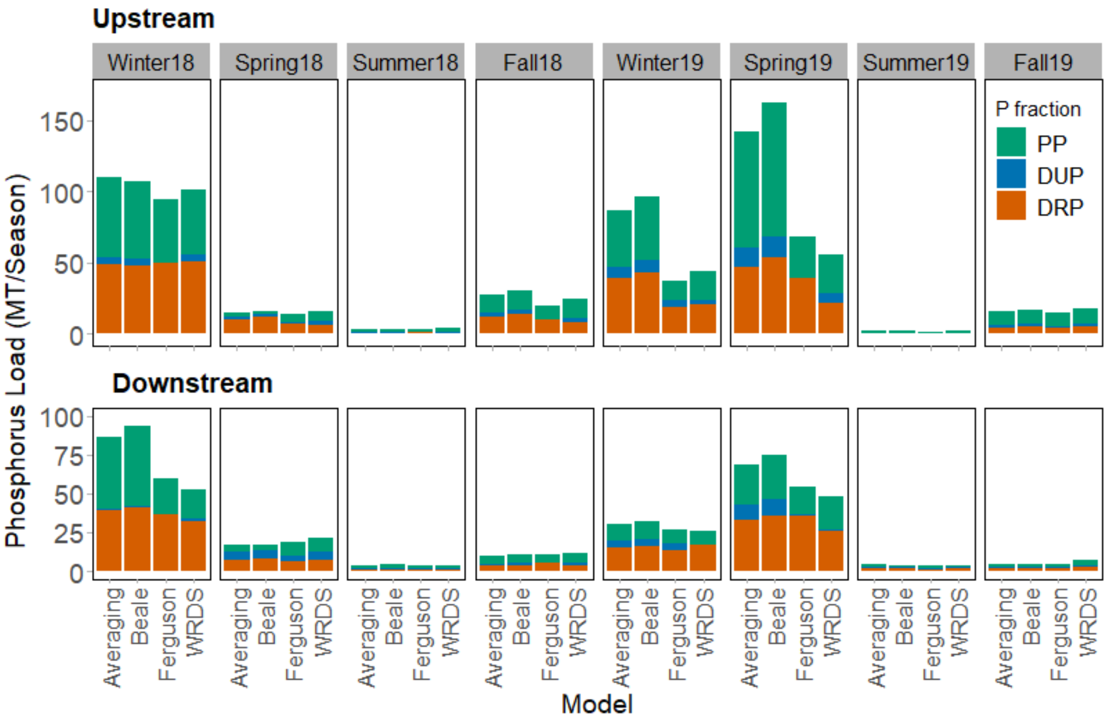
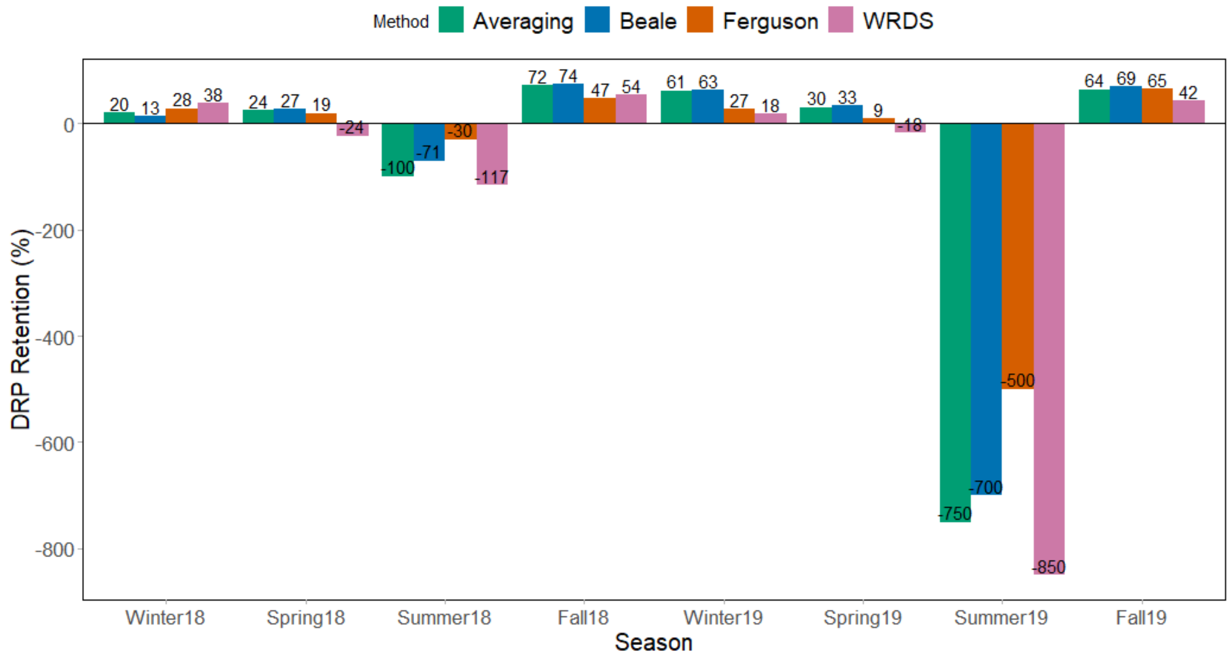


Figure 2.6 Seasonal phosphorus (P) loads from winter 2018 to fall 2019 of upstream (top 8 panels) and downstream (bottom 8 panels). TP was further separated into particulate phosphorus (PP), dissolved unreactive phosphorus (DUP), and dissolved reactive phosphorus (DRP) fractions.

TP retention efficiencies varied widely between seasons (Figure 2.7), ranging from sink (winter and fall of both years and 2019 spring) to source (summers and 2018 spring). The most negative TP retention efficiency was observed in the summer of 2019 (-113% on average between models). However, P loads delivered by the Thames River during summers were orders of magnitude lower than the high-flow seasons (winter and spring) (e.g. mean upstream TP loads was 1.8 MT in summer 2019 compared to 106.9 MT in spring 2019). Therefore, the mass of P released downstream during seasons with negative retention efficiencies was much smaller than the mass retained during the remaining seasons. For example, on average, 61 MT of TP was retained in spring 2019 at 35% retention efficiency, while only 4 MT of TP was released in summer 2019 at -113% retention efficiency. Seasonal retention of PP (Figure A.3Figure A.3 Seasonal particulate phosphorus (PP) retention in 2018 and 2019.



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and DRP (Figure A.4) followed similar trends to TP with exceptions during 2018 spring and summer: Net release of PP and retention of DRP was observed in spring 2018, while retention of PP and net release of DRP occurred in summer 2019. Downstream DRP:TP ratios were variable seasonally and there was no clear agreement across the ensemble of loading models for most seasons (Figure A.5). However, pronounced increases to DRP:TP were shown by all models during the summers of 2018 and 2019 (Figure 2.8). Conversely, in spring 2018, DRP:TP decreased markedly across all model outputs.

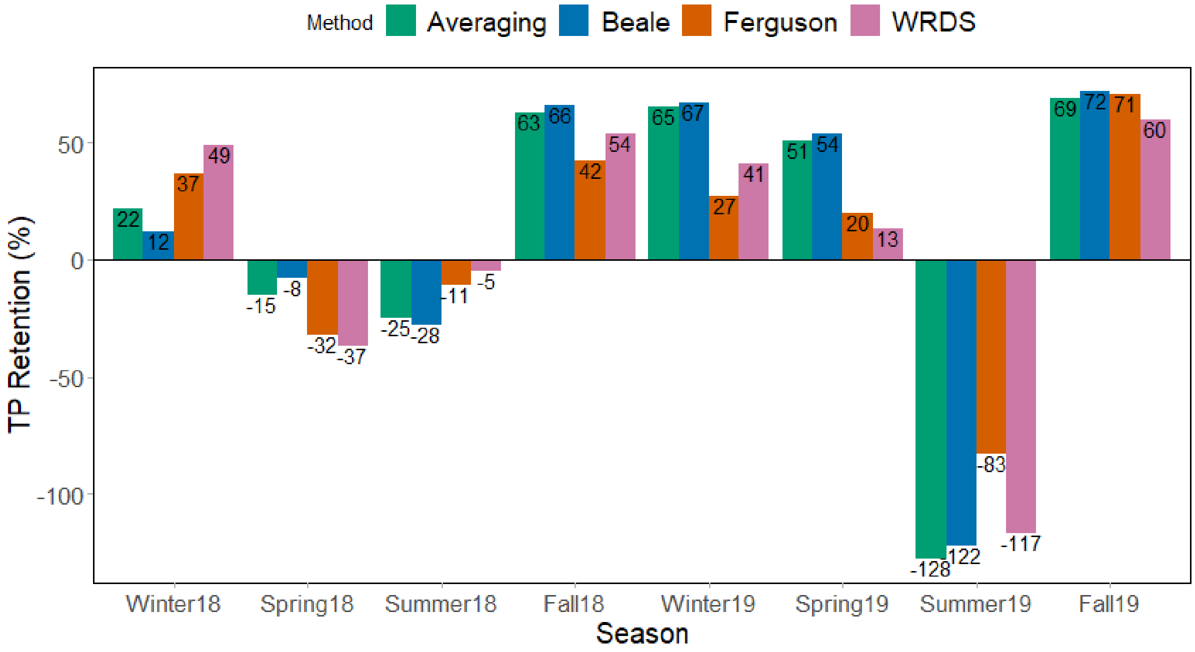

Figure 2.7 Fanshawe Reservoir seasonal total phosphorus (TP) retention efficiencies from winter 2018 to fall 2019.

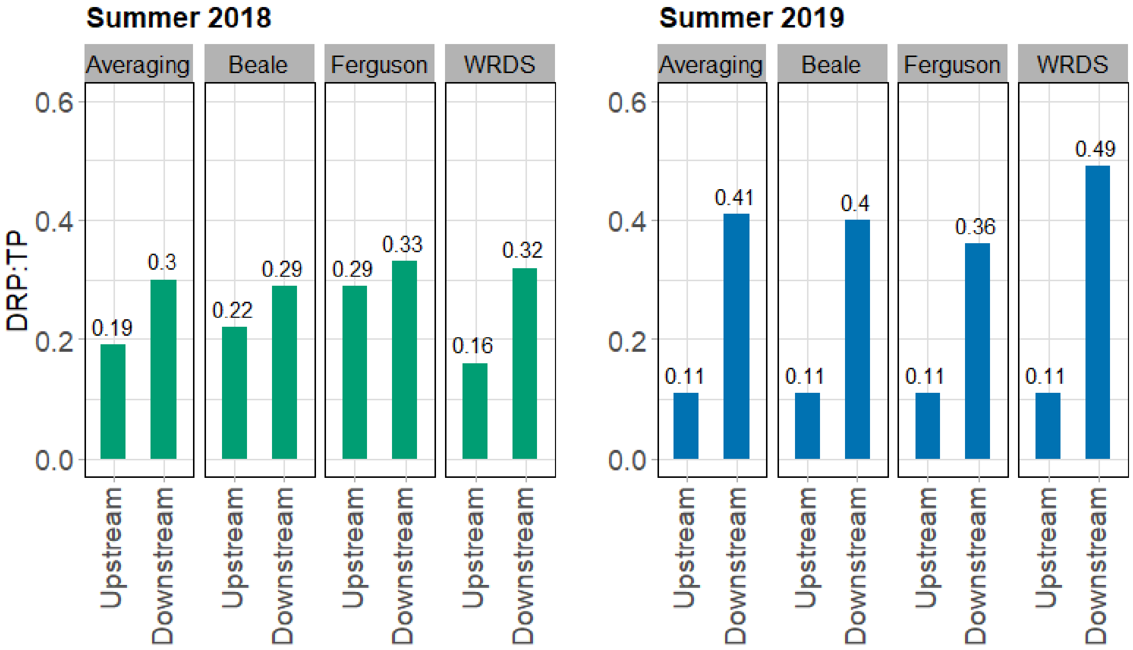

Figure 2.8 Summer seasonal speciation changes in 2018 (green) and 2019 (blue) between upstream and downstream loads using ratio of dissolved reactive phosphorus to total phosphorus (DRP:TP) as bioavailability indicator.

2.4.4 In-reservoir conditions

Based on dissolved oxygen profiles, in-reservoir stratification was observed in 2018 from May to September (no profiler data available in 2018 after September due to instrument errors) and in 2019 from July to September (**Figure A.6**). DRP concentrations measured at the lentic site showed noticeable deviation between hypolimnion and epilimnion depths during the summer seasons (Figure 2.9). Hypolimnion DRP concentrations were consistently higher from June to September in 2018 and from July to September 2019, during which the reservoir was stratified. For the complete water chemistry dataset collected (excluding ECCC data), see Annex A.

