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

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ABSTRACT

Extensive efforts are underway to reduce phosphorus (P) export from the Lake Erie 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 dams in retaining and modifying riverine P loading to the lake has not been comprehensively evaluated. We assessed whether Fanshawe Reservoir, the largest dam reservoir on the Thames River, acts as a source or sink of P, using year-round discharge and water chemistry data collected in 2018 and 2019. We also determined how in-reservoir processes alter P speciation by comparing the dissolved reactive P to total P ratio (DRP:TP) in upstream and downstream loads. Annually, Fanshawe Reservoir was a net sink for P, retaining 25% (36 tonnes) and 47% (91 tonnes) of TP in 2018 and 2019, respectively. Seasonally, the reservoir oscillated between a source and sink of P. Net P release occurred during the spring of 2018 and the summers of 2018 and 2019, driven by internal P loading and hypolimnetic discharge from the dam. The reservoir did not exert a strong influence on DRP:TP annually, but ratio increases occurred during both summers, concurrent with water column stratification. 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 P loads. We therefore propose that the potential of using existing dam reservoirs to attenuate downstream P loads should be more thoroughly explored alongside source based P mitigation strategies.

Introduction

To address widespread eutrophication and the resurgence of harmful algal blooms (HABs) in Lake Erie, Canadian and U.S. federal, state and provincial governments have committed to a 40% reduction of spring total phosphorus (TP) and dissolved reactive phosphorus (DRP) loads from priority tributaries that discharge to the western and central basins of Lake Erie by 2025 (Government of Canada, 2016). On the Canadian side of the watershed, the Thames River (via Lake St. Clair and the Detroit River) constitutes the largest tributary P source to the lake's western basin (Maccoux et al., 2016) and has been 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 concerted and renewed efforts to mitigate non-point source (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, Ministry of the Environment and Climate Change, 2018; Upper Thames River Conservation Authority, 2018). However, a quantitative understanding of the processes influencing P transformations, retention and remobilization within the Thames River, from source areas to the river mouth, remains lacking.

Dammed reservoirs modify nutrient flows and speciation along the river continuum (Friedl and Wüest, 2002; Maavara et al., 2020;

BMP, best management practice; DRP, dissolved reactive phosphorus; DUP, dissolved unreactive phosphorus; HAB, harmful algal bloom; NPS, non-point source; PP, particulate phosphorus; RE, retention efficiency; TDP, total dissolved phosphorus; TP, total phosphorus.

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Teodoru and Wehrli, 2005; Van Cappellen and Maavara, 2016). On a global scale, reservoirs retain an estimated 12% of the riverine TP load (Maavara et al., 2015). However, the retention efficiency (RE) of individual reservoirs varies widely, with some reservoirs even acting as a source rather than a sink (Maavara et al., 2020; Maavara et al., 2015); Némery et al., 2016; Teodoru and Wehrli, 2005). Predicting the influence of any individual reservoir on P retention and transformation is challenging due to the complex interactions of multiple physical and biogeochemical processes in the reservoir's water column and sediments (Donald et al., 2015; Powers et al., 2015).

Compared to the inflowing river channel, a reservoir experiences a longer water residence time, decreased flow velocity and turbidity, and deeper light penetration (Friedl and Wüest, 2002). That is, the reservoir exhibits more lake-like properties that enhance in-reservoir primary production and the biogeochemical cycling of P, typically leading to retention of P through accumulation of both organic and mineral particulate matter during sediment deposition and burial (Van Cappellen and Maavara, 2016). Generally, the RE of P correlates with the reservoir's water residence time (Donald et al., 2015; Kõiv et al., 2011; Maavara et al., 2015). However, net remobilization of P can occur in reservoirs with a history of high external P inputs, particularly when the external P load from the watershed decreases, as legacy P in the sediments may be mobilized through internal loading (O'Connell et al., 2020; Orihel et al., 2017; Søndergaard et al., 2001; Teodoru and Wehrli, 2005). Furthermore, the chemical speciation and, therefore, the bioavailability of P flowing out through the dam may be altered by in-reservoir biogeochemical processes. For example, for the Iron Gate I Reservoir on the Danube River, in-reservoir transformation of particulate P to dissolved P (DP) causes a 20% increase of the DP:TP ratio leaving the reservoir (Teodoru and Wehrli, 2005).

There are three major dammed reservoirs on the Thames River: Pittock, Wildwood, and Fanshawe (Fig. 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 $\times$ 10^6 m^3) (Nürnberg and 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 on Fanshawe Reservoir. The first, completed by the Ontario Ministry of Environment between 1988 and 1989, was based on relatively high frequency water chemistry and discharge measurements but was limited to the summer season (May to September). This study concluded that the reservoir was a sink of P in 1988 but a source of P in 1989 (Vandermeulen and Gemza, 1991). The second, more recent, study estimated a long-term P RE of −28%, implying that the reservoir has been a net source of TP to the Thames River over several decades (1975–2004) (Nürnberg and LaZerte, 2005). However, as recognized by the authors, the P concentration data used were sparse (e.g. four data points in 2004) and did not provide good coverage of high flow events, hence, limiting the accuracy of the loading calculations on which the P retention estimates were based (Lee et al., 2016; Nürnberg and LaZerte, 2015; Nürnberg and LaZerte, 2005). Given the context of Fanshawe Reservoir within a watershed of regional and binational importance, an updated and more robust mass balance for P is of considerable interest. Therefore, in this study we conducted an intensive two-year sampling of water chemistry, spanning all seasons and a comprehensive range of flow regimes, to better characterize P cycling in Fanshawe Reservoir.

Changes to the riverine P load, caused by physical and biogeochemical processes in the reservoir, can potentially mask improvements to water quality in the upstream watershed following the implementation of nutrient BMPs. Therefore, an assessment of the efficacy of such management practices requires an understanding of how in-reservoir processes alter the magnitude and speciation of the riverine P load delivered by the North Thames River watershed. Specifically, in this study we aimed to: (1) determine the reservoir's annual and seasonal RE for the following P fractions: DRP, dissolved unreactive P (DUP) and particulate P (PP), (2) assess the relative changes in the bioavailability of the P load using the DRP:TP ratio as a proxy, and (3) explore the implications of our findings for nutrient management strategies at the watershed scale.

Study site and methods

Fanshawe Reservoir

Fanshawe dam was constructed in 1953, primarily for flow regulation and to avoid flooding in the city of London, Ontario, which is located approximately 12 km downstream of the dam (Vandermeulen and Gemza, 1991). Operated and maintained by the Upper Thames River Conservation Authority (UTRCA), Fanshawe Reservoir also provides hydroelectricity generation (2860 megawatt $year^{-1}$) and recreational opportunities (Upper Thames River Conservation Authority (UTRCA), n.d.). According to stream flow data collected between 1981 and 1991 by Water Survey Canada (WSC), Fanshawe Reservoir receives about 97% of its inflow from the Thames River, while the remaining 3% is accounted for by a minor tributary, Wye Creek (Fig. 2). Primary outflow from the reservoir is controlled by the dam, which discharges downstream to the Thames River through bottom draw valves 8–10 m below the water surface. Under normal operating conditions, the outflow closely balances the upstream inflow. 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 dammed reservoirs based on morphology and hydrological behavior: 1) a fluvial zone where the river first discharges into the reservoir, 2) a lentic zone closest to the dam wall where water is the deepest and slowest moving, and 3) a transitional zone between the fluvial and lentic zones (Soares et al., 2012). The morphology and hydrology of Fanshawe Reservoir follows this longitudinal zonation quite closely, with a mean water depth of 4.8 m and a maximum depth of 12 m close to the dam wall (Nürnberg and LaZerte, 2005). Based on historical data collected between 1954 and 2004, the average water residence time of Fanshawe Reservoir is estimated at approximately 10 days (Nürnberg and LaZerte, 2005). The water residence time, however, is highly variable. For instance, during our study the values ranged from 43 days (summer 2018) to 6.5 days (spring 2019).