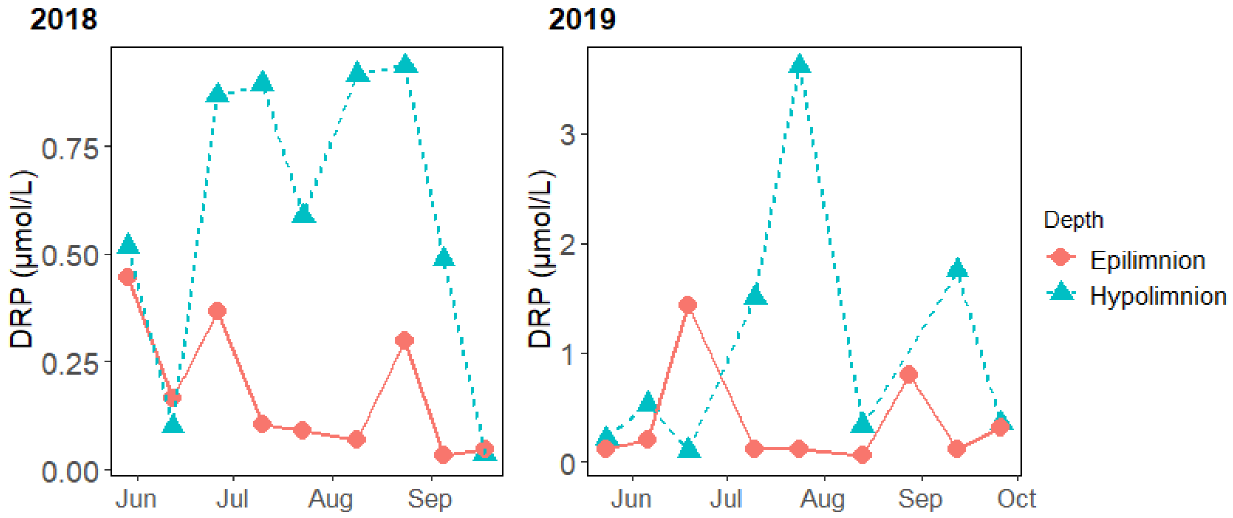

Figure 2.9 Concentrations of DRP at Fanshawe Reservoir's lentic site measured at epilimnion (solid line) and hypolimnion (dashed line) depths in summer of 2018 (left) and summer of 2019 (right).

2.5 Discussion

2.5.1 Influence of Fanshawe Reservoir on Annual P load

In contrast to a previous mass balance study which showed that Fanshawe Reservoir acted as a source of P over several decades (Nürnberg & Lazerte, 2005), our results show that Fanshawe Reservoir acted as a net sink for P in both 2018 (20-39% TP retained) and 2019 (27-58% TP retained). Although there was no temporal overlap between our study and that of Nürnberg and Lazerte, this disparity is likely due to data limitation associated with the previous study, with was confined to the growing season. Despite some variation between the various load estimation models considered here, all models are in broad qualitative agreement. These estimates taken together indicate that annual P retention efficiency in Fanshawe Reservoir is relatively high compared to other dammed reservoirs with similar water residence time (Maavara et al., 2015) and approximately twice of Lake St. Clair (Scavia et al., 2019a).

Despite its location upstream of P source areas including the City of London and the extensive agricultural areas that dominate much of the Lower Thames River watershed, Fanshawe dam exerts a major control on P transport in the Thames River. The reservoir retained 41 MT and 92 MT of TP in 2018 and 2019, respectively (Table 2.1) compared to the total annual P load from the Thames River to Lake St. Clair of 323 MT (Maccoux et al., 2016). Our TP retention estimates for 2018 and 2019 are equivalent to a reduction of 0.29 to 0.64 kg P ha^{-1} yr^{-1} from the upstream watershed. Therefore, P retention within the reservoir results in load reductions comparable in magnitude to the most optimistic modelling scenarios for nutrient management whereby multiple best management practices (cover crops, subsurface placement of fertilizer and a 25% reduction in fertilizer application rate) are simultaneously implemented on all appropriate land within the watershed (Scavia et al., 2019b).

As high order streams integrate P loads from large areas, dammed reservoirs across the Great Lakes basin collectively represent a relatively unexplored and spatially focused opportunity for phosphorus management in comparison to land-based strategies. We contend that an integrated approach that incorporates nutrient management actions in suitable reservoirs to maximize P retention, in supplement to continued land-based actions would likely result in faster and more easily measurable decreases to P loading (Macintosh et al., 2018). We therefore argue that the extent to which dam operation decisions and reservoir management influence P retention efficiency in reservoirs, particularly those in priority tributaries such as the Thames River, warrant further investigation.

Fanshawe Reservoir's role as an important P sink along the Thames River corridor also raises questions regarding the geographic placement of future P loss mitigation strategies. Since a significant portion of riverine P is retained in the reservoir, it could be argued that resources to mitigate P losses from the landscape should focus on areas downstream of the reservoir to maximize P load reduction to Lake St. Clair (Donald et al., 2015). However, it has also been shown that the magnitude, timing, and speciation of NPS P losses from Canadian agricultural lands vary considerably depending on geomorphology, soil type, and other physiographic characteristics (Plach et al., 2019). Therefore, allocating resources to mitigate P losses from agricultural areas upstream of reservoirs that exhibit high retention efficiencies may still be a defensible strategy depending on the P loss characteristics within each sub-watershed.

The significant P retention in Fanshawe Reservoir implies accumulation of a considerable legacy P within reservoir sediments, an unknown fraction of which may be at risk for remobilization by internal loading should external P loads to the reservoir or in-reservoir conditions change (Orihel et al., 2017). Assessment of the extent and stability of P legacies within sediments in Fanshawe Reservoir and in other reservoirs within the Great Lakes basin should therefore be considered a future research priority.

2.5.2 Influence of Fanshawe Reservoir on DRP:TP ratio

While Fanshawe Reservoir functions as a sink for TP, retention efficiency differs between particulate and dissolved fractions (Figure A.2), with impacts on apparent bioavailability of the P load downstream of the reservoir (Figure 2.5). Typically, PP is retained more efficiently than its dissolved counterpart in low energy waterbodies (Jossette et al., 1998). This effect was observed in 2019, during which PP was preferentially retained over DRP, resulting in elevated DRP:TP downstream of the reservoir relative to upstream. In 2018, however, the reservoir retained PP and DRP with similar efficiencies, and the DRP:TP of the P load remained relatively unchanged by P cycling within the reservoir. The different effects on P load's DRP:TP between the two years is likely due to different PP retention efficiencies during the high flow seasons (winter and spring). In 2019, PP was retained particularly efficiently in winter and spring (Figure A.3), indicating sedimentation of particulate matter. In contrast, net release of PP was observed during the spring of 2018 (Figure A.3), during which the estimated discharge at downstream was considerably greater (>10%) than upstream (discussed in section 2.5.3).

2.5.3 Seasonal effects

The quantity of P delivered to the reservoir from upstream Thames River varies seasonally by orders of magnitude and is strongly related to flow. The majority of P is delivered during the high flow seasons, in either winter or spring, and the smallest P loads from the watershed were delivered during low flow summer seasons (Figure 2.6). For example, the mean estimated upstream TP load in winter 2018 was over 30 times greater than in the summer 2018 (Table A.1). Since transport of P from non-point sources (agricultural and urban runoff) is more dependent on high flow events in comparison to point sources (Withers & Jarvie, 2008), the observed seasonal pattern here is expected considering the agricultural-dominated land use (83.5%) within the upstream watershed (Ontario Ministry of Natural Resources and Forestry, 2020). Furthermore, previous studies have demonstrated that a very high proportion of total annual P loads from agricultural watersheds may be exported in just a few large events, typically outside of the growing season (e.g. Long et al., 2015, Macrae et al., 2007, Plach et al., 2019). However, our dataset reinforces the importance of sampling consistently throughout the entire year, and targeting high flow events, for the most accurate load and retention estimates (Lee et al., 2016). If a reservoir's annual retention efficiency was extrapolated from selected seasons only, most likely the growing seasons during which field sampling is most accessible, the final estimates may be unreliable and potentially misleading for nutrient management decisions.

Fanshawe Reservoir's P retention efficiency varies systematically across seasons, ranging from a minor source during the summer to a strong sink during winter or spring. Changing reservoir conditions such as flow regime (natural and artificial) and the presence or absence of stratification likely control the seasonal pattern of P retention efficiency. The majority of P retention occurs during the high flow seasons, likely due to rapid deposition of particulate P loads. Net release of P during the summer is ostensibly driven by internal P load induced by in-reservoir stratification. Prolonged stratification during the summers creates anoxic or hypoxic conditions at the sediment-water interface favorable for internal P loading via reductive dissolution of iron (Fe III) (hydr)oxides and subsequent release of dissolved P from bottom sediments (Mortimer, 1941; Søndergaard et al., 2001; Orihel et al., 2017, Parsons et al., 2017). Hypolimnion water with elevated DRP concentration is then preferentially released from the reservoir by bottom draw valves. Dam discharge occurs exclusively through bottom draw valves during the summer since reservoir water level is maintained relatively low, in part to facilitate recreation activities around the reservoir. In addition, dam outflow rate is slightly higher than inflow rate during the summer. This seasonal effect is reflected by notably higher DRP:TP leaving the reservoir during the summers (Figure 2.8). However, when considering each season's contribution to annual P retention, loads released in summer are essentially negligible in comparison to loads retained during the high flow seasons.

To improve P retention in the summer, stratification monitoring programs could provide practical information for nutrient management decisions. Water column profiles and oxygen levels within the reservoir can be measured at a higher frequency (e.g. daily) and are less labor intensive than P concentration measurements. With onset of stratification, release of hypolimnion water can be avoided by shifting discharge location vertically from bottom draw valves to surface gates. However, this would require reservoir management to maintain higher water level during the summer, opposite to current operations. Practical methods to increase retention of dissolved P could also be experimented, such as the addition of artificial sorbents and flocculants. Aluminum sulfate (alum) and Phoslock^{TM} are common chemical techniques that are non-redox sensitive and thus can bind with DRP under anoxic conditions (Hickey & Gibbs, 2009). However, the long-term effectiveness and potential repercussion of these techniques will require careful consideration at Fanshawe Reservoir. For example, the addition of sulfate via alum may increase the molar ratios of S:Fe and S:P in the sediments, with potential impact on permanent P retention capacity (Gächter & Müller, 2003).

Although retention of dissolved P could potentially be enhanced artificially, it alone may not be sufficient to achieve net P retention. During spring of 2018, negative TP retention is due to net release of PP instead of DRP load from bottom sediments observed during the summers. Release of PP is likely due to sediment resuspension driven by elevated outflow rate relative to inflow, which may have been in response to high flow conditions from previous season (2018 winter). Elevated outflow rate is also observed during the summer, although flow augmentation is not one of the primary purposes of Fanshawe Reservoir (UTRCA, n.d.). The correlation between seasonal P release and elevated outflow rate indicates that flow manipulation can unintentionally decrease the reservoir's P retention efficiency, an effect worth considering by reservoir management. Furthermore, timing of high flow and snow melt events will likely influence flow control decisions and therefore in-reservoir P retention. Historically, Thames River's high flow season usually occurred in spring due to snow melt events. In 2018, however, highest average flow was recorded during winter, potentially causing increased dam discharge in spring to alleviate high water levels. In 2019, the majority of high flow days occurred during spring, and significant increase to dam outflow was implemented in the summer only. The changing climatic patterns in Canada, such as warmer winters and seasonal displacements (Champagne et al., 2019; Vincent et al., 2015) will introduce additional challenges for reservoir nutrient management and may result in more years similar to 2018 and fewer similar to 2019. The implications of these climatic changes on the P retention efficiency in Fanshawe Reservoir, and other large reservoirs in the Great Lakes Basin, and the potential ripple effects to P export from the watershed to the lakes, are not well understood and should be considered a research priority for future studies.

2.6 Conclusion

Fanshawe Reservoir acts as an important P sink on the Thames River by retaining 28% and 48% of TP in 2018 and 2019, respectively. However, the reservoir's P retention efficiency can fluctuate substantially between seasons, ranging from a strong sink to a weak source. Net P release during the summer is ostensibly driven by internal P loading induced by in-reservoir stratification, and further exacerbated by flow augmentation and bottom draw discharge practices that preferentially release hypolimnion water with elevated DRP concentration. The amount of P released in the summer, however, only makes up a small portion of the annual P load and is unlikely to offset retention from other seasons. Flow augmentation alone could also result in net P release, an effect observed in spring of 2018 that saw a preferential release of PP, likely as a result of sediment resuspension. The mechanisms behind seasonal P release indicate that retention efficiency may be influenced by flow manipulation at the dam, namely discharge location and outflow rate relative to inflow. Load bioavailability (estimated by DRP:TP) generally increases from upstream to downstream during the summer months due to more efficient in-reservoir retention of PP over DRP and the release of DRP through internal loading processes.

Our results provide a better understanding of Fanshawe Reservoir's effects on P flow along the Thames River corridor, with implications to HAB developments in downstream Lake St. Clair and ultimately the western basin of Lake Erie. With the GLWQA target deadline for 40% P load reduction to Lake Erie rapidly approaching in 2025, we contend that exploring nutrient management actions to maximize in-reservoir P retention, in addition to land-based P loss mitigation strategies, should receive more careful consideration.

Chapter 3

Fanshawe Reservoir's influence on Nitrogen, Phosphorus, and Silicon fluxes and ratios of the Thames River

3.1 Summary

Globally, dammed reservoirs are known to alter riverine nutrient flow and nutrient ratios to varying degrees. Within the Lake Erie watershed, nutrient loss mitigation efforts are focused on reducing excess P loads from the landscape, but the influences of dammed reservoirs on nutrient flow and ratios have not been evaluated comprehensively. In this study, we used a mass balance approach to calculate the retention efficiencies of dissolved inorganic nitrogen (DIN), dissolved reactive phosphorus (DRP), and dissolved silicon (DSi) and the changes to nutrient ratios exerted by Fanshawe Reservoir on the Thames River, Ontario. Furthermore, we analyzed the concentration to flow (CQ) relationships of DRP, DIN, and DSi to determine the general transport behaviors in the watershed. From 2018 to 2019, Fanshawe Reservoir retained DRP (28.6%) and DSi (5.6%) but released DIN (-6.2%) (retention efficiencies in parentheses). The preferential retention of DRP over DSi and DIN increased nutrient loads' DIN:DRP and DSi:DRP ratios leaving the reservoir, and potentially increased N availability and P limitation to downstream Lake Erie. Algal bloom toxicity could increase with N availability, however, P retention by the reservoir represents an important nutrient sink along the river corridor and a potential point of mitigation to implement nutrient management actions. Upstream of the reservoir, DRP and DIN exhibited mobilization transport behaviors, and DSi was characterized as chemostatic. Downstream of the reservoir, however, DRP transitioned to chemostatic behavior, driven by the combined effect of internal P loading during low flow summer and enhanced retention during high flow events. Overall, our results showed that Fanshawe Reservoir decoupled Thames River's nutrient fluxes by altering both the quantity and relative ratios of nutrients with further modifications to DRP's transport behavior.

3.2 Introduction

Through flow regulation and river fragmentation, damming has impacted 48% of the world's river, and that value is expected to rise to 93% by 2030 with the completion of currently planned dams (Grill et al., 2015). In addition to altering the natural flow regime, damming reduces the connectivity between upstream and downstream water bodies by impeding the exchange of energy and matter (Grill et al., 2019). Furthermore, damming disrupts the natural riverine nutrient cycles by converting a segment of free-flowing river into a reservoir, an intermediate waterbody with both river and lake characteristics (Friedl & Wüest, 2002). Compared to the original riverine environment, a reservoir lengthens hydraulic residence time, lowers flow velocity and turbidity, and allows more light to penetrate the water column. Cumulatively, these effects promote in-reservoir primary production and nutrient retention through deposition of particulate matter, adsorption and biological uptake of dissolved nutrients, and gaseous removal (Van Cappellen & Maavara, 2016). From a biogeochemical perspective, dammed reservoirs are essentially "in-stream reactors" along the river corridor that enhance riverine nutrient recycling and transformation processes (Maavara et al., 2020a).

Although reservoirs tend to retain nutrients, retention efficiencies differ among nitrogen (N) and phosphorus (P), two essential elements for life (Galloway et al., 2003), and silicon (Si), an essential element for diatoms (Kristiansen & Hoell, 2002; Struyf et al., 2009). Globally, reservoirs retain 7.4% of N, 12% of P, and 5.3% of Si; the differing retention efficiencies between nutrients indicate that, reservoirs are altering both the absolute and relative magnitudes of river nutrient flow (Maavara et al., 2020a). Additionally, human activities on the landscape have disproportionately impacted these three elements. Attributed mainly to wastewater discharge and fertilizer runoffs, riverine N and P loads have approximately doubled since pre-industrial time, driving widespread eutrophication in both inland and marine waters (Galloway, 1998; Filippelli, 2008; Le Moal et al., 2019). In comparison to N and P, riverine Si load has remained relatively constant and may fluctuate depending on the type of land use changes (Conley, 2002). For example, conversion of a forested area to an urban center increases riverine Si load as a result of enhanced runoffs from impervious surfaces (Carey & Fulweiler, 2012) In contrast, agricultural activities decreases riverine Si loads by removing biogenic Si from the local terrestrial ecosystem during crop harvesting (Struyf et al., 2010).

The disproportionate increase of N and P relative to Si from the landscape, coupled with the effect of reservoirs along the river corridors, are changing the ratios at which nutrients are delivered to downstream water bodies, with impacts on phytoplankton community structures and ecosystem health (Billen & Garnier, 2007; Andersen et al., 2020; Maavara et al., 2020b). The average molar ratio at which phytoplankton uptake N, P, and Si is described by the Redfield-Brzezinski ratio C:N:P:Si = 106:16:1:15 (Redfield, 1934; Brzezinski, 1985). However, different phytoplankton species have different preferred N:P:Si uptake ratios. Therefore, an environment's N:P:Si availability can favor the growth of certain species, and drastic changes to N:P:Si abundance can alter the dominant phytoplankton community (Davidson et al., 2012). In Si-rich environment, diatom species, most of which are not toxic, are favored due to their rapid growth rates (Conley, 2002; Paerl et al., 2006). In Si-limited environment, however, non-siliceous phytoplankton such as dinoflagellate and cyanobacteria are favored, which contain a higher proportion of species capable of producing toxins (Officer & Ryther, 1980; Royer, 2019). In N-rich environment, both the growth and toxicity of cyanobacterial blooms are enhanced due to the positive correlation between N availability and toxin production by certain strains of cyanobacteria, such as *Microcystis* (Gobler et al., 2016). So while P is often the primary limiting nutrient in freshwater environment that controls the overall growth of phytoplankton (Schindler, 1977), the relative abundance of N, P, and Si can influence the community assemblage and the severity of harmful algal blooms (HABs).

In Lake Erie (USA-Canada), severe eutrophication symptoms such as HABs, oxygen depletion, and fish kill have been documented since the 1960s. This initial deterioration of ecosystem health of Lake Erie was mainly driven by a combination of unregulated industrial and domestic discharges, insufficient wastewater treatment processes, and agricultural runoffs (De Pinto et al., 1986). In the 1970s, regulations and by-laws initiated by the Great Lakes Water Quality Agreements (GLWQA) led to successful reduction of point source P pollutions, resulting in a decrease of HABs and overall improvements to lake water quality (De Pinto et al., 1986). However, algal blooms and near shore fouling have returned since the 1990s, with the most severe cases documented in the western basin of Lake Erie (EPA, 2010). One of the main drivers behind this resurgence of HABs is the excess amount of tributary P loads with non-point source origins, which have emerged as the main source of P pollution to Lake Erie (Dolan, 1993; Scavia et al., 2014).

From the Canadian side, the Thames River is the largest tributary P source into Lake Erie's western basin (Maccoux et al., 2016). As such, strategies to reduce P loss and nutrient pollution within the Thames River watershed are of great interests. Thus far, nutrient management strategies implemented within the Thames River watershed have focused on reducing runoffs from the landscape, such as soil erosion control in agricultural fields and small-scale storm water retention in urban areas (UTRCA, 2018). The effect of dammed reservoirs on Thames River's nutrient fluxes and their potential as points of intervention for nutrient management have not been fully evaluated yet. While global average retention efficiencies of N, P, and Si by reservoirs are known, large spatial variation exists between regions, watersheds, and reservoirs (Maavara et al., 2015). Estimating an individual reservoir's retention efficiency by simply downscaling the global average could be inaccurate and could potentially misinform future nutrient management decisions (Van Cappellen & Maavara, 2016). In this study, we use a mass balance approach to 1) determine the retention efficiencies of DIN, DRP, and DSi by the largest dammed reservoir on the Thames River, Fanshawe Reservoir, and 2) evaluate modifications to riverine DIN:DRP and DSi:DRP ratios by Fanshawe Reservoir. Additionally, we identify the primary limiting nutrient on the Thames river and characterize the general transport behaviors within the watershed by examining the relationships between concentration (C) and flow (Q).

3.3 Study site and methods

3.3.1 Site description

Fanshawe Reservoir is a eutrophic run-of-the-river reservoir located on the upper Thames River, in southwestern Ontario, Canada (Vandermeulen & Gemza, 1991; Nürnberg & LaZerte, 2005). Construction of the dam was completed in 1952 to provide flood control and flow regulation services for London, the largest urban area in the Thames River watershed located approximately 12 km downstream (Vandermeulen & Gemza, 1991). Under normal operation, the surface area of the reservoir is about 2.6 km^2 with an average water depth of 4.8m (UTRCA, n.d.; Nürnberg & LaZerte, 2005). Under high flow condition, the reservoir could cover up to 6.5 km^2 at a maximum water depth of 21.6 m (UTRCA, n.d.). The dam's primary outflow is bottom draw discharge through intake valves approximately 8 to 10 m below the water surface, and surface sluice gates are only used during high water levels (UTRCA, n.d.). Agricultural activities dominate land use within Fanshawe Reservoir's watershed (83.5%) (Ontario Ministry of Natural Resources and Forestry, 2020).

3.3.2 Flow and chemistry data

Fanshawe Reservoir receives most of its water inflow from upstream Thames River (97%) with minor contribution (3%) from a tributary source, Wye Creek; the main outflow is at the dam wall, which discharges directly to downstream Thames River (Fig.1). Flow rate of Thames River is continuously monitored by Water Survey Canada (WSC) at upstream (station ID: 02GD015) and downstream (station ID: 02GD003) of the reservoir. However, WSC station at Wye Creek (station ID: 02GD013) is no longer in service (operated from 1953 to 1991). Therefore, we estimated Wye Creek's flow rate based on a regression relationship between upstream Thames River and Wye Creek stations (see Appendix A, Figure S1 and Equation S1).

From March 2018 to November 2019, we collected water chemistry samples on the Thames River upstream and downstream of the reservoir, and at Wye Creek once every two weeks with additional high flow event sampling (Figure 3.1). Upon collection, all samples were filtered to <0.45 μm using nylon membrane filters and stored in polyethylene or glass bottles. Concentrations of DRP was measured using the blue molybdate complex method (Murphy and Riley, 1962) on a UV-Vis spectrometer (Thermo Scientific Evolution 260 Bio) (MDL 0.05 μmol L^{-1}). Concentrations of DSi was measured using ICP-OES

(Thermo Scientific iCAP 6300) after acidification with HNO_3 to < pH 2 (MDL 1 µmol L^{-1}). Nitrate and nitrite samples were further filtered to <0.2 µm and measured using ion chromatography (Dionex ICS 5000) (MDL nitrate 4 µmol L^{-1}, nitrite 9.7 µmol L^{-1}). We also measured total dissolved N (TDN) using a Shimadzu TOC-LCPH/CPN analyzer (MDL 3 µmol L^{-1}). Additionally, we obtained water chemistry data from Environment and Climate Change Canada (ECCC) collected at the same locations as our upstream and downstream Thames River sites between December 2017 and October 2018. The dataset from ECCC included: DRP, nitrate and nitrite combined, total Kjeldahl N (TKN), and ammonia concentrations. Since we did not directly measure ammonia concentrations, we combined ours and ECCC's nitrate and nitrite concentrations as "DIN", neglecting the ammonia component, which is one of the fractions of DIN (Ran et al., 2017). However, based on ECCC's data, ammonia concentrations were relatively low compared to nitrate and nitrite; on average, ammonia was 1.5% and 2.9% of the combined concentration of nitrate and nitrite at upstream and downstream Thames River sites, respectively. Lastly, we estimated the combined concentration of ammonia and dissolved organic N by taking the difference between TDN and DIN (nitrate and nitrite), which gave comparable result to TKN measured by ECCC (Sáez-Plaza et al., 2013).

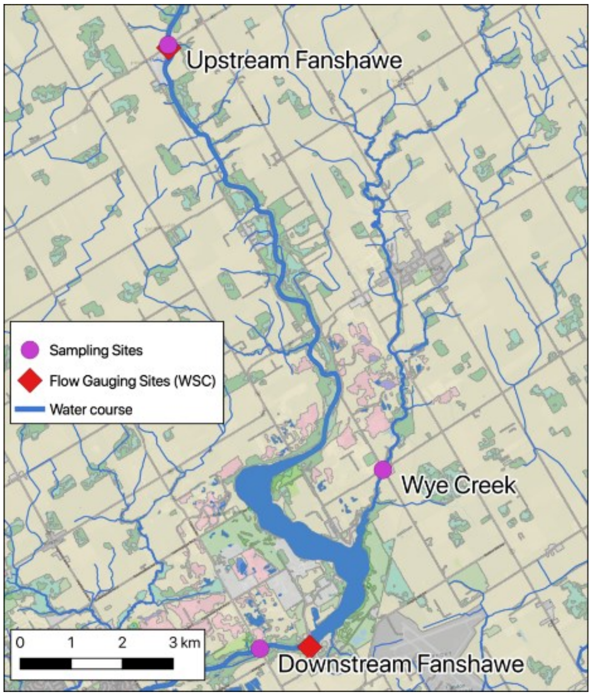

Figure 3.1 Water chemistry sampling sites (purple) and Water Survey Canada (WSC) flow gauging stations (red) on the Thames River upstream and downstream of Fanshawe Reservoir and at Wye Creek.

3.3.3 Load estimation models

To determine Fanshawe Reservoir's nutrient retention efficiencies, we took a mass balance approach by first quantifying the inflow and outflow loads using load estimation models. While there are many load estimation models available with different mathematical bases and assumptions, a universally superior model does not exist (Lee et al., 2016; Preston et al., 1989). The "correct" choice of model depends on a variety of factors that need to be considered, such as: land use within the watershed, frequency of concentration data, strength of correlation of CQ relationship, and flow variability (Richards & Holloway, 1987; Quilbe et al., 2006). Thus, recognizing the intrinsic uncertainties of load estimation, we took an ensemble approach by using four different load estimation models to establish a range of load. The four models we used were: flow-weighted averaging estimator (Walling & Webb, 1981), Beale ratio estimator (Beale, 1962), Ferguson regression (Ferguson, 1986), and Weighted Regression on Time, Discharge, and Season (WRTDS) under a modified setting (Hirsh et al., 2010). These four models cover the three main groups of load estimation models: averaging method, ratio estimators, and regression methods (Nava et al., 2019). For equations and detailed descriptions of these models, see Appendix B. All model calculations were performed in R. To accommodate our relatively short-term dataset (2 year) in comparison to what WRTDS was originally designed for (> 20 years), we modified the default settings by muting the "time" component of the regression equation, which accounts for long term variations. Therefore, "WRDS" is a more accurate description of the modified version, which we will use in reference to WRTDS for the remaining section. After nutrient loads were estimated, the retention efficiencies were calculated using:

$$Retention\ (\%) = \frac{Load_{in} - Load_{out}}{Load_{in}} \times 100 \tag{3.1}$$

where $Load_{in}$ is the combined load of upstream Thames River and Wye Creek, and $Load_{out}$ is the downstream Thames River load exiting the reservoir. When retention efficiency is expressed in percentage, negative values indicate net release, and positive values indicate retention.