Mass balance approach

To determine RE (Eq. (1)), we used a mass balance approach accounting for the riverine inflow and outflow P loads (Electronic Supplementary Material ((ESM) Fig. S1) For inflowing loads, the Thames River upstream of the reservoir is the dominant source, with a very small additional contribution from Wye Creek. We further accounted for the TP load from a local wastewater treatment plant (Thorndale WWTP), which discharges into the Thames River between the upstream sampling point and the reservoir (Fig. 2 with further details provided in ESM Appendix S1). The only discharge location from the reservoir is at the dam wall, which represents the outflowing load.

$$\boldsymbol{Retention}(\%) = \left(\frac{\boldsymbol{Load_{in}} - \boldsymbol{Load_{out}}}{\boldsymbol{Load_{in}}}\right) \times 100 \quad (1)$$

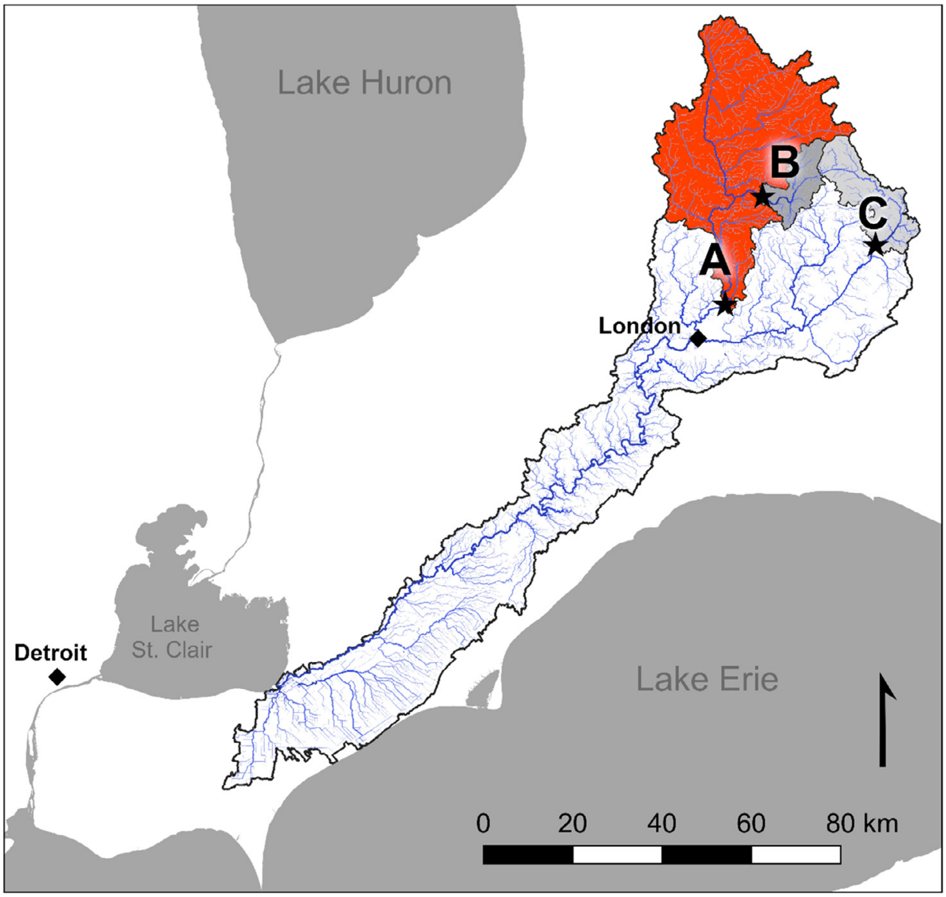

Fig. 1. Thames River watershed (black outlined area) and locations of reservoirs (black stars) Fanshawe (A), Wildwood (B), and Pittock (C) with respective subwatersheds colorized in the order of red, dark grey, and light grey. Thames River discharges to Lake St. Clair and subsequently to Lake Erie through the Detroit River. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Expressed as a percentage, positive RE indicates net retention of P within the reservoir (i.e., the reservoir is a P sink), and negative values indicate net release of P from the reservoir (i.e., a source). In comparison to riverine loads, the estimated P inputs via precipitation and groundwater are negligible and hence excluded from our calculations (Keup, 1968; Nürnberg and LaZerte, 2005). We conducted mass balance calculations at annual and seasonal scales. The seasons were based on meteorological definitions: winter (December 1–February 28), spring (March 1–May 31), summer (June 1–August 31), and fall (September 1–November 30) (Kutta and Hubbart, 2016).

Streamflow data

Daily discharge values for the Thames River upstream (station ID: 02GD015) and downstream (station ID: 02GD003) of Fanshawe Reservoir were calculated based on level measurements recorded at 5-minute intervals and the corresponding rating curves. The data were obtained from WSC between December 1, 2017 and November 30, 2019 (ESM Fig. S2). Unfortunately, similar data collection at a hydrometric station on Wye Creek (station ID: 02GD013) ended in 1991. Therefore, we estimated daily discharge from Wye Creek using a regression relationship between the Thames River upstream and Wye Creek WSC stations based on discharge data collected between 1981 and 1991 (r^2 = 0.76, RMSE = 0.39) (ESM Fig. S3).

River water sampling

Between December 2017 and October 2018, water grab samples were collected at the upstream and downstream sites approximately once every two weeks by Environment and Climate Change Canada (ECCC) under the Great Lakes Nutrient Initiative. Between March 2018 and December 2019, water grab samples were also collected at the upstream, downstream and Wye Creek sites (Fig. 2) once every two weeks by researchers from the University of Waterloo (UW), with additional sampling during high flow events. Both datasets were combined for load calculations. The combined dataset included 72 samples at each of the upstream and downstream sites, and 51 samples at the Wye Creek site.