3.3.4 CQ relationship

Using all data collected in 2018 and 2019, we determined the 2-year CQ relationships of DIN, DRP, and DSi by fitting linear regression trendlines between C and Q on a double-log scale (equivalent to power-law relationships):

$$\log_{10}(C) = \log_{10}(a) + b\log_{10}(Q) \tag{3.2}$$

where a is the intercept and b is the slope of the CQ relationship (Knapp et al., 2020). Based on the slope of the CQ relationship, the dominant transport mechanism and source of a solute within the watershed can be interpreted (Dolph et al., 2019). A positive slope ($b > 0$) indicates mobilization behavior where solute concentration increases with flow, typically due to enhanced erosion and transport during high flow condition (Dolph et al., 2019). In contrast, a negative slope ($b < 0$) indicates dilution behavior, and an inverse relationship exists between C and Q, likely a result of constant solute sources being diluted by varying water flow (Godsey et al., 2009). A slope close to zero ($b \approx 0$) indicates chemostatic behavior where concentration remains relatively constant over the entire flow range, a common pattern for mineral weathering products (Godsey et al., 2009) or a sign of widespread legacy stores of solute attributed by a long history of fertilization (Basu et al., 2011). Similar to the method defined by Zimmer et al. (2018), we characterized transport behaviors as chemostatic if the slope of CQ relationship was between -0.3 and 0.3, mobilization when slope was > 0.3, and dilution when slope was < -0.3. Separately, we normalized C by the average C over the time series, highlighting the range and factor at which C increased or decreased with varying flow.

3.4 Results

3.4.1 Retention efficiencies and nutrient ratios based on load estimation models

Fanshawe Reservoir preferentially retained DRP over DSi and had a net release of DIN: on average, 29% of DRP and 6% of DSi were retained, and 6% of DIN was released (Figure 3.2). The more efficient DRP retention relative to DIN and DSi resulted in higher DIN:DRP and DSi:DRP ratios leaving the reservoir: from upstream to downstream, model average showed DIN:DRP increased from 105 to 153, and DSi:DRP increased from 30 to 39 (Figure 3.3). Both upstream and downstream loads are P-limited based on the Redfield-Brzezinski ratio. The release of DIN coupled with retention of DRP resulted in higher net increase of DIN:DRP compared to DSI:DRP. Relative magnitude between DIN and DSi did not vary much from upstream to downstream in comparison to ratios involving DRP. Ratio of DIN:DSi increased slightly from upstream (3.5) to downstream (3.9).

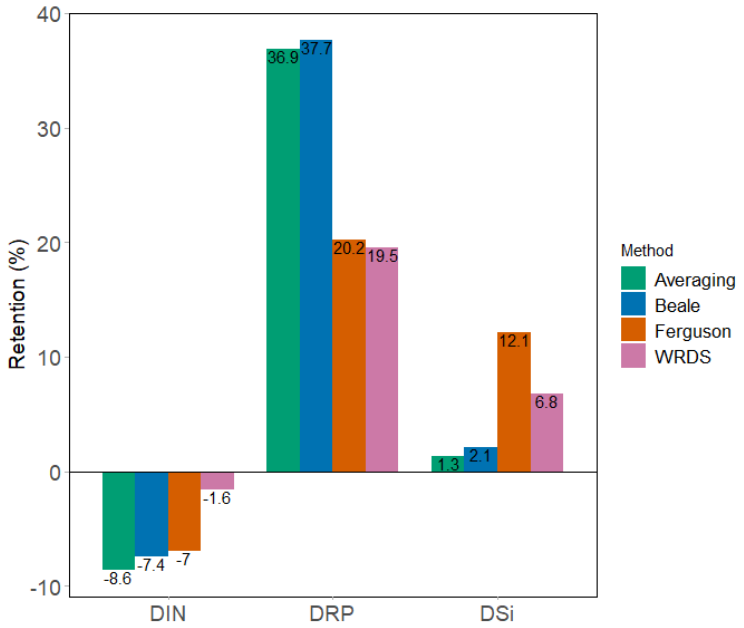

Figure 3.2 Retention efficiencies (%) of DIN (left), DRP (center), and DSi (right) by Fanshawe reservoir (2018-2019). Positive values indicate net sink and negative values indicate net release. "Averaging" (green), "Beale" (blue), “Ferguson" (orange), and "WRDS" (pink) correspond to the four load estimation models used: flow-weighted averaging estimator, Beale Ratio estimator, Ferguson regression, and modified version of WRTDS, respectively.

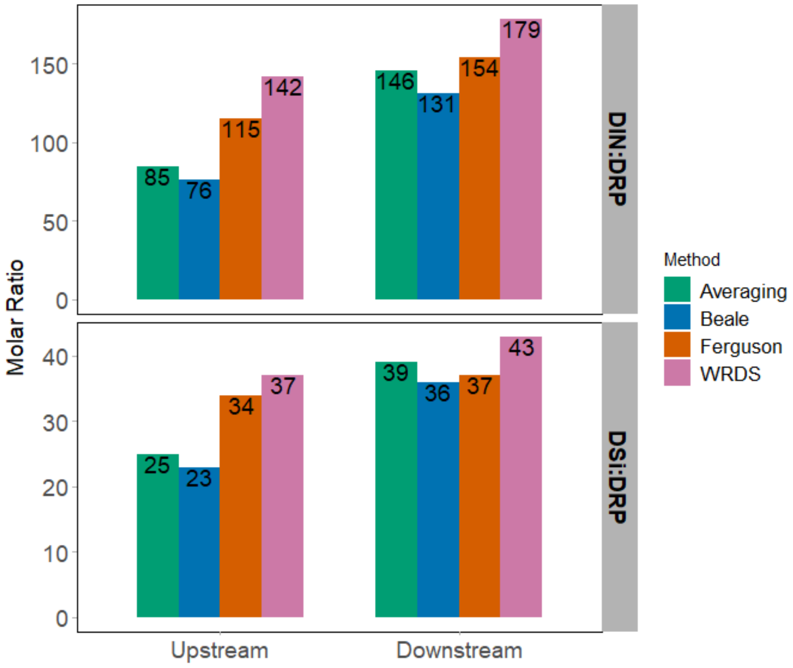

Figure 3.3 Molar ratios DIN:DRP (top) and DSi:DRP (bottom) of Thames River’s nutrient loads upstream (left) and downstream (right) of Fanshawe Reservoir.

3.4.2 Limiting nutrient and nutrient ratios based on concentration data

In a separate approach, we determined the primary limiting nutrient of Thames River using discrete concentration data points collected at the upstream and downstream locations (Figure 3.4). Based on the Redfield-Brzezinski ratio, four different nutrient limitation scenarios are possible when plotting DIN:DRP (y-axis) against DSi:DRP (x-axis): P-limited, N-limited, Si-limited, or N and Si co-limited (Harrison et al., 2013). Out of 133 data points, the majority (n=129) were classified as P-limited, while the remaining few (n=4) were Si-limited. None were N-limited or N and Si co-limited. All four Si-limited days occurred during high flow events in either winter or spring of 2019. Although no data points were classified as N-limited, few approached the DIN:DRP = 16 threshold during the low-flow summer and fall seasons at the downstream location.

Both DIN:P and DSi:DRP were significantly lower at the downstream location compared to the upstream location (*p*=0.0395 for DIN:DRP; *p*=0.01384 for DSi:DRP). Figure 3.5 shows the mean and distribution of DIN:DRP and DSi:DRP data points at the upstream and downstream locations. The lower DSi:DRP and DIN:DRP ratios leaving the reservoir imply greater DSi and DIN retention efficiencies compared to DRP, in contrast to the results based on load estimation models (3.4.1 Retention efficiencies and nutrient ratios based on load estimation models).

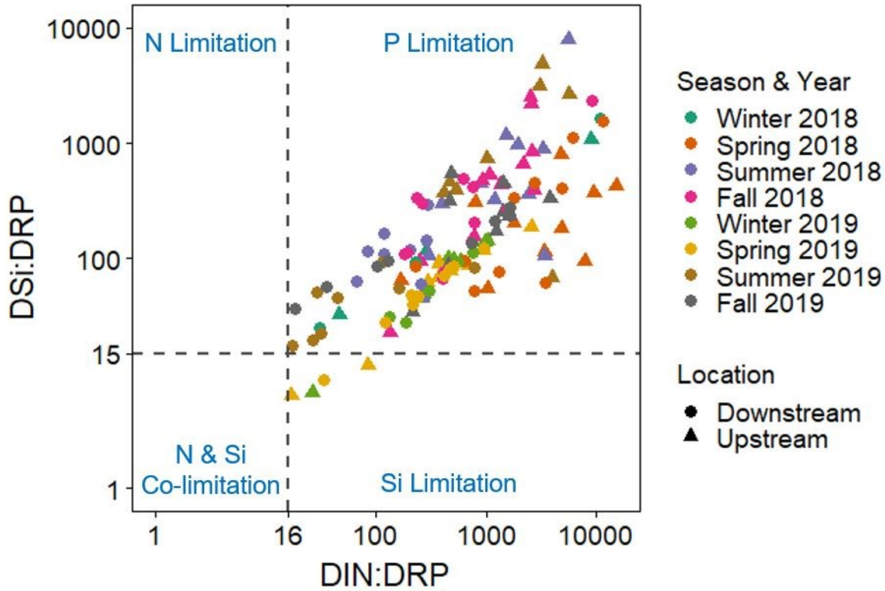

Figure 3.4 Molar ratios DSi:DRP (y-axis) vs DIN:DRP (x-axis) and discrete concentration data points collected on Thames River upstream and downstream of Fanshawe Reservoir (2018-2019). Four quadrants identified showing the potential limiting nutrient based on Redfield-Brzezinski ratios of N:P:Si = 16:1:15.

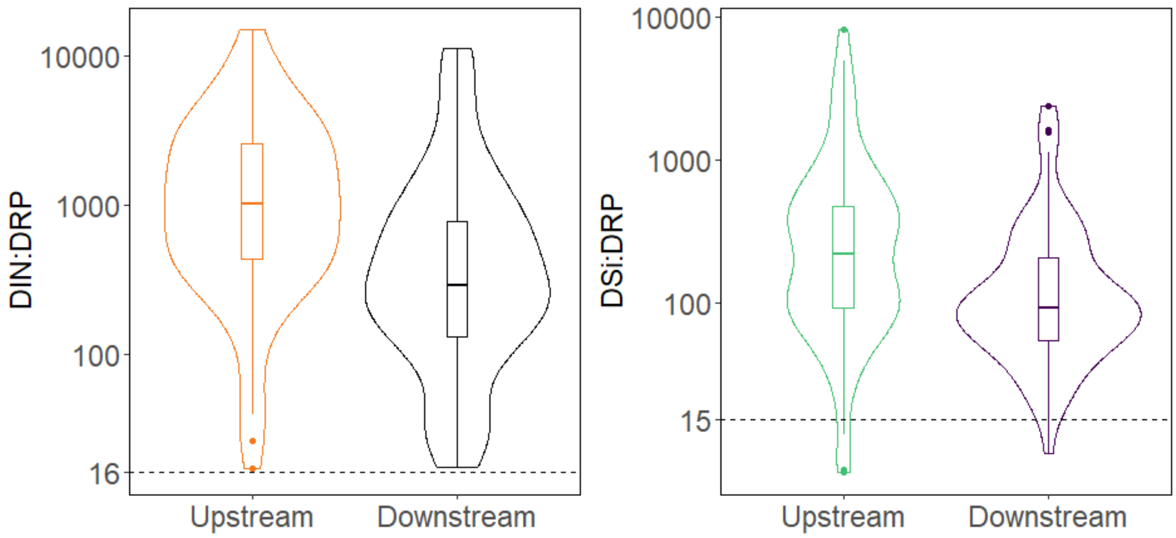

Figure 3.5 Violin plots overlayed with boxplots of DIN:DRP ratios (left) and DSi:DRP ratios (right) on Thames River upstream and downstream of Fanshawe Reservoir based on discrete concentration data points. Horizontal lines showing potential nutrient limitation threshold at y=16 (DIN:DRP) and y=15 (DSi:DRP) based on Redfield-Brzezinski ratios of N:P:Si = 16:1:15.

3.4.3 CQ relationships

The 2-year CQ relationships of all three nutrients are shown in Figure 3.6. At upstream Thames River, DRP concentrations increased with flow and demonstrated clear mobilization behavior (b = 1.0) at a strong correlation (r^2 = 0.69); DIN is weakly mobilized (b = 0.34) with a weaker correlation (r^2 = 0.31) in comparison to DRP; DSi showed chemostatic behavior (b = 0.24) and had the weakest correlation (r^2 = 0.10). At downstream of the dam, DRP's slope (b = 0.22) and correlation (r^2 = 0.05) decreased markedly from upstream, shifting from mobilization to chemostatic behavior; DIN maintained almost identical slope (b = 0.35) and correlation (r^2 = 0.29); DSi's slope (b = 0.06) and correlation (r^2 = 0.01) slightly decreased from upstream.