In-reservoir water sampling

Sampling was also conducted at three sites within the reservoir (Fig. 2). Site locations were selected to represent the lentic (site 1), transitional (site 2), and fluvial (site 3) zones. Sites 1 and 2 were further separated into two sampling depths to represent the epilimnion and hypolimnion. Water samples within the reservoir were collected using a peristaltic pump (Pegasus Alexis). Epilimnion samples were collected 1 m below the water surface, hypolimnion samples 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 the loading model calculations but provided insights into the in-reservoir P-cycling processes respon-

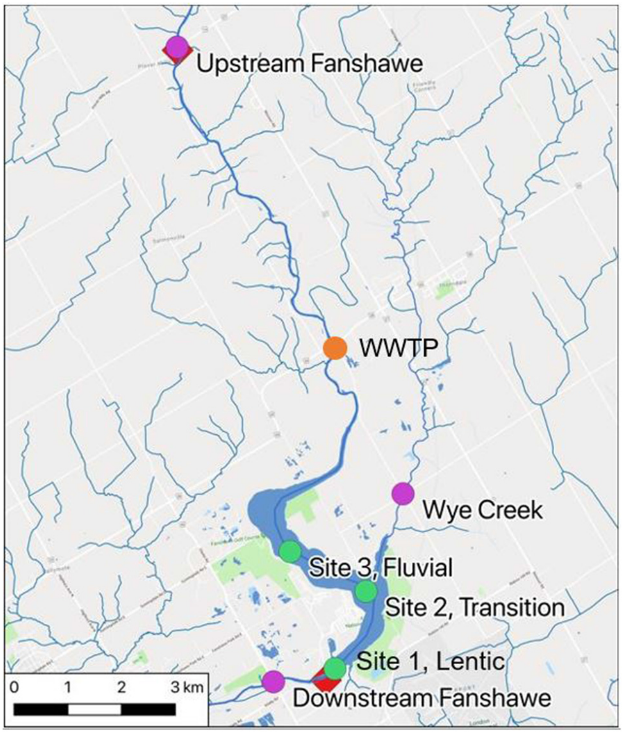

Fig. 2. Sampling sites at Fanshawe Reservoir and the Thames River. River water sample site, reservoir water sample site, and Water Survey Canada stations are colorized in purple, green, and red, respectively. Location of Thorndale WWTP appears in orange. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sible for the seasonal patterns in RE and DRP:TP changes. Water column profiles of temperature and dissolved oxygen concentration were obtained using a profiler (RBR XR-620) at the three reservoir sites prior to the collection of water chemistry samples.

Analytical methods

The concentrations of the following three operationally defined P fractions were determined for 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 pore size 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 from UW (76% of samples) and ECCC (24% of samples) were analyzed in the UW Ecohydrology Laboratory and the Burlington National Laboratory for Environmental Testing (NLET), respectively. Each laboratory analyzed an equal number of samples from upstream and downstream of the reservoir. At both laboratories, DRP was measured colorimetrically using the molybdate 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 at NLET following an acid persulfate autoclave digestion (MDL 0.016 μmol L^{-1}). In both laboratories, TP samples were subjected to acid persulfate autoclave digestion prior to analysis (Dayton et al., 2017; Ontario Ministry of the Environment, Laboratory Services Branch, 2015). 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 were <10% RSD based on triplicate measurements of samples, and ±10% with respect to certified reference materials (orthophosphate, NS-QCI-141, Canadian Life Science; ICP QC standard 1 CRM, ICPQC-1, NSI Lab Solutions). Matrix matched 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). Consistency between results obtained from the UW laboratory and NLET was evaluated for all parameters (TP, TDP and DRP) via Mann-Whitney-Wilcoxon and Kruskal-Wallis rank sum tests performed in the R statistical computing environment (R Core Team, 2020). No statistical differences between the results obtained from the two different laboratories were found at the 0.05 confidence level for any parameters. Non-parametric tests were used after checking for normality with the Shapiro-Wilk test and by visual inspection of quantile–quantile plots.

Weather and streamflow

We obtained daily records of precipitation and air temperature between 2003 and 2019 to assess whether weather during our study period was representative of long-term conditions. Data were obtained from the Meteorological Service of Canada's London CS station (Climate ID: 6144478), which is located approximately 2.5 km from Fanshawe Reservoir. Using the definition of 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 the WSC upstream station (ID: 02GD015) to determine the natural inter-annual 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 operations, the dam's discharge is managed to roughly mimic the upstream inflow (Upper Thames River Conservation Authority (UTRCA), n.d.).

Phosphorus loads

Many different riverine nutrient loading models have been comprehensively evaluated in previous literature (e.g. Lee et al., 2016; Lee et al., 2019; Nava et al., 2019, Preston et al., 1989). Optimal method selection is controversial and dependent on a wide variety of factors, such as sample frequency and distribution, watershed size, human activities, flow variability, and the strength of correlation between concentration and discharge (Quilbé et al., 2006; Richards and Holloway, 1987).

Traditionally, loading estimation models are divided into three main classes;

(1) Interpolation methods, which involve averaging of either sampled concentration values, flows or loads, calculated over different time intervals. These methods provide accurate estimates of load when both flow and concentration data are abundant and representative of the entire range of flow, concentration and time.
(2) Ratio estimator methods, which attempt to correct for differences between average flow conditions during the study period and average flow conditions at the times when concentration values were determined. Ratio estimator methods are particularly suitable when large amounts of flow data

and comparatively little concentration data are available. The Beale's ratio estimator allows for flexibility in the relationship between flow and concentration, which improves estimation accuracy.

(3) Regression methods, which employ either simple linear relationships or more complex weighted formulations linking concentration with flow to estimate missing concentration data from more abundant flow data. These methods are most appropriate when a strong relationship between concentration and flow exists.

While no single model, or class of models, is superior to others in all situations, Beale's ratio estimator and regression methods such as the Weighted Regression on Time, Discharge, and Season (WRTDS) have been found to provide accurate loading estimates under a broad range of conditions (Lee et al., 2016; Nava et al., 2019). Further, a modification of WRTDS, in which a Kalman filter is applied to the model output based on the residuals, has recently been shown to yield even better loading estimates, particularly in situations where water chemistry is sampled frequently (Lee et al., 2019, Zhang and Hirsch, 2019).

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 different commonly used load estimation models spanning all three classes and including those reported to generally exhibit the highest estimation accuracy. The models selected were the flow-weighted averaging estimator (Walling and Webb, 1981), Beale ratio estimator (Beale, 1962), Ferguson regression (Ferguson, 1986), and a modified Weighted Regression on Time, Discharge, and Season – Kalman Filter (WRTDS-K) estimation (Hirsch et al., 2010; Zhang and Hirsch, 2019). In our study the "Time" component of WRTDS-K, which accounts for multi-year variations, was muted to accommodate our shorter sampling timeframe. This was achieved by increasing the half-window width for time weighting to over-smooth trends over time (Hirsch and De Cicco, 2015). Therefore, "WRDS-K" is used herein. All model calculations were performed in the R statistical computing environment (R Core Team, 2020); WRDS-K was calculated using the Exploration and Graphics for RivEr Trends (EGRET) package. The equations, detailed descriptions of the load estimation models used and any modifications of the models, are provided in ESM Appendix S1.

We further classified and separated TP loads according to the following operational fractions: 1) DRP, the most bioavailable fraction of TP, 2) particulate P (PP), defined as the difference between TP and TDP, and 3) dissolved unreactive P (DUP), defined as the difference between TDP and DRP (Effler et al., 2009; Worsfold et al., 2016). The DRP:TP ratio was used as a measure of changes in the relative bioavailability between upstream and downstream loads (Baker et al., 2014).

Results

Weather and water flow regime

The average annual TAP for the period 2003–2019 was 954 mm. Comparatively, 2018 was a wet year (TAP: 969 mm) and 2019 was an extreme wet year (TAP: 1057 mm). The heavier than average precipitation was reflected in the discharge measured on the Thames River upstream of the reservoir: both 2018 and 2019 were high flow years averaging 21.2 and 20.8 cubic meters per second (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, calculated downstream flows were slightly higher than upstream in 2018 and 2019, by 1.4% and 5.9%, respectively. Seasonally, downstream and upstream flows generally balanced well (<10% difference), except in three seasons for which downstream flows were greater (>10%) than upstream flows: 2018 spring (11%), 2018 summer (23.6%), and 2019 summer (13.5%). Records of water level within the reservoir also indicate net water drawdown during spring and summer followed by net increases to stored water volumes during fall and winter. Our sampling program captured water chemistry covering close to 100% of the variation in flow at both upstream and downstream sites during the study period (ESM Fig. S4).

Annual P loads, retention, and speciation

In 2018, the four loading models provided similar estimates of annual TP loads (Fig. 3). Upstream loads ranged from 115.6 to 156.3 metric tons (MT) (12.3% RSD between model outputs), while downstream loads ranged from 86.2 to 124.7 MT (15.3% RSD) (Table 1). In 2019, the different models yielded higher variability, especially between the interpolation methods (flow-weighted averaging and Beale Ratio) and the regression methods (Ferguson regression and WRDS-K). Upstream TP loads ranged from 122.5 to 277.7 MT (36.7% RSD), while downstream TP loads ranged from 89.2 to 115.4 MT (11.1% RSD). In both years, the annual DRP and PP loads were of comparable magnitudes, indicating that at least half of the P load was readily 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 acted as a net P sink in both 2018 and 2019 (ESM Fig. S5). On an annual basis, 20% to 29% of total incoming TP was retained in 2018, and 26% to 58% was retained in 2019. The larger range in RE in 2019 reflects the greater variability in the 2019 load estimates by the four models. Although retention of PP and DRP were approximately equal in 2018 (RE of 26% for PP and 28% for DRP), PP was more efficiently retained than DRP in 2019 (RE of 55% for PP vs 29% for DRP).

Changes to the DRP:TP ratio of the annual loads between upstream and downstream sites are shown in ESM Fig. S6. In 2018, the averaging, Beale ratio estimator and WRDS-K methods all yielded slight decreases in DRP:TP (−0.03), while the Ferguson regression method produced no change. In 2019, however, all models showed minor increases to the DRP:TP ratio in the downstream loads, ranging from +0.07 to +0.10 relative to the upstream loads.

Seasonal P loads, retention, and speciation

Across 2018 and 2019, the mean upstream TP loads predicted by the four load estimation models ranged widely between seasons, from 1.7 MT (summer 2019) to 108.9 MT (spring 2019). Downstream TP loads followed a similar seasonal pattern, ranging from 3.8 MT (summer 2019) to 73.5 MT (winter 2018) (Fig. 4). 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 occurred during summer for both years. All models produced similar seasonal patterns of loading of the different P fractions, except during winter and spring of 2019 at the upstream location, when the regression methods produced smaller TP load estimates compared to the interpolation models. For the model results of all seasonal TP loads, see ESM Tables S1 and S2.

The RE of TP also varied widely between seasons (Fig. 5), ranging from sink (winter and fall of both years plus spring of 2019) to

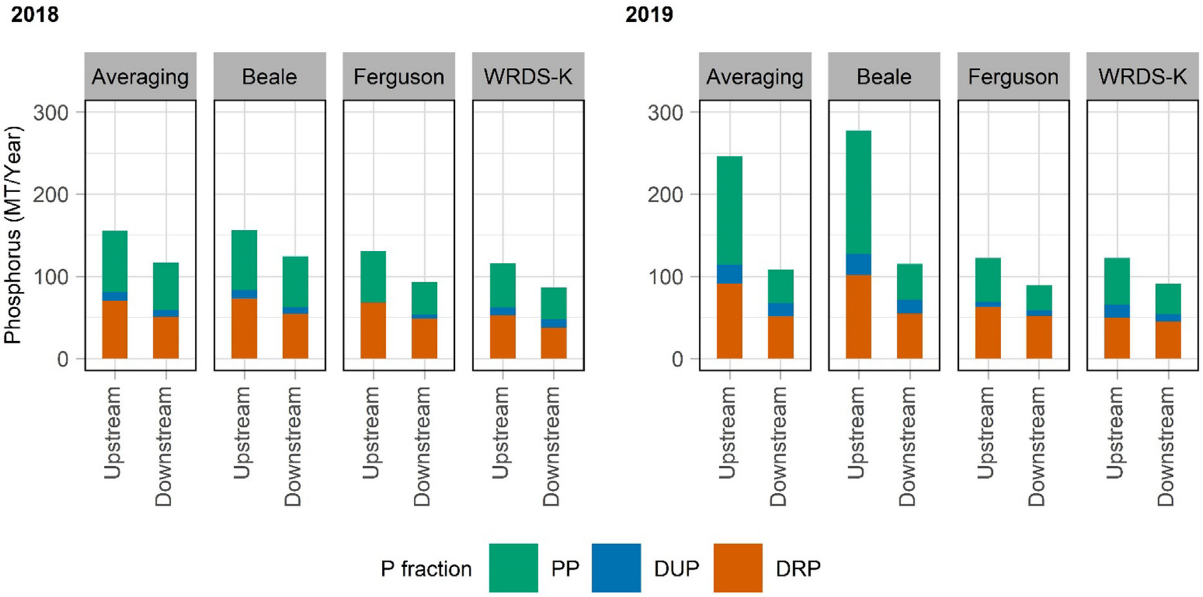

Fig. 3. Model estimates of 2018 and 2019 annual total phosphorus (TP) loads in metric tons (MT). TP was further separated into particulate phosphorus (PP), dissolved unreactive phosphorus (DUP), and dissolved reactive phosphorus (DRP) fractions. "Averaging", "Beale", "Ferguson", and "WRDS-K" correspond to the four models used: flow-weighted averaging estimator, Beale ratio estimator, Ferguson regression, and modified version of WRTDS-K, respectively.

Table 1
Model estimates of 2018 and 2019 annual total phosphorus (TP) loads in metric ton (MT) per year. "Averaging", "Beale", "Ferguson", and "WRDS-K" correspond to the four models used: flow-weighted averaging estimator, Beale ratio estimator, Ferguson regression, and modified version of WRTDS-K, respectively.

		TP load estimates (MT/year)				
Model	2018 Upstream	2018 Downstream	2018 Retained	2019 Upstream	2019 Downstream	2019 Retained
Averaging	155.1	117.0	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-K	115.6	86.2	29.4	122.6	90.9	31.8
Mean	139.5	105.2	35.7	192.2	101.0	91.2

source (both summers plus spring of 2018). The most negative RE was observed in the summer of 2019 (−118% on average between the models). However, inflow P loads delivered to the reservoir by the Thames River during summers were orders of magnitude lower than during the high-flow seasons (winter and spring). Therefore, the mass of P released downstream during seasons with negative RE was much smaller than the mass retained during the remaining seasons. For example, on average, 46 MT of TP was retained in spring 2019 at 42% RE, while only 2 MT of TP was released in summer 2019 at −124% RE. Seasonal retention of PP (ESM Fig. S7) and DRP (ESM Fig. S8) followed similar trends to TP except for spring and summer of 2018. 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 varied seasonally with good agreement across the ensemble of loading models for most seasons (ESM Fig. S9). Pronounced increases to DRP:TP were shown by all models during both summers and the spring of 2019 (Fig. 6 and ESM Fig. S9). Conversely, in spring 2018, DRP:TP decreased markedly across all model outputs.