The relative change of concentration over the entire flow range at upstream and downstream is shown in Figure 3.7. At upstream, DRP concentration had the largest maximum change (8.5 factors) over the flow range, followed by DSi (3.2 factors) then DIN (2.6 factors). At downstream, the maximum relative changes of DSi and DIN decreased slightly from upstream, at 2.5 factors and 2.1 factors, respectively. A more drastic difference is shown by DRP, with a maximum change of 5.3 factors at downstream, a clear decrease from upstream.

All three nutrients had a higher average concentration at downstream relative to upstream. From upstream to downstream, DIN increased from 314 μmol L^{-1} to 319 μmol L^{-1}, DRP increased from 0.91

μmol L^{-1} to 1.2 μmol L^{-1}, and DSi increased from 72 μmol L^{-1} to 83 μmol L^{-1}. In terms of relative change, DRP had the largest increase (29%), followed by DSi (15%) and DIN (1.4%). The average concentration of total Kjeldahl N is also higher at downstream (52 μmol L^{-1}) than upstream (44 μmol L^{-1}). Lastly, slightly higher average flow was measured at downstream (21.76 cubic meter $second^{-1}$) in comparison to the combined flow of upstream and Wye Creek (21.66 cubic meter $second^{-1}$).

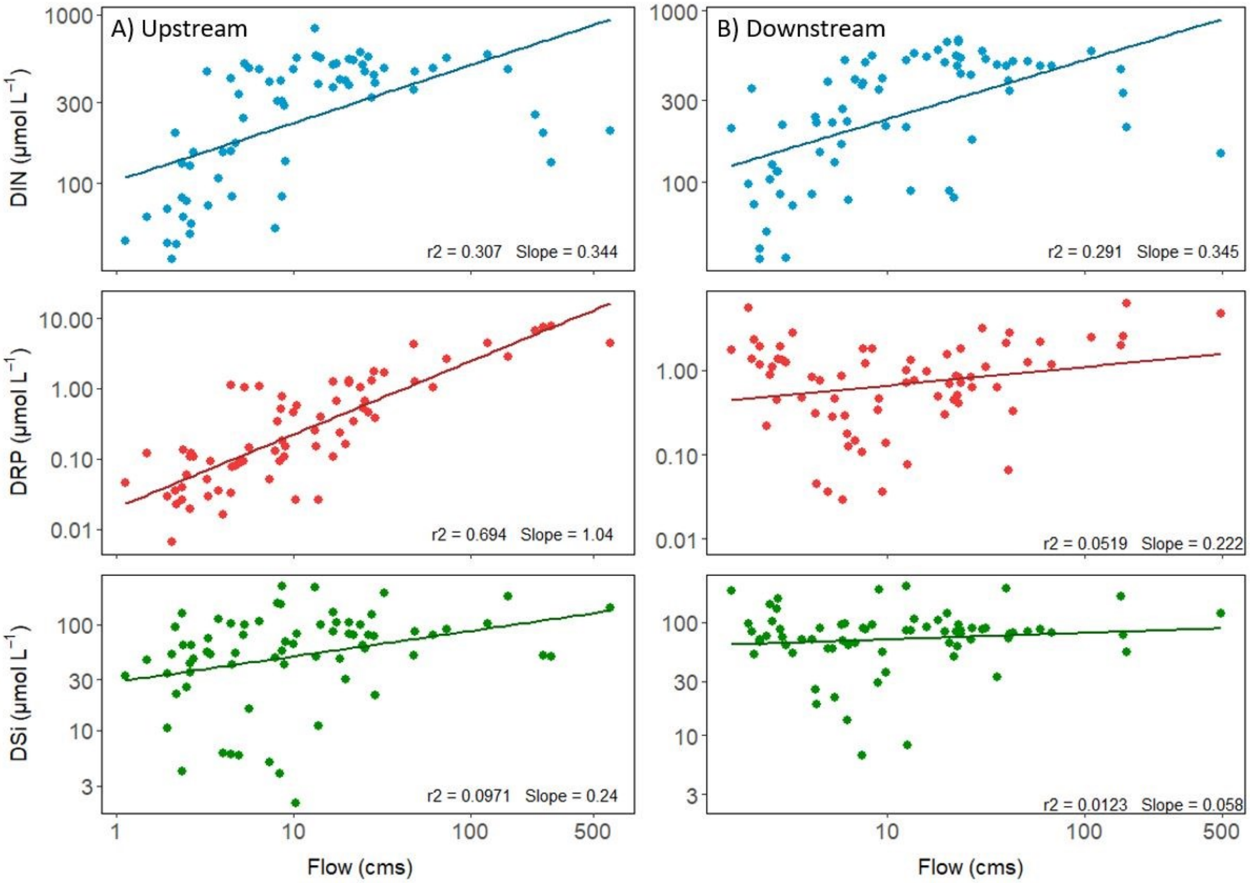

Figure 3.6 CQ relationships of DIN (blue), DRP (red), and DSi (green) on double log scale of the Thames River A) upstream and A) downstream. Coefficient of determination (r2) and slope of fitted linear regression line displayed on bottom right corner of each panel.

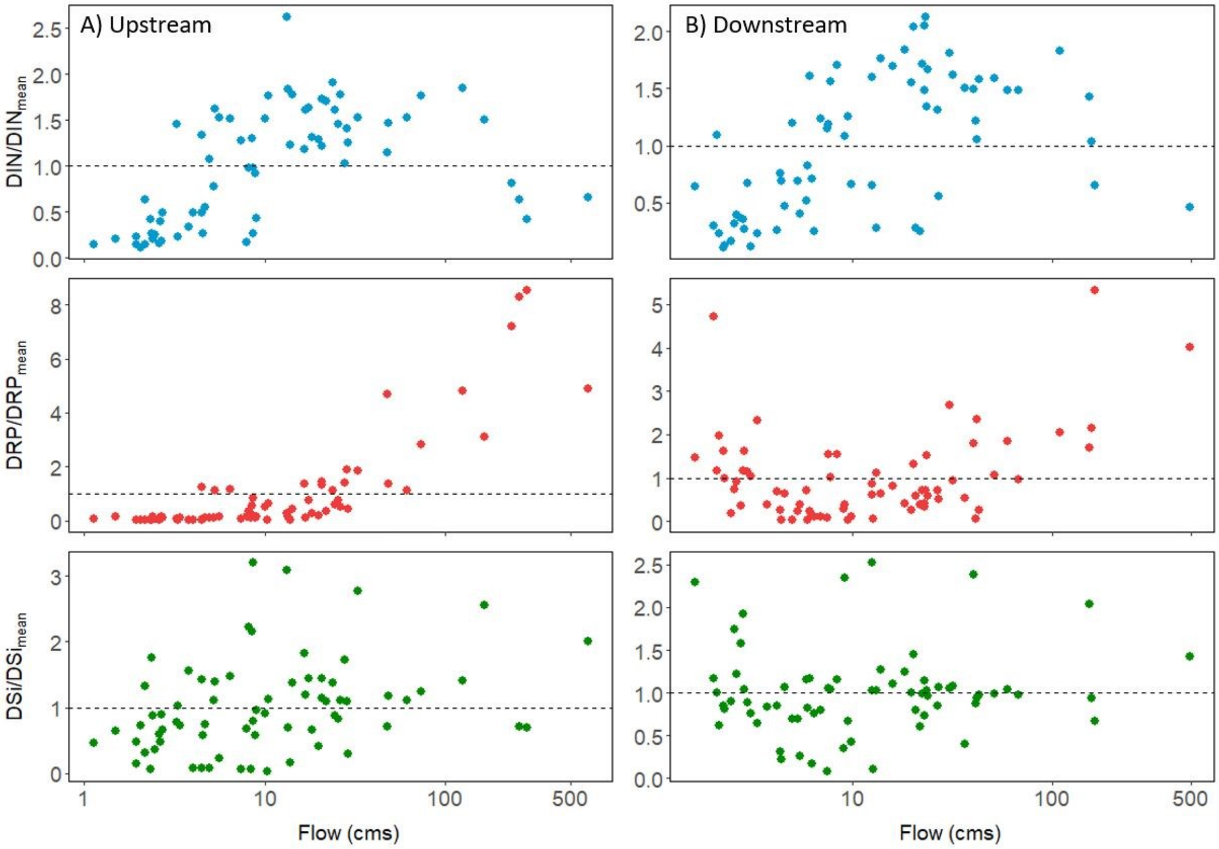

Figure 3.7 Normalized concentration (C/C$_{mean}$) over the entire flow range of DIN (blue), DRP (red), and DSi (green) on the Thames River A) upstream and B) downstream. Note y axis range difference between upstream and downstream for DRP.

3.5 Discussion

3.5.1 Retention efficiencies and changes to nutrient ratio: Implications for nutrient management

Fanshawe Reservoir alters both the absolute and relative magnitudes of Thames River's nutrient fluxes by retaining DIN, DRP, and DSi loads at markedly different efficiencies. DRP fluxes are preferentially retained over DIN and DSi, which increases riverine DIN:DRP and DSi:DRP at the outlet of the reservoir relative to the inlet. This modification to nutrient ratios can potentially enhance P-limitation status in receiving waters, which further heighten the importance of reducing excess P loads to control downstream eutrophication. The additional increase to the already high DIN:DRP (>50) indicates an increased risk of developing more toxic HABs given the ability of certain cyanobacteria, such as *Microcystis*, to produce more toxin at higher N:P ratios (Baker et al., 2018; Gobler et al., 2016). This increase of N availability to downstream water bodies emphasizes the need to develop N reduction goals in conjunction with P reduction goals within the watershed to mitigate HABs in Lake Erie. On the other hand, the reservoir's strong DRP retention efficiency demonstrates its ability to serve as an important P sink along the river corridor and reduce P loads originating from the landscape upstream. However, while P retention within Fanshawe Reservoir could alleviate downstream eutrophication, it comes at the expense of in-reservoir nutrient enrichment and potential deterioration to reservoir water quality (Maavara et al., 2020b), as the buildup of legacy P in sediments could be released through internal loading, delaying the recovery of water quality even after reduction to external nutrient loads (Sharpley et al., 2013; O'Connell et al., 2020). Depending on the desired outcome, experimental nutrient management strategies could be implemented to further enhance P retention in Fanshawe Reservoir, and to prevent future sediment P release.

While the stronger P retention efficiency relative to N and Si is consistent with the predicted global trend (Maavara et al., 2020b), the observed net DIN release is unexpected. There are a few potential contributors to this net DIN release: N fixation, N transformation (Ran et al., 2017), groundwater discharge, and atmospheric deposition (Galloway, 2003). Under N-limited conditions, some phytoplankton can acquire N through biological N fixation, an energy intensive process carried out by specialized species (Galloway et al., 2003). However, this process is unlikely to occur rapidly at Fanshawe Reservoir since the external nutrient load is P-limited, which reduces the demand and rates of N fixation (Howarth et al, 1988; Baker et al., 2018). Although, N fixation rate could vary spatially within a reservoir from inlet to outlet; Scott et al. (2009) showed that, despite having relatively high N availability compared to the rest of the reservoir, transition zone is the hotspot for N fixation of three reservoirs in Texas (Scott et al., 2009).

Furthermore, based on compiled data from 30 lakes and reservoirs, the contribution to reservoir N pool by N-fixation are reduced but not completely absent in waters with above Redfield ratio of N:P = 16, and a definitive N:P threshold at limiting N fixation does not exist (Akbarzadeh et al., 2019). In-reservoir N cycling could also contribute to net DIN release through transformation of particulate N and dissolved organic N to DIN (Ran et al., 2017). However, we did not measure particulate N, and the combined concentration of organic N, ammonia, and ammonium is higher at downstream than upstream, contradicting the likelihood of this mechanism. We also did not measure groundwater nutrient fluxes nor atmospheric deposition. Based on the available data, we cannot confidently identify the reason for Fanshawe Reservoir's net DIN release. To bridge this data gap, we recommend further research and sampling that specifically investigate in-reservoir N cycling, such as in-situ N fixation and denitrification rates. Advancing our understanding of in-reservoir N cycling at Fanshawe Reservoir would fill an important data gap for inland waters globally (Maranger et al., 2018), and specifically for Fanshawe Reservoir, could help design better nutrient management strategies targeting the landscape, and in the reservoir.

Lastly, deviations from the global trend, such as Fanshawe Reservoir's DIN retention efficiency, demonstrates the value of assessing a dammed reservoir's effect on nutrient flow comprehensively, especially on a river acting as a major source of nutrients to downstream water bodies. Simple downscaling from the global average would have produced drastically different result for Fanshawe Reservoir, potentially misleading future nutrient management decisions.