In-reservoir conditions

Based on dissolved oxygen profiles, in-reservoir stratification was observed in 2018 from May to September (no profiler data are available for 2018 after September due to instrument failure) and in 2019 from July to September (ESM Fig. S10). All profiles collected during winter indicated a well-mixed water column. DRP concentrations measured at the lentic site showed noticeable deviation between hypolimnion and epilimnion depths during the summer seasons (Fig. 7). Hypolimnion DRP concentrations were consistently higher from June to September in 2018 ($p = 0.0001$, $n = 6$) and from July to September in 2019 ($p = 0.088$, $n = 4$), that is, when the reservoir was stratified.

Discussion

P retention in Fanshawe Reservoir

In contrast to previous P mass balance studies, which implied that Fanshawe reservoir acted as a source of P for the period 1974–2004 (Nürnberg and LaZerte, 2005) and during 1989 (Vandermeulen and Gemza, 1991), our results demonstrate that Fanshawe Reservoir acted as a net sink for P in both 2018 (20–29% TP retained) and 2019 (26–58% TP retained). These RE values correspond to an average retention of 36 MT TP in 2018 and 91 MT TP in 2019 (Table 1). For comparison, the annual TP load from the Thames River to Lake St. Clair in on the order of 323 MT (Maccoux et al., 2016). Based on these results, we conclude that Fanshawe Reservoir represents an important TP trap along the land to lake continuum, at least in 2018 and 2019. In other words, the reservoir helps mitigate the P export from the upper watershed with its intensive agricultural production and consistent P surplus on the landscape (Van Staden et al., 2021).

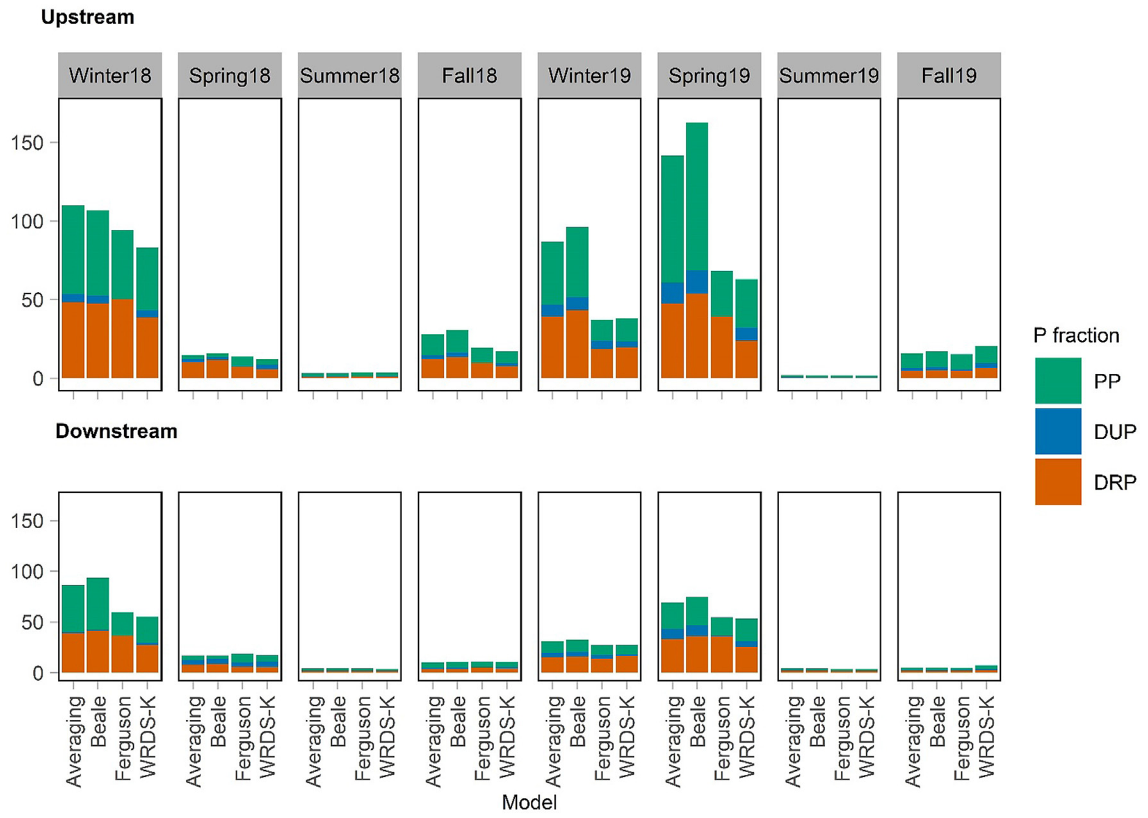

Fig. 4. Seasonal phosphorus (P MT) loads from winter 2018 to fall 2019 of upstream (top 8 panels) and downstream (bottom 8 panels). TP was further separated into particulate phosphorus (PP), dissolved unreactive phosphorus (DUP), and dissolved reactive phosphorus (DRP) fractions.

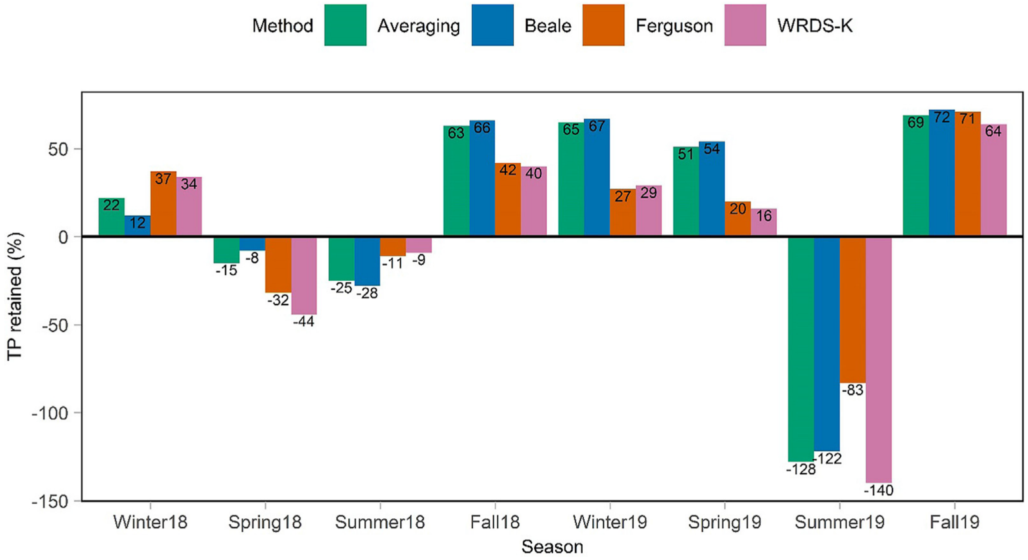

Fig. 5. Fanshawe Reservoir seasonal total phosphorus (TP) retention efficiencies from winter 2018 to fall 2019.

Our results further indicate that the P RE of the reservoir is subject to substantial, yet poorly constrained, inter-annual variability. This variability is likely largely modulated by inter-annual variations in the upstream river discharge and P loading, driven by stochastic variations in weather conditions and compounded by physical and biogeochemical processes within the upstream watershed and the reservoir. However, to fully characterize and predict the range of inter-annual variability of P retention in Fanshawe reservoir empirically will require extending the data acquisition over many more years.