3.5.2 CQ relationships

The responses to flow variation exhibited by DRP and DSi concentrations on the Thames River upstream of the reservoir are consistent with the general patterns observed in watersheds dominated by agricultural land use: mobilization behavior by DRP indicates flushing of P with increasing flow (Withers and Jarvie, 2008; Dolph et al., 2019); chemostatic behavior of DSi reflects the chemical weathering nature of silicon (Godsey et al., 2009). Similar to DRP, mobilization behavior is also exhibited by DIN, reflecting the agricultural-dominated land use (83.5%) in the upstream watershed (Ontario Ministry of Natural Resources and Forestry, 2020), where excess fertilizers from the upper soil layers are transported to streams and rivers under high flow conditions (Zimmer et al., 2018). Losses of DIN and DRP from the landscape may be exacerbated by the emerging climatic pattern in Canada: increasing annual precipitation and streamflow (Vincent et al., 2015), and increasing frequency of extreme precipitation events (Zhang et al., 2019). In comparison to DRP and DSi, CQ relationship of DIN is not widely characterized and can fluctuate greatly both spatially and temporarily depending on factors such as land use and cover, biological interactions, and flow regime (Zimmer et al., 2019; Knapp et al., 2020). In intensively managed watersheds with long histories of agricultural land use, chemostatic behavior of nitrate have been observed due to legacy N pools acting as consistent and long-lasting source of N to stream waters (Basu et al., 2011; Van Meter et al., 2016). The lack of chemostatic behavior by DIN and DRP on the Thames River may indicate that full nutrient saturation has yet to occur, or that legacy N pool are not distributed evenly in the landscape (Zimmer et al., 2018). However, our sampling locations are at the upper portion of the Thames River watershed, and the CQ relationships observed here may not accurately represent transport behaviors further downstream of the river closer to Lake St. Clair.

Downstream of the reservoir, DRP's transport behavior transitions from mobilization to chemostatic. This change in CQ relationship is attributed by higher DRP concentrations during low flow conditions downstream of the reservoir, which decreases the slope of the fitted regression line. In Chapter 2 (*2.4.4 In-reservoir conditions*), in-reservoir stratification and elevated hypolimnion DRP concentrations (relative to epilimnion) near the dam wall were observed during the low flow summer, indicative of internal P loading from the sediments. Throughout the summer, while the reservoir water level is low, preferential discharge of hypolimnion water is the typical operation at Fanshawe Reservoir, which ensures the increase to downstream DRP concentrations. Additionally, DRP concentrations during high flow events are markedly lower at downstream relative to upstream, which further decrease the slope of DRP's CQ relationship. Damming reduces peak flow velocity and increases contact time between sediment and dissolved solutes, promoting sorption with bottom sediments and suspended particulate matter; furthermore, lowered flow velocity also reduces the disturbance to bottom sediments and mobilization of porewater DRP (House, 2003; Withers & Jarvie, 2008). The cumulative effect of these in-reservoir processes lowers DRP concentrations leaving the reservoir during high flow events. In contrast, DIN's CQ relationship is consistent between upstream and downstream. This may be explained by the different biogeochemical properties between N and P; nitrate is highly soluble and can remain dissolved for a longer duration, while orthophosphate have a higher affinity to mineral surfaces and particulate matters (Goyette et al., 2019). Thus, while the reservoir is able to retain a portion of DRP during high flow events through sorption and subsequent sedimentation, majority of DIN remains in the dissolved phase and flushes out of the reservoir. The reservoir's modification to DRP's transport behaviors imply that further flow manipulation could be experimented to maximize DRP retention by increasing residence time during high flow events.

3.5.3 Discrepancy between model and concentration data approaches

Based on discrete concentration datapoints, Thames river is a P-limited environment with occasional Si-limited days driven by high flow events. Due to different CQ relationships exhibited by DRP (mobilization) and DSi (chemostatic or near-chemostatic), the range and magnitude at which concentration increases with flow is much larger for DRP than DSi. During some high-flow events, this can lower DSi:DRP to below Redfield-Brzezinski ratio of Si:P = 15. These events are rare, however, and their effect is not reflected by nutrient load, which remains P-limited at both upstream and downstream. The average downstream DIN:DRP and DSi:DRP are significantly lower compared to upstream based on concentration data points, which implies stronger DIN and DSi retention efficiencies relative to DRP. This directly contradicts the results from load estimation models. However, this discrepancy is due to higher average DRP concentration at downstream in comparison to upstream, not because of higher DRP load exiting the reservoir relative to DIN or DSi load. The calculation of nutrient ratio based solely on concentration data does not consider the effect of flow on nutrient transportation, which can generate misleading information such as this case. While nutrient concentration represents a river's ambient water quality, load is the primary control to condition in downstream water body (Hirsch et al., 2010). In the context of assessing a reservoir's effect on nutrient flow, load estimation should be prioritized over analyses based on concentration data exclusively.

3.6 Conclusion

A decoupling of Thames River's nutrient fluxes is exerted by Fanshawe Reservoir, where DIN, DRP, and DSi fluxes are subjected to different retention efficiencies. Our mass balance approach shows that 29% of DRP and 6% of DSi are retained, while 6% of DIN is released by the reservoir. The preferential retention of DRP over DIN and DSi is increasing DIN:DRP and DSi:DRP ratios leaving the reservoir, further solidifying P-limited conditions in downstream water bodies. Furthermore, elevated N availability relative to P and Si could alter downstream algal community structure and increase the toxicity of algal blooms (Gobler et al., 2016). Retention of DRP by the reservoir can alleviate downstream eutrophication, at the expense of in-reservoir eutrophication (Maavara et al., 2020b). Depending on the desired outcome, in-reservoir nutrient management strategies could be implemented to maximize P retention, as supplement to the more widely adapted land-based strategies such as land use management changes. Net release of DIN, however, implies that in-reservoir N cycling may create additional anthropogenic pressure to downstream Lake St. Clair and ultimately the western basin of Lake Erie. This unexpected increase of N flow reveals an anomaly from the global average and highlights the need to develop N reduction goals alongside P reduction goals in the Thames River watershed to mitigate downstream eutrophication.

The general nutrient transport behaviors of DIN, DRP, and DSi on the Thames River are identified by their CQ relationships. At upstream of the reservoir, DIN and DRP exhibit mobilization behaviors, and DSi is chemostatic. The observed pattern is consistent with many agricultural-dominated landscapes, where excess fertilizers are mobilized under high flow conditions, and silicon is derived from mineral weathering (Dolph et al., 2019; Godsey et al., 2009). Mobilization behaviors of DRP and DIN indicate that nutrient losses from the landscape may be exacerbated by higher frequency of extreme precipitation events and higher annual average precipitation/streamflow, an emerging climatic trend in Canada driven by warmer temperature (Goyette et al., 2019; Zhang et al., 2019; Vincent et al., 2015). Downstream of the reservoir, DRP's transport behavior shifts to chemostatic, likely driven by internal P loading during the low flow summer and enhanced retention during high flow events. The cumulative effect of these in-reservoir processes lowers the long-term variability of DRP concentration with flow. In contrast, DIN's CQ relationship remains consistent between upstream and downstream, likely due to nitrate's high solubility which limits sorption and retention under high flow conditions (Goyette et al., 2019; Sommer et al., 2006).

Based on discreate concentration data, Thames River is a predominately P-limited environment with occasional Si-limited days driven by high flow events, during which DRP concentration increases markedly more than Si concentration. The effects of these flashy events, however, are not observed on a longer timescale reflected by the load's nutrient ratios, which remain P-limited.

Overall, the findings of this projects improve the understanding of Fanshawe Reservoir's impact on Thames River's DIN, DRP, and DSi flows to Lake Erie and further identify their general transport behaviors within the Thames River watershed. The combination of these findings may help inform future nutrient management decisions targeting the landscape and the reservoir.

Chapter 4

Conclusions and future directions

4.1 Summary of main findings

In this thesis, Fanshawe Reservoir's influences on N, P, and Si flows of the Thames River are evaluated. Results from Chapter 2 show that the reservoir acts as an important P sink on the Thames River by retaining 28% and 48% of TP in 2018 and 2019, respectively. However, P retention efficiency can fluctuate substantially between seasons, ranging from a strong sink to a weak source. During the summer, P release is ostensibly driven by internal P loading induced by in-reservoir stratification, and further exacerbated by flow augmentation through bottom draw valves that preferentially discharge hypolimnion water with elevated DRP concentration. The amount of P released during the summer, however, only makes up a small portion of the annual P load and is unlikely to offset retention from other seasons. Net P release could also be driven by flow augmentation alone, an effect observed in spring of 2018 that saw a preferential release of PP, likely as a result of sediment resuspension. The mechanisms behind seasonal net P release indicate that reservoir retention efficiency is influenced by flow manipulation, namely discharge location and rate of outflow relative to inflow. Besides altering the quantity of P flow, increases to P load bioavailability (DRP:TP) is observed during the summer, driven by preferential retention of PP over DRP and release of DRP through internal loading.

In Chapter 3, results show that Fanshawe Reservoir is decoupling Thames River's nutrient flow by retaining DIN, DRP, and DSi at markedly different efficiencies: 29% of DRP and 6% of DSi are retained, while 6% of DIN is released. Preferential retention of DRP over DIN and DSi increases DIN:DRP and DSI:DRP ratios downstream of the reservoir, and potentially increases N availability and P limitation of receiving water bodies. Elevated N availability may promote more toxic HABs, however, in-reservoir P retention serves as an important P sink along the river corridor that could reduce the extent of HABs. Net release of DIN from the reservoir represents an additional source of nutrient pollution to downstream water bodies and highlights the need to develop dual nutrient reduction strategies addressing both N and P sources within the watershed. Additionally, CQ relationships reveal the general transport behaviors of DIN, DRP, and DSi in the Thames River. Upstream of the reservoir, DIN and DRP exhibit mobilization behaviors, and DSi is characterized as chemostatic. Downstream of the reservoir, however, DRP shifts to chemostatic transport, likely due to internal P loading during low flow summer and enhanced retention during high flow events within the reservoir.

Overall, the major findings of this thesis indicate that Fanshawe Reservoir exerts a major influence on nutrient flow of the Thames River. Although nutrient management actions typically focus on reducing nutrient losses from the landscapes, the effects of dammed reservoirs along river corridors warrant further consideration within the Thames River watershed.

4.2 Future Directions

The findings of this thesis are limited to data collected between 2018 and 2019 water years. Both 2018 and 2019 were wet years based on precipitation and flow data. This may create a biased understanding of Fanshawe Reservoir's influence on nutrient flow since retention efficiency may fluctuate with changing in-reservoir conditions such as water residence time, stratification, and water turbulence. It is currently unclear what the long-term variations are for Fanshawe Reservoir's retention efficiency. To address this knowledge gap, a continuous water chemistry sampling program would be necessary. Bi-weekly or weekly (if possible) sampling frequency with additional high flow events should be sufficient for accurate load estimations (Young et al., 1988; Lee et al., 2016). Furthermore, measurements of groundwater and atmospheric fluxes could improve the mass balance method herein, which only addressed riverine fluxes.

To understand the mechanisms behind in-reservoir retention and speciation transformation, in-situ measurements of different cycling processes should be conducted. Internal P loading rates under different conditions (e.g. oxygen level, temperature, and pH) can be estimated using core-incubation experiments. Particle settling rates can be measured using sediment traps deployed in the water column to identify the timing of major sedimentation fluxes. This approach was attempted during this thesis project; however, data were limited due to equipment failures. Measurements of in-situ N fixation and denitrification rates could provide important insights on the fluxes driving net release of DIN observed in Chapter 3. Analyses of total N (TN) and biogenic Si (BSi) concentrations could also be beneficial. Only dissolved nutrient species were examined in Chapter 3; however, total nutrient loads (dissolved and particulate) could be important at predicting primary production rates at longer timescales (Håkanson et al., 2007).

To increase in-reservoir P retention, nutrient management actions that specifically target in-reservoir P cycling processes will need to be experimented with. Results from Chapter 2 indicate that majority of P load are delivered during the high flow seasons; thus, maximizing retention during those seasons will have the most impact on annual retention efficiency. During high flow events, mobilization of particulate P is enhanced, which could be efficiently retained in the reservoir through sedimentation. This mechanism is like to be rapid at the fluvial site where Thames River discharges to Fanshawe Reservoir.

Dredging at this location will increase sedimentation capacity and remove accumulated P in the sediments. However, at deeper locations of the reservoir where stratification can occur, dredging could exacerbate internal P loading by increasing water depth (Kõiv et al., 2011).

To reduce internal P loading in reservoirs and lakes, numerous mitigation strategies have been developed which include both physical and chemical techniques (Søndergaard et al., 2001). At Fanshawe Reservoir, physical mixing of water by artificial circulation was recommended in the past to break up stratification and increase bottom water oxygen levels (Vandermeulen & Gemza, 1991). However, artificial circulation can have adverse effects on reservoir water quality by resuspending particulate matters and redistributing P-rich bottom waters to the surface, fueling in-reservoir algal blooms (Søndergaard et al., 2003; Hickey & Gibbs, 2009). Another physical technique to increase bottom water oxygen levels is hypolimnetic oxygenation, which involves the injection of pure oxygen to bottom waters (Hickey & Gibbs, 2009). Successful implementation of this method was observed in five eutrophic Danish Lakes that saw significant reduction of bottom water P concentrations during oxygenation (Liboriussen et al., 2009). However, long-term oxygenation can be expensive and may not reduce internal P loading if sedimentation and decomposition of organic matters were occurring rapidly, which can quickly consume dissolved oxygen at the sediment water interface (Gächter & Wehrli., 1998).

Chemical techniques through the addition of sorbents or flocculants in either particulate or liquid forms are also potential options to reduce internal P loading. Alum (aluminum sulfate) is a commonly used flocculation agent that binds with DRP in the water column before settling to the sediments (Hickey & Gibbs, 2009). One of the advantages of alum is that it is non-redox sensitive, so oxygenation of hypolimnion water would not be required to maintain P retention (Søndergaard et al., 2001). Phoslock^{TM}, a lanthanum modified clay, is another popular chemical technique that removes DRP through the formation of lanthanum phosphate, or rhabdophane (van Oosterhout & Lürling, 2013). Similar to alum, Phoslock^{TM} is also non-redox sensitive. However, an advantage of Phoslock^{TM} over alum is its faster settling rate (Hickey & Gibbs, 2009), which will be an important factor to consider due to the low water residence time at Fanshawe Reservoir.

If no mitigation strategies were deemed feasible at Fanshawe Reservoir, an alternative method to increase summer P retention efficiency may simply be altering the discharge location from the dam. If surface water could be discharged instead of bottom water with elevated DRP concentrations, the reservoir's P retention should improve during periods of stratification. However, this will come at the cost of in-reservoir nutrient enrichment. Interestingly, previous study by Nürnberg and LaZerte (2005) recommended hypolimnetic discharge coupled with flow augmentation as the method of choice to improve Fanshawe Reservoir’s water quality.

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Appendix A

Supplementary Material

The complete water chemistry dataset (excluding ECCC data) can be accessed on Mackenzie Datastream (DOI: 10.25976/a5ve-nk95).

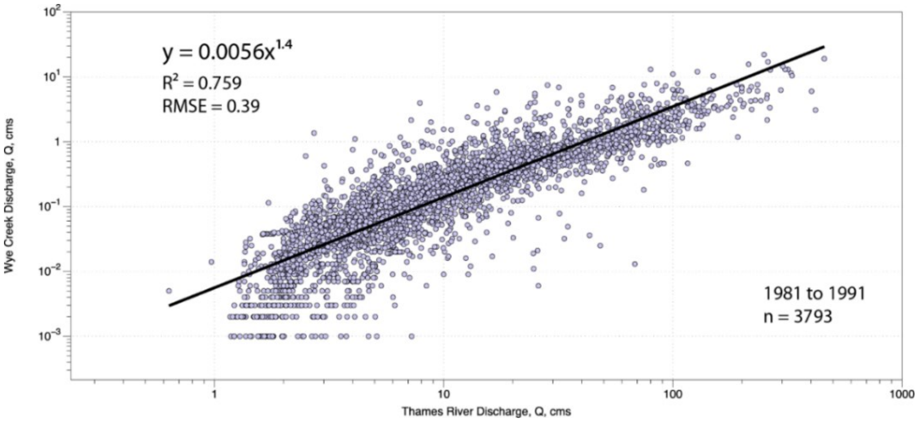

Figure A.1 Regression relationship between Wye Creek flow (y-axis) and upstream Thames River flow (x-axis). Data collected between 1981 and 1991, which were the last ten years Wye Creek WSC station's operation (station ID: 02GD013).

$$Wye\ Creek\ Flow = 0.0056(Upstream\ Thames\ River\ flow)^{1.4} \tag{A1}$$

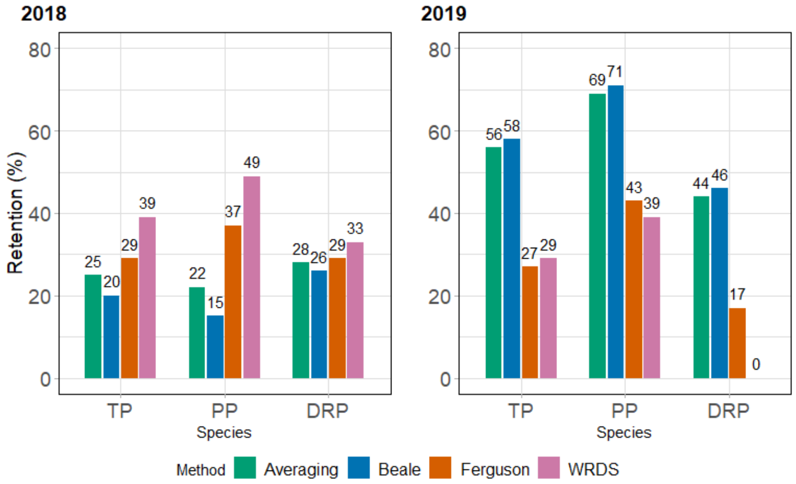

Figure A.2 Annual retention efficiencies (%) of total phosphorus (TP), particulate phosphorus (PP), and dissolved reactive phosphorus (DRP) in 2018 and 2019. "Averaging", "Beale", "Ferguson", "WRDS" correspond to the models: flow-weighted averaging estimator, Beale ratio estimator, Ferguson regression, and modified version of WRTDS, respectively.

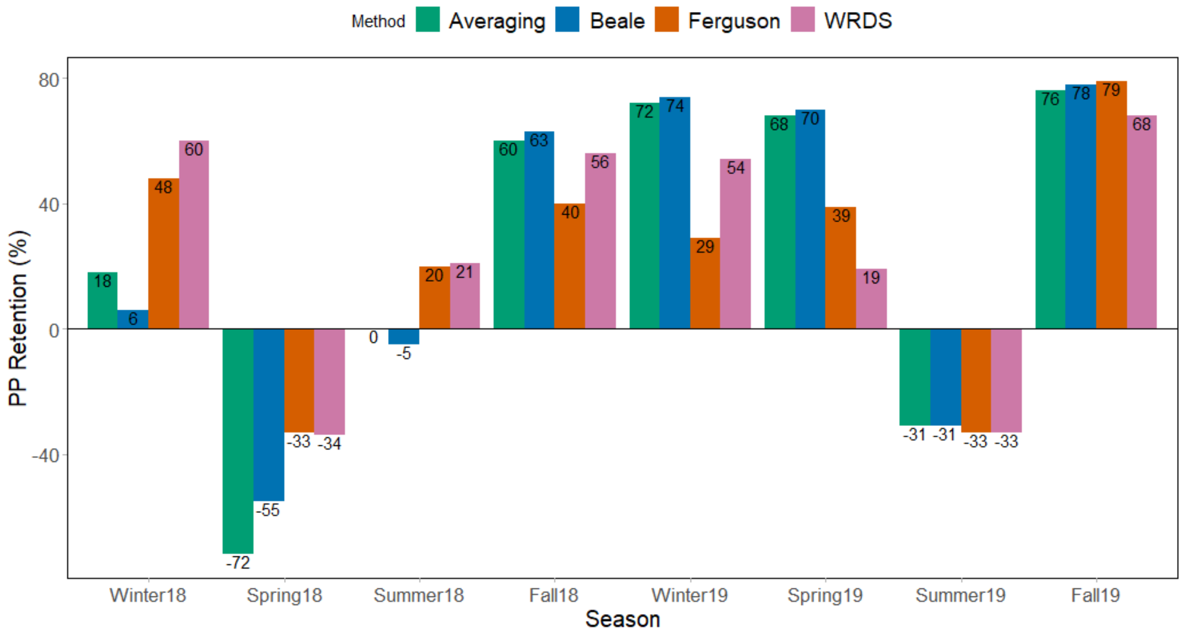

Figure A.3 Seasonal particulate phosphorus (PP) retention in 2018 and 2019.

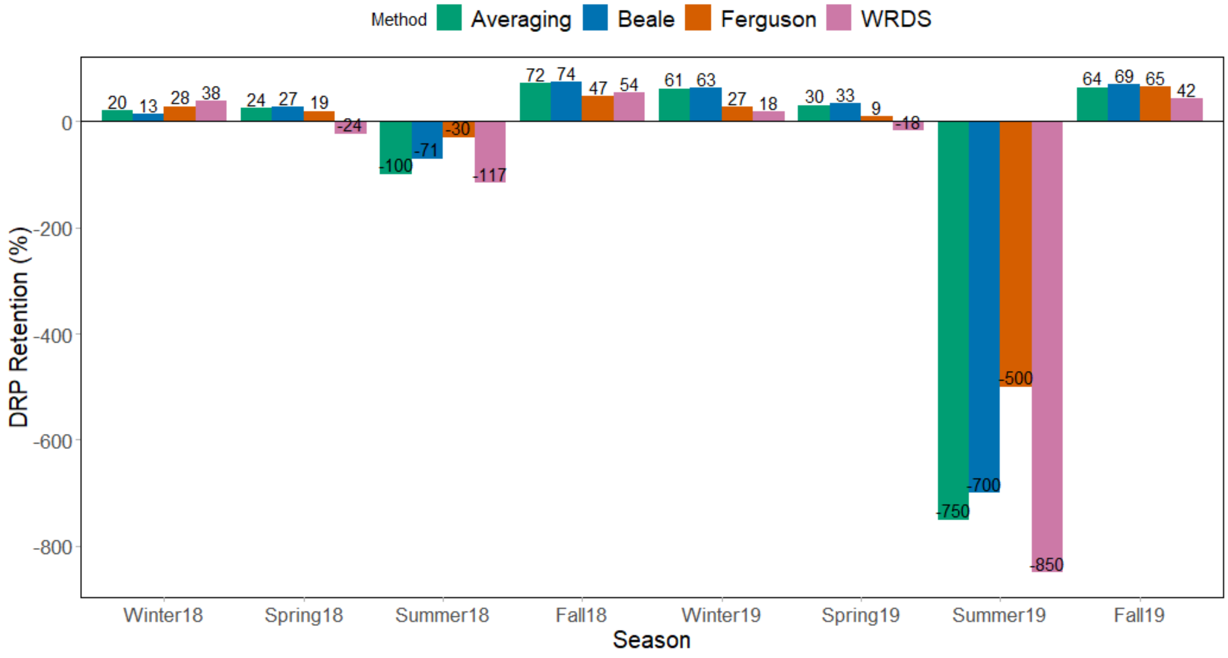

Figure A.4 Seasonal dissolved reactive phosphorus (DRP) retention in 2018 and 2019.

Table A.1 Upstream Thames River seasonal total phosphorus (TP) loads from 2018 and 2019 in metric ton (MT)

	Upstream TP loads (MT/season)							
	2018				2019			
Method	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Averaging	109.8	14.5	3.2	27.6	86.8	141.6	1.8	15.6
Beale	106.7	15.7	3.2	30.7	96.3	162.6	1.8	17
Ferguson	94.2	14	3.5	19.2	37.1	68.3	1.8	15.3
WRDS	101.2	15.5	3.8	24.2	43.5	55.2	1.8	18.1
Mean	103	14.9	3.4	25.4	65.9	106.9	1.8	16.5

Table A.2 Downstream Thames River seasonal total phosphorus (TP) loads from 2018 and 2019 in metric ton (MT)

	Downstream TP loads (MT/season)							
	2018				2019			
Method	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Averaging	86.1	16.7	4.0	10.2	30.6	69	4.1	4.8
Beale	93.4	16.9	4.1	10.3	32.2	74.5	4	4.7
Ferguson	59.4	18.5	3.9	11.1	27.0	54.4	3.3	4.5
WRDS	52.1	21.2	4.0	11.1	25.8	47.8	3.9	7.2
Mean	72.8	18.4	4.0	10.7	28.9	61.4	3.8	5.3

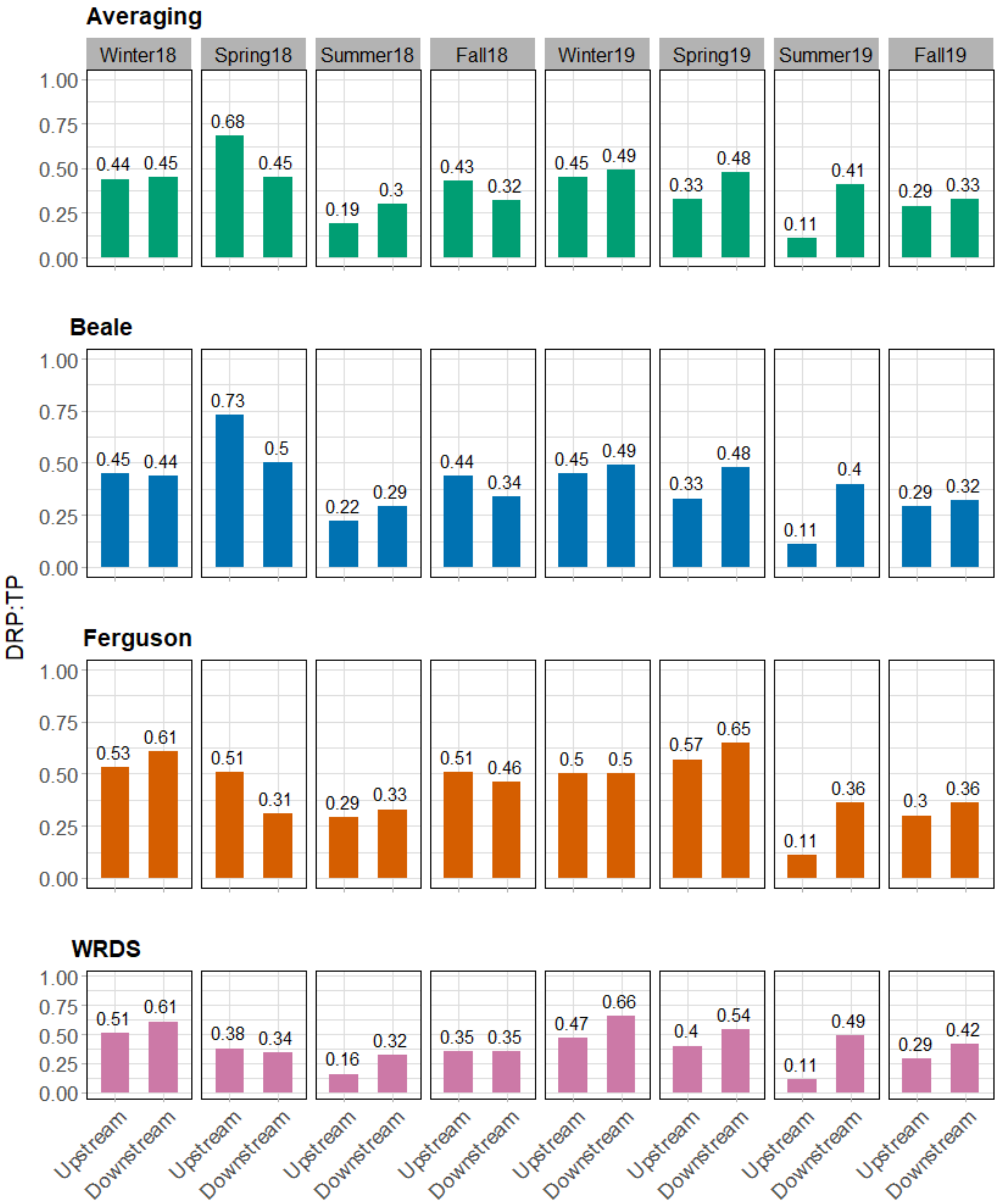

Figure A.5 Seasonal changes to load bioavailability (DRP:TP) between upstream and downstream Thames River.