Despite the sometimes large differences between the RE estimates obtained with the four load estimation models considered here (Table 1 and Fig. 3), there is broad qualitative agreement in the general trends. Collectively, the annual RE estimates indicate that Fanshawe reservoir is quite efficient in retaining TP compared to other dammed reservoirs with similar water residence times

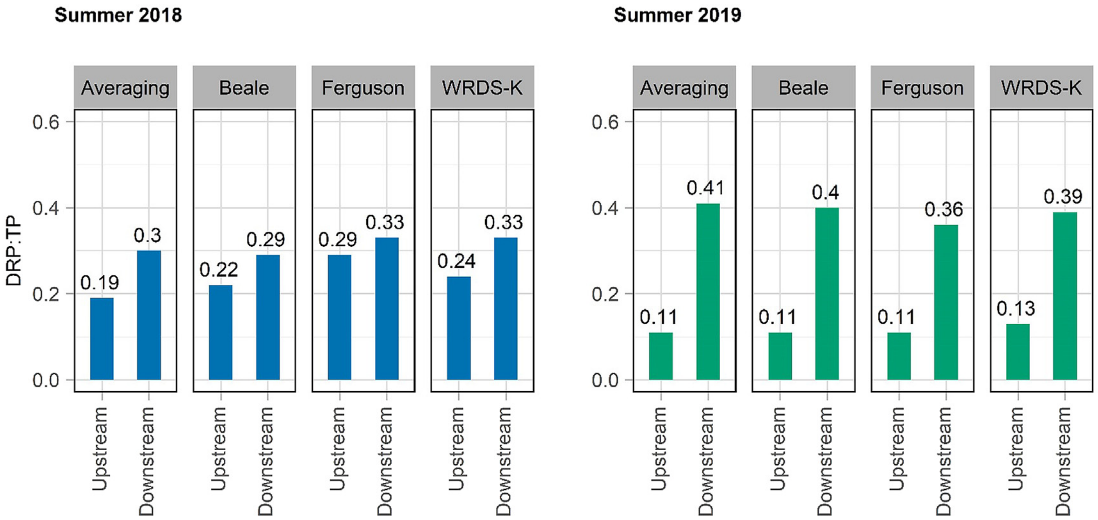

Fig. 6. Summer seasonal speciation changes in 2018 (green) and 2019 (blue) between upstream and downstream loads using ratio of dissolved reactive phosphorus to total phosphorus (DRP:TP) as bioavailability indicator. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

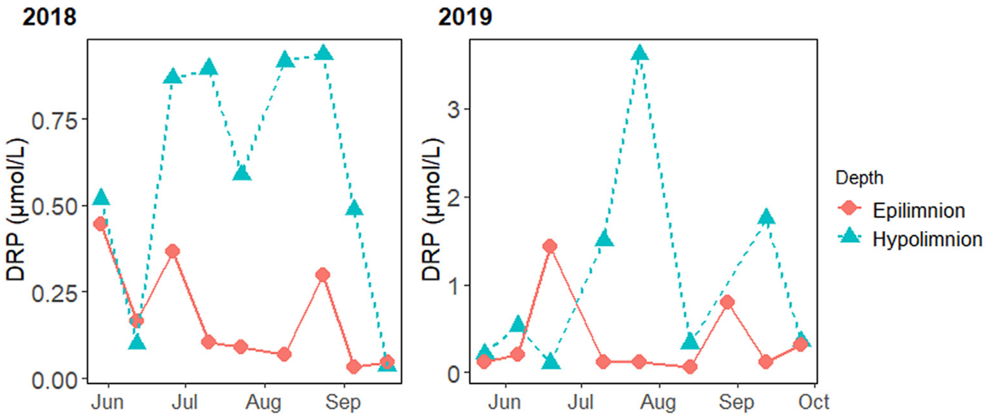

Fig. 7. Concentrations of DRP at Fanshawe Reservoir's lentic site measured at epilimnion (solid line) and hypolimnion (dashed line) depths in summer of 2018 (left) and summer of 2019 (right).

(Maavara et al., 2015), or even the much larger Lake St. Clair (Scavia et al., 2019b). For context, P export from the Thames River and Sydenham River watersheds together has recently been estimated to range between 0.78 and 1.38 kg P ha^{-1} yr^{-1} (Scavia et al., 2019a). The TP retention estimates in Fanshawe Reservoir for 2018 and 2019 are equivalent to a reduction of 0.25–0.64 kg P ha^{-1} yr^{-1} from the upstream watershed. Such P load reductions are comparable in magnitude to the most optimistic modelling scenarios for landscape nutrient management whereby multiple BMPs (cover crops, subsurface placement of fertilizer plus a 25% reduction in fertilizer application rate) are simultaneously implemented on all appropriate land within the watershed (Scavia et al., 2019a). Considering the magnitude of these reductions, we propose that adaptive reservoir management represents a promising, but insufficiently explored, opportunity to minimize P export to the receiving lake environment.

Although there is no temporal overlap between our study and those of Nürnberg and LaZerte (2005) and Vandermeulen and Gemza (1991), our contrasting findings are most likely due to data limitations associated with the earlier studies. These limitations were recognized by Nürnberg and LaZerte (2005) who recommended improvements to water chemistry sampling to more accurately constrain the P load estimates upon which their RE estimates were based. Most notably, chemistry data used in prior studies were either sparse, not representative of the full range of flow (Nürnberg and LaZerte, 2005), or biased to the growing season (Stammler et al., 2017; Vandermeulen and Gemza, 1991) when internal P loading is most prevalent. While our much higher temporal data resolution overcomes the limitations of the previous studies, the large differences between 2018 and 2019 point to the need to better understand the inter-annual variability in reservoir P retention and transformation processes. In particular, with the available data it is not possible to infer the RE of Fanshawe reservoir during dry years, as these data are not represented in our dataset. A decrease in the annual P load entering the reservoir would be expected during drier years due to transport-limited mobilization of P from the watershed (Dolph et al., 2019). However, the net responses of in-reservoir P cycling and downstream export are more challenging to predict without the help of a mechanistic model incorporating all the relevant hydrodynamics and biogeochemical processes (e.g. Carr et al., 2019).

A fully predictive understanding of P retention by Fanshawe Reservoir, as well as the other dam reservoirs along the Thames River, would help inform ongoing efforts to achieve the domestic and binational TP load reductions for the Thames River, which are based on the 2008 TP load close to the river mouth (Annex 4

Objectives and Targets Task Team, 2015; Maccoux et al., 2016). Current approaches to decrease NPS P loads to meet these targets focus almost exclusively on the upstream source areas (Agriculture, Food and Rural Affairs, 2015; Environment and Climate Change Canada, Ministry of the Environment and Climate Change, 2018; Upper Thames River Conservation Authority, 2018). Our results strongly suggest that reservoir trapping of P needs to be accounted for when assessing the efficacy of land-based nutrient management actions and predicting the P export flux and speciation at the river mouth. Notwithstanding the associated costs, we recommend continued year-round and event-based monitoring of inflow and outflow P loads of Fanshawe reservoir, while also investing efforts in calibrating and validating a predictive in-reservoir hydrodynamic-water quality model.