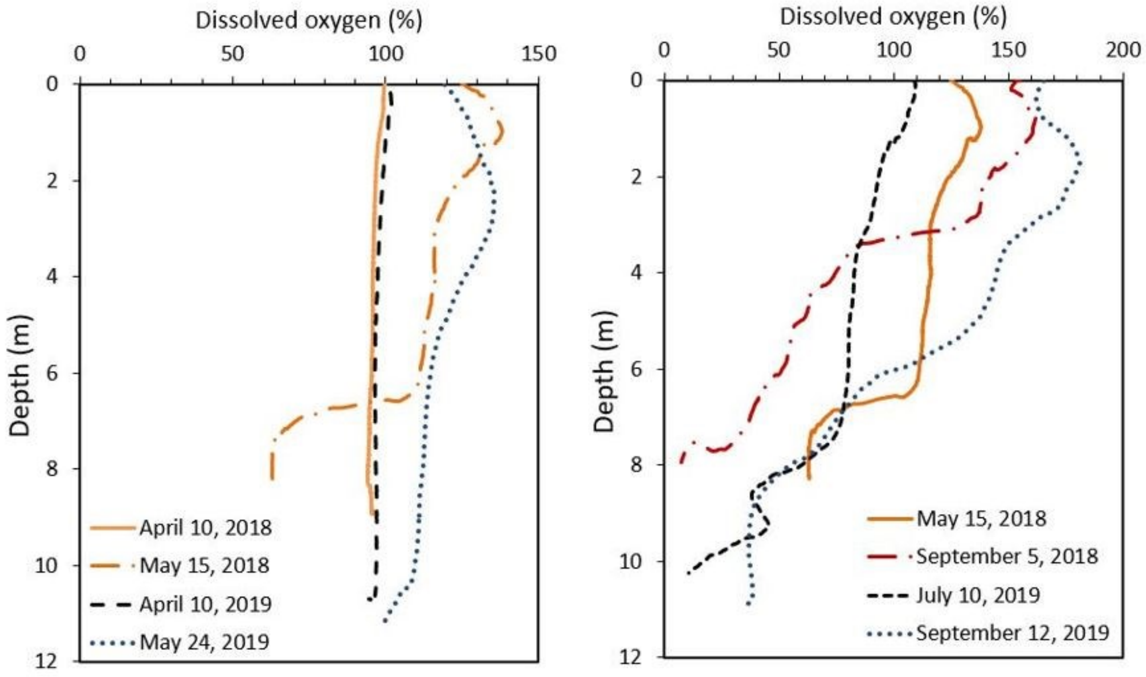

Figure A.6 Dissolved oxygen (% relative to atmospheric oxygen) water column profile taken at Fanshawe Reservoir's lentic site. Left panel shows earlier signs of stratification in 2018 starting in May, while in 2019 the water column was still well mixed. Right panel shows the earliest and latest dates of stratification in 2018 and 2019.

Table A.3 Flux bias statistics of WRDS for total phosphorus (TP) dissolved reactive phosphorus (DRP), total dissolved phosphorus (TDP), dissolved inorganic nitrogen (DIN), and dissolved silicon (DSi) on the Thames River upstream and downstream of Fanshawe Reservoir.

	Upstream	**Downstream**
TP	0.23	-0.14
DRP	0.33	0.35
TDP	0.25	0.11
DIN	-0.06	0.03
DSi	-0.05	0.05

Appendix B

Load Estimation Models

Four different load estimation models (flow-weighted averaging estimator, Beale ratio estimator, Ferguson regression, and WRTDS) were used in this study to calculate riverine phosphorus loads on Wye Creek and the Thames River upstream and downstream of Fanshawe Reservoir. Their fundamental equations, assumptions, and some advantages and disadvantages are discussed below. Additionally, due to limited available data, loads from Thorndale wastewater treatment plant were calculated in a separate method (also discussed below).

1) Flow-weighted averaging estimator

In general, averaging methods are used as a first approximation to estimate nutrient loads due to their mathematical simplicity (Quilbe et al., 2006; Booty et al., 2014), and typically require higher sampling frequency to achieve comparable accuracy to ratio methods and regression methods (Meals et al., 2013). However, in comparison to other averaging methods, the flow-weighted averaging estimator can achieve results of higher accuracy (Walling & Webb, 1981) and was recommended by Moatar & Meybeck (2005) for DRP and nitrate load calculations, and by the Paris Commission for estimating river inputs of Red list and other substances to the North Seas (Littlewood, 1992). The flow-weighted averaging estimator equation is shown below (Eq. S2), where N is the total number of days during the period of interest, C_i is the measured concentration at day i, q_i is flow at day i, n is the number of samples measured, and Q is the mean flow during the entire estimated period.

$$Load_{AVG} = N \frac{\sum_{i=1}^{n} C_i q_i}{\sum_{i=1}^{n} q_i} Q \tag{A2}$$

2) Beale ratio estimator

In cases where abundant flow data are available, but concentration data are relatively sparse, the Beale ratio estimator consistently performs better with greater precision and lower bias in comparison to other estimation methods such as linear regression and averaging methods (Dolan et al., 1981; Richards & Holloway, 1987; Young et al., 1988; Quilbe et al., 2006; Lee et al., 2016;). The Beale ratio estimator was mandated by the International Joint Commission (Canada & U.S.) in the Great Lakes Region for loading calculations (Richards & Holloway, 1987). The Beale ratio estimator equation is given below (Equation A3), where *I* is the mean load on days when samples were taken, *Q* is the mean daily flow of the entire period, *q* is the mean daily flow of the sampling days, *N* is the number of days in the entire period, and *F* is the correction factor.

$$Load_{Beale} = I\frac{Q}{q}N \cdot F \tag{A3}$$

The correction factor, *F*, is provided below (Equation A4), where *n* is the number of samples taken, S_{lq} is the covariance of load and flow from sampling days, and S_{qq} is the variance of flow of the sampling days.

$$F = \frac{1 + \frac{1}{n}\frac{S_{lq}}{Iq}}{1 + \frac{1}{n}\frac{S_{qq}}{q^2}} \tag{A4}$$

The Beale ratio estimator could be further stratified for greater precision and less error (Cochran, 1977; Dolan et al., 1981). The flow regime of the entire year could be highly heterogenous, but when divided seasonally, the internal homogeneity of each season, or strata, may be improved. Each variable of the Beale Ratio Estimator is then calculated for each individual season, summing to provide an estimation of the annual load with greater precision than calculating the annual load as one single strata (Richards & Holloway, 1987; Young et al., 1988). We applied the same approach to the flow-weighted averaging estimator and Ferguson regression (discussed below).

3) Ferguson Regression

In general, regression methods first establish a log-log linear regression between concentration (*C*) and discharge (*Q*) from sampling days:

$$log_{10}(C) = a + b \cdot log_{10}(Q) \tag{A5}$$

where *a* is the y-intercept and *b* is the slope of the fitted line. Using Equation A5, daily concentrations may be predicted using the measured daily flow data, and the total load is obtained by summing the predicted daily loads across the entire period of interest:

$$Load_{simple} = \sum_{i=1}^{N} C_i \cdot Q_i \tag{A6}$$

where C_i is the predicted concentration on day *i*, and Q_i is the measured flow on day *i*.

Ferguson (1986) stated that the back-transformation of log values between Equation A5 and Equation A6 could generate underestimations to the actual load, and proposed the Ferguson regression method (Equation A7) as a modification to Equation A6 to mitigate underestimations:

$$Load_{Ferguson} = Load_{simple} \cdot \exp\,(2.651\,\sigma^2) \tag{A7}$$

where σ is the standard error of the estimate of the log-log linear regression (Equation A8) in $\log_{10}$ units:

$$\sigma = \sqrt{\frac{\sum\left(\log_{10} C_i - \log_{10} \hat{C}_i\right)^2}{n-2}} \tag{A8}$$

where $\hat{C}_i$ is the actual documented concentration on day *i*.

The performance of regression methods is dependent on the strength of correlation between concentration and discharge (Preston et al., 1989; Richards, 1998), which can be evaluated by the coefficient of determination (r^2) of the fitted line (Eq. S5), but a comprehensively agreed upon threshold value that validates the use of regression methods does not exist. Several authors have recommended different r^2 values as the deciding factor for choosing between regression or interpolation (ratio and averaging methods) methods. For example, Quilbe et al. (2006) proposed $r^2 > 0.5$, while Aulenbach et al. (2016) recommended $r^2 \geq 0.3$ for selecting regression methods. With satisfactory correlation between C and Q, regression methods require less extensive data to achieve comparable accuracy as interpolation methods. However, the data points used to generate the fitted line (Eq. S5) should cover the entire flow range of the period, and any predicted concentrations extrapolated from beyond the measured flow range will introduce error to the model (Freund & Wilson, 2003; Quilbe et al., 2006). Booty et al. (2014) stated however, loading estimates can be extrapolated outside of the measured range if a strong CQ correlation exists ($r^2 > 0.5$).

4) Weighted Regression on Time, Discharge, and Seasons (WRTDS)

Formulated by Hirsch et al. (2010), WRTDS is a regression method that can be used through the U.S. Geological Survey R package: Exploration and Graphics for RivEr Trends (EGRET) (Hirsch & De Cicco, 2014). In comparison to Ferguson regression, WRTDS is mathematically more complex and offers more flexibility and robustness at the cost of requiring longer records of data (Lee et al., 2016). Unlike most simple regression methods (e.g. Ferguson regression), which rely on a single, rigid equation based on the observed CQ relationship, WRTDS does not assume that the CQ relationship remains static with time; the mathematical structure of WRTDS is flexible in the way that it is a non-linear and time-varying equation that changes with the flow condition ("discharge" component) at multi-year ("time" component) and seasonal ("seasons" component) timescales (Hirsch et al., 2010). With WRTDS, Hirsch et al (2010) looked to address some of the common conditions that introduce errors to regression models such as poor CQ relationships and varying CQ relationships between seasons (Lee et al., 2016). The equation of WRTDS is given below:

$$\ln(c) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon \tag{A9}$$

where *c* is concentration, *β* values are the fitted coefficients, Q is flow, t is time in years, and *ε* is the unexplained variation (Hirsch et al., 2010). Originally designed for long-term datasets that require at least 200 concentration data points collected over 10 years or longer, WRTDS can also be used on smaller datasets with modifications to the default settings (Hirsch & De Cicco, 2014). The timeframe of our dataset is much shorter than WRTDS' original requirement (e.g. TP data at upstream Thames River has 72 data points over 2 years), which means the "time" component that adjusts for long-term trends is unnecessary; to eliminate this, we changed the half window width for time weighting ("windowY" in EGRET) from the default setting of 7 years to 100 years, essentially over-smooth any long-term trends, leaving the "seasons" component as the only time trend. We recognize that even with this maneuver, our dataset is still shorter than the suggested timeframe, possibly introducing errors to the model.

4.1) Flux bias statistic

Flux bias statistic is one of the built-in outputs of the EGRET package to evaluate the performance of WRTDS. Flux bias statistic (*B*) represents the difference between the sum of predicted loads (*P*) and the sum of observed loads on days of sampling:

$$B = \frac{(P - O)}{P} \tag{A10}$$

The bias of the model is estimated by B, where values near zero suggest approximately unbiased results, negative values suggest underestimation, and positive values suggest overestimation. For example, a B value between -0.15 and +0.15 suggests the bias of the estimated long term mean flux is within 15 percent. In cases where severe biases are estimated, the user should consider using a different load estimation model (Hirsch & De Cicco, 2014).

For the flux bias statistics of nutrient elements considered in this thesis, see Table A.3.

5) Thorndale WWTP calculation

Due to limited data availability, we calculated the WWTP loads differently than the riverine loads (upstream and downstream Thames River, and Wye Creek). Only monthly averaged TP concentration and effluent flow data were available from the Thorndale WWTP. Under this constraint, we assumed the monthly averaged values to be representative of the daily values throughout their respective month, and calculated WWTP load of a given month with the following equation:

$$Load_{WWTP} = C_m \cdot Q_m \cdot N_m \tag{A11}$$

where C_m is the monthly averaged concentration, Q_m is the monthly averaged flow, and N_m is the number of days in the month. Each monthly load is then added to the corresponding seasonal upstream TP load.