Reservoir P legacy

Our findings indicate that dammed reservoirs represent a potential opportunity to minimize P export from watersheds. However, P accumulating within reservoir sediments forms a long-term legacy that, in turn, may represent a potential future risk to downstream water quality. Further, the RE of dammed reservoirs often decreases over time as sediment accumulates, reducing reservoir water volume and water residence time (Maavara et al., 2020). For example, approximately 70 years after dam closure, a gradual decrease in P retention has been observed for the Conowingo dam reservoir in the United States (Zhang et al., 2016). Therefore, the long-term P load mitigation by current dammed reservoirs and their RE trajectory are both uncertain and likely site specific. A variable fraction of PP deposited in a reservoir's sediments could be remobilized via the efflux of DRP or resuspension of PP should external P loads decrease or in-reservoir conditions change (North et al., 2015; Orihel et al., 2017; Xu et al., 2021). Release of legacy-P from sediments may mask and delay anticipated improvements to downstream water quality after the implementation of management actions aimed at decreasing P export from the landscape (Haygarth et al., 2014; Jarvie et al., 2013, Zhang et al., 2016). However, the risk of P remobilization from sediments varies widely depending on the P speciation, the particle size with which P is associated and the depositional environment (Heinrich et al., 2021; Katsev et al., 2006; Nguyen et al., 2020; O'Connell et al., 2020; O'Connell et al., 2015; Orihel et al., 2017; Parsons et al., 2017).

A study on three cascade dams along the Creuse River, France, showed that P concentrations in reservoir sediments were 3–7 times higher compared to free-flowing river sediments, and that the majority of sediment P was vulnerable to release under anoxic bottom water conditions (Rapin et al., 2020). Further work on the same river also revealed that approximately 4% of sedimentary P in the Champsanglard reservoir is associated with water-mobilizable colloids (Nguyen et al., 2020). Phosphorus associated with the colloidal fraction is likely at greater risk of resuspension and subsequent export than P associated with larger particle size fractions. Therefore, the assessment of the chemical speciation, size fractionation and stability of P legacies accumulating within sediments of Fanshawe Reservoir, and in other reservoirs within the Great Lakes basin deserves further research. Increased focus on this sedimentary record may also yield insights on the history and trajectory of sedimentary P accumulation, and those of other pollutants (Copetti et al., 2019; O'Connell et al., 2020).

Bioavailability: DRP:TP ratio

In this study the DRP:TP ratio is used as a simple proxy for the relative bioavailability of the TP load. This ratio is a convenient metric for P bioavailability because DRP and TP are commonly measured in nutrient monitoring programs of aquatic systems. However, we fully recognize that the DRP:TP ratio does not capture the highly diverse speciation of P and its complex relationship to P bioavailability in freshwater environments (Boström et al., 1988; DePinto, 1982; DePinto et al., 1981; Ellison and Brett, 2006; Li and Brett, 2013; Pacini and Gächter, 1999; Prestigiacomo et al., 2016; Shinohara et al., 2018; Young et al., 1985). Although it is reasonable to assume that the greater the DRP fraction, the higher the bioavailability of the TP load, DRP is not the only bioavailable form of P. For example, PP within algal biomass may be readily recycled upon senescence and can therefore be considered to be relatively bioavailable (Shinohara et al., 2018; Shinohara et al., 2012). However, PP bound within the crystalline structure of recalcitrant minerals such as detrital apatite is unavailable to algae (Ruttenberg, 1992).

By only considering the DRP:TP ratio, we are unable to account for the variable bioavailability of PP. This is a potential limitation of our study given that in-reservoir primary production may cause a highly variable contribution of algal biomass to PP. Actively growing algae are capable of decreasing DRP concentrations to extremely low levels during blooms (Hudson et al., 2000), which can result in low DRP:TP values, yet a high P bioavailability. Thus, by only considering the DRP:TP ratio we are likely underestimating the potential bioavailability of the downstream P load relative to the upstream load (Mohamed et al., 2019). The latter may be expected to contain more recalcitrant mineral P forms within the PP fraction eroded from the upstream watershed (Pacini and Gächter, 1999). While a detailed evaluation of P bioavailability in the suspended load upstream and downstream of Fanshawe Reservoir is beyond the scope of the current study, more research on this topic would serve to further elucidate the role of the reservoir in modulating the eutrophication potential of P exported from the Thames River watershed.

Our results show that while Fanshawe Reservoir acts as a sink for TP, the RE values differ between the particulate and dissolved P fractions (ESM Fig. S5), thus changing the DRP:TP ratios of the outflowing P load (Fig. S6). Typically, PP is retained more efficiently than dissolved P (Jossette et al., 1999). This effect was observed in 2019, when PP was preferentially retained over DRP, resulting in more elevated DRP:TP values downstream of the reservoir relative to upstream (ESM Fig. S6). In 2018, however, the reservoir retained PP and DRP with similar efficiencies, and the DRP:TP of the P load remained relatively unchanged. The inter-annual difference is mostly due to different PP RE during the high flow seasons: in 2019, PP was retained particularly efficiently in winter and spring (ESM Fig. S7), indicating relatively high sedimentation of particulate matter, likely eroded from agricultural land and river channels. The effect is seen in 2019, a much wetter year than 2018, resulting in higher peak flows with correspondingly higher erosive power. In contrast, release of PP was observed during the spring of 2018 (ESM Fig. S7), a period when estimates of downstream discharge exceeded upstream values, indicating reservoir drawdown as also seen in the reservoir level data (ESM Fig. S11). Therefore, enhanced PP export could have been due to sediment resuspension in response to increased flow through the dam.

Elevated DRP:TP downstream of a reservoir can also be driven by internal (dissolved) P load from the sediments, an effect observed at the Iron Gate I Reservoir with a reported increase of 20% of the dissolved fraction in the TP load (Teodoru and Wehrli, 2005). However, the DRP loads released by Fanshawe Reservoir during the stratified summer months (see next section) are orders of magnitude smaller than the annual TP loads. For example, in 2019, the summer DRP load only contributed 1.4% of the downstream TP load. Thus, internal P loading does not have a large impact on the annual DRP:TP ratio.

Seasonal trends

The influx of P delivered to the reservoir from the upstream watershed varies seasonally by orders of magnitude, as a result of seasonal flow variations and increasing P concentrations with river discharge. The latter mobilization-transport pattern is typical for agriculturally dominated watersheds and reflects precipitation-driven export of P from the landscape (Dolph et al., 2019; Van Meter et al., 2020; Withers and Jarvie, 2008). The majority of P is delivered during the high flow seasons, that is, either winter or spring, and the smallest P loads occur during the low flow summer seasons (Fig. 4). For example, the estimated mean TP load in winter 2018 was over 30 times greater than in the summer of 2018. The seasonal pattern of P inflow to the reservoir is thus consistent with the 83.5% agricultural land use within the upstream watershed (Ontario Ministry of Natural Resources and Forestry, 2020).

In agricultural watersheds in general, a very high proportion of total annual P loads 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; Nelligan et al., 2021; Plach et al., 2019). Hence, our study reinforces the critical importance of sampling across all seasons, as well as targeting high flow events, in order to derive accurate load and retention estimates (Lee et al., 2016). Extrapolating a reservoir's annual RE from data covering selected seasons only, usually the growing seasons during which field sampling is most accessible, is likely to be inaccurate and potentially misleading for nutrient management decisions. The same is true when considering high flow events that may dominate P loads but are often underrepresented in standard monitoring programs.

Fanshawe Reservoir's P RE values varied systematically as a function of season during the study period, with the reservoir ranging from a minor P source during the summers to a strong sink during winters and spring of 2019. The seasonal RE pattern reflects variations in flow regime (due to upstream inflow and dam operation) and the presence or absence of stratification. The majority of P retention occurs during the high flow seasons, likely due to rapid deposition of riverine particulate P loads that include eroded detrital material exhibiting high densities and correspondingly high settling velocities. Net release of P through the dam during the summer is ostensibly driven by internal P load induced by in-reservoir stratification. Prolonged stratification during the summer promotes hypoxic conditions in the hypolimnion that favor the reductive dissolution of ferric iron (hydr)oxides and subsequent efflux of dissolved P from the bottom sediments (Mortimer, 1941; Orihel et al., 2017; Parsons et al., 2017; Søndergaard et al., 2001). Hypolimnion water with elevated DRP concentration is then released from the reservoir through bottom draw discharge. During the summer, discharge occurs almost exclusively through the bottom draw valves as the reservoir level is maintained relatively low, hence, limiting the release of epilimnetic water through sluice gates. Moreover, dam outflow rate was slightly higher than inflow rate during the 2018 and 2019 summers, which further decreased the calculated summer RE values. The seasonal effect on the RE value is also accompanied by notably higher summer DRP:TP leaving the reservoir (Fig. 6).

The P loads released through the dam in summer are essentially negligible in comparison to loads retained during the high flow season. Nonetheless, the timing of delivery of highly bioavailable P during the period of reservoir stratification may exacerbate eutrophication issues downstream at the time when algal growth is peaking (Ho and Michalak, 2017). Options to disrupt hypoxic bottom waters to alleviate internal P loading in lakes and reservoirs have been explored extensively in the literature (e.g., Gächter and Müller, 2003, and references therein). However, these strategies have not always resulted in decreases in P internal loading due to the complexity of coupled elemental cycling (e.g., C, Fe, S, P) during early diagenesis (Caraco et al., 1989; Gächter and Müller, 2003; Orihel et al., 2017). The mechanical disruption of stratification has also been suggested previously for Fanshawe Reservoir but never implemented (Vandermeulen and Gemza, 1991). Other methods to increase retention of dissolved P include chemical amendments, such as ferric iron (Heinrich et al., 2021; Engstrom, 2005; Markelov et al., 2019; Markovic et al., 2019; Orihel et al., 2016), aluminum (Huser et al., 2016; Schütz et al., 2017) and Phoslock™, in order to enhance inorganic sorption or flocculation (Hickey and Gibbs, 2009).

In contrast to the summers, during spring 2018 the negative TP retention was driven by net export of PP rather than DRP. The enhanced export of PP may have been due to sediment resuspension driven by elevated outflow rates in response to high flow conditions during the preceding season (2018 winter). Alternatively, it may have reflected enhanced export of autochthonous algal biomass though the sluice gates. Overall, our observations are in line with previous studies indicating that reservoir operation can influence the RE of P (Xu et al., 2021). Because the primary function of the Fanshawe dam has been flood control, the timing and magnitude of high flow and snowmelt events dominates flow control decisions thus far. The development of a predictive hydrodynamics-biogeochemistry model (e.g., Carr et al., 2019; Lindenschmidt et al., 2019) for the reservoir may help support more sophisticated multi-criteria decision making that combines flood regulation and P retention.

Historically, the Thames River's high flow season mostly occurred in spring following snowmelt. In 2018, however, the 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 a significant dam outflow surplus was only implemented in the summer. The changing climatic patterns in Canada, such as warmer winters and seasonal displacements (Champagne et al., 2019; Vincent et al., 2018; Vincent et al., 2015), will introduce additional challenges for reservoir nutrient management and may result in more years similar to 2018 and fewer to 2019. The implications of these climatic changes on P retention and speciation in Fanshawe Reservoir, and other reservoirs within the Great Lakes watershed, are not well understood and should be considered a research priority for future studies.

Implications for nutrient management

Construction of new dams to mitigate agricultural P discharge to the Great Lakes is unlikely to be met with much public support. In addition, locations with physiographic suitability for new reservoirs are limited. However, as higher order streams integrate P loads from large areas, the existing large reservoirs within the Great Lakes drainage basin collectively represent a comparatively unexplored and spatially focused potential opportunity for phosphorus management. The P RE of any given reservoir is largely controlled by attributes that are inherently unmanageable, such as the reservoir size and morphology, as well as the hydrology of the upstream watershed (Maavara et al., 2020). However, as implied by our results, reservoir operation may potentially be used to optimize P retention. This is consistent with other recent work, such as modelling studies by Carr et al. (2019) and Xu et al., (2021), that implies that controlling the withdrawal elevation and water storage level could be used to alter a reservoirs' thermal regime and downstream nutrient export. Even relatively modest increases of P retention via a multi-criteria reservoir management approach (Xu et al., 2021) may be worth pursuing as part of a whole watershed nutrient management strategy. We contend that an integrated approach, including maximizing the interception of P in suitable reservoirs, in concert with continued on-land actions to reduce P losses would likely result in faster and more easily measurable decreases to riverine P loadings to the Great Lakes (Macintosh et al., 2018). Research advancing the quantitative understanding of the influence of dam operation decisions on P RE of Fanshawe reservoir, and other reservoirs within priority watersheds, is therefore strongly recommended.

Given the significant retention of P within Fanshawe reservoir, it could be argued that resources to mitigate P export to Lake Erie should focus on areas downstream of the reservoir (Donald et al., 2015). However, the benefits of limiting P losses from the landscape are not restricted to alleviating downstream eutrophication. Retaining P on the landscape is important for long-term soil health, sustainable agriculture, and the ecological health of receiving streams and rivers. In addition, further reducing P losses in the catchment upstream of a reservoir will also help reducing the risk of algal blooms in the reservoir itself, which negatively impact associated recreational activities. Therefore, allocating resources to mitigate P losses from agricultural areas upstream of reservoirs that exhibit high RE for P is still a defensible strategy depending on the P loss dynamics within each sub-watershed and the specific objectives of management actions.

Conclusions

Together, our results demonstrate that on an annual time scale Fanshawe reservoir acts as an important P sink along the river continuum. During 2018 and 2019, Fanshawe Reservoir retained 25 and 47% of TP exported from the upstream watershed, respectively. The retention and speciation changes of P also exhibit large seasonal variations. Over the two-years of field sampling presented here, the reservoir ranged from a strong sink during winter and fall to a weak source during one spring (2018) and both summers. The DRP:TP ratio also increased from upstream to downstream of the reservoir during the summer months when water column stratification enhanced DRP release from the bottom sediments. Although the net release of P by the reservoir during the summer accounted for only a small fraction of the annual P load (0.6–2% of the TP load through the dam), the increased bioavailability of the P during the growing season may exacerbate eutrophication impacts downstream.

Fanshawe reservoir helps remove a large portion of riverine P exported from agricultural land in the watershed of the North Thames River. Our work provides a better understanding of Fanshawe Reservoir's effects on the flow of P along the Thames River corridor, with implications for algal bloom development in the receiving 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, deserves full consideration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jglr.2021.11.008.

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