NUTRIENT DYNAMICS AND STOICHIOMETRY IN STORMWATER MANAGEMENT PONDS

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Abstract

Nutrient dynamics and stoichiometry in stormwater management ponds

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Although stormwater management ponds (SWMPs) are frequently used to mitigate flooding in urban areas, we still do not fully understand how these systems impact water quality in a watershed. Currently, most research focuses on the effectiveness of SWMPs to retain nutrients during high flows, even though there is potential for internal nutrient releases to occur in these systems during low flows. To investigate if SWMPs act as nutrient sources or sinks during low flow conditions, we analyzed how sewershed characteristics, pond properties, and hydrological and limnological factors influenced nutrient dynamics and stoichiometry in 10 SWMPs. Our study ponds were located in Peterborough, Whitby, and Richmond Hill, which are urbanized municipalities in southern Ontario, Canada. During October 2010 to 2011, we took monthly measurements of various carbon (C), nitrogen (N), and phosphorus (P) forms. We collected samples in the inlets, permanent pools, and outlets to determine any changes in concentrations, loads, and stoichiometric ratios into and out of the ponds. At the time of sampling, we also measured a variety of hydrological and limnological parameters. Our findings indicate that more urbanized sewersheds with higher drainage densities tend to have higher inflowing particulate and dissolved nutrient loads. In addition, we found that pond properties such as depth, length-to-width ratio, volume, and age differentially influence the retention of particulate and dissolved C, N, and P forms. Influential hydrological and limnological factors were antecedent moisture conditions, season, and thermal stratification. We found higher particulate P concentrations near the sediments when the catchments were drier and the ponds were ice-free and stratified. As well, we found higher outflowing stoichiometric ratios for DOC:TDN and DOC:TDP. This indicates an enrichment of C compared to N and P and suggests biogeochemical processes may be occurring in SWMPs. Overall, our results demonstrate that SWMPs are complex aquatic systems and we need to consider biogeochemical processes in our design and maintenance activities, so that the effectiveness of SWMPs is not compromised during low flow conditions as a result of internal nutrient releases.

Key words: urban stormwater pond, particulate organic carbon, particulate organic nitrogen, particulate phosphorus, dissolved organic carbon, total dissolved nitrogen, total dissolved phosphorus, urban biogeochemical cycling.

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Chapter 1: General Introduction

Urbanization transforms landscapes by removing vegetation while concomitantly increasing engineered structures and impervious surfaces (Arnold & Gibbons, 1996). Increased impervious surface cover (e.g., roads, parking lots, and rooftops) can impede the infiltration of precipitation causing surface runoff (Arnold & Gibbons, 1996; Booth, 1991; Schueler, 1994). Surface runoff can also occur when pores in the soil matrix become saturated and precipitation cannot infiltrate; however, this process depends on the presence and type of vegetation, soil properties, and antecedent moisture conditions (Booth, 1991; Boyd et al., 1993).

Regardless of the generation mechanism, increased surface runoff volumes can produce more frequent and intense flooding (Leopold, 1968). This can lead to shorter lag time until peak flow, increased peak flow, and quicker storm recession time in water bodies (Arnold et al., 1982; Hasenmueller et al., 2017; Leopold, 1968; Rose & Peters, 2001). These hydrological impacts cause bank erosion in streams and rivers, which in turn, contributes to habitat loss and reduced biodiversity in urban aquatic ecosystems (Paul & Meyer, 2001; Walsh et al., 2005).

To mitigate the adverse hydrological effects of increased impervious surface cover, stormwater management ponds (SWMPs) are constructed to collect runoff and slowly release it (Ontario Ministry of the Environment [OMOE], 2003). There are different kinds of SWMPs, but ponds with a permanent pool of water are frequently constructed and are referred to as wet ponds or retention ponds (Blecken et al., 2017). These SWMPs gradually release stormwater to primarily reduce flooding, and their secondary function is to remove nutrients such as nitrogen (N) and phosphorus (P) from the water column through the process of sedimentation (OMOE, 2003; Troitsky et al., 2019).

The main sources of N, P, and carbon (C) in urban areas are from atmospheric deposition, leaf litter, grass clippings, pet waste, eroded sediments, fertilizers, and leaky sewer pipes (Bratt et al. 2017; Decina et al., 2018; Hobbie et al., 2017; Kaushal et al., 2011; Selbig, 2016; Yang & Toor, 2016; Yang & Toor, 2017). Although nutrients are essential to maintain urban ecosystems, excess N and P in watersheds can accelerate the process of cultural eutrophication, which in turn can lead to issues such as toxic algae blooms, reduced biodiversity, and degraded drinking water quality (Carpenter et al., 1998).

However, some field studies have found that SWMPs may not retain nutrients (especially dissolved forms) effectively and their performance may also decrease as they age (Comings et al., 2000; Mallin et al., 2002; Sønderup et al., 2016). This variability in SWMP performance may be due to a wide range of factors including pond design and maintenance activities. A key design consideration is water retention time, and the underlying assumption is that a longer water retention time allows particulate bound nutrients to settle and for dissolved nutrient forms to be assimilated or converted to less bioavailable forms (Gu et al., 2017; Wong et al., 1999). Retention time can be influenced by the size and shape of a pond and its length-to-width ratio (Persson, 2000; Persson et al., 1999; Persson & Wittgren, 2003).

Aside from retention time, storage volume also impacts SWMP performance and a facility's volume can decrease over time due to sediment build up (Graham & Lei, 2000). One of the primary maintenance activities that can help a SWMP return to its original design is the removal of sediment by dredging (Blecken et al., 2017; Drake & Guo, 2008). However, due to the high costs associated with dredging sediments and a lack of comprehensive monitoring and maintenance plans for SWMPs, many ponds are poorly maintained (Drake & Guo, 2008; Erickson et al., 2018).

Beyond maintenance activities and design considerations, variability in SWMP performance may also be influenced by conditions within the ponds (Troitsky et al., 2019). For example, SWMPs can stratify diurnally or for longer periods which can lead to hypoxic or anoxic conditions near the sediments and result in P release to the water column (Ahmed et al., 2022; Ahmed et al., 2023; He et al., 2015; McEnroe et al., 2013, Song et al., 2013; Taguchi et al., 2020). In contrast, denitrification (i.e., the microbially-mediated process where NO_3^- is converted to N_2) occurs more frequently in anoxic conditions (Collins et al., 2010). Thus, this N removal process would take place under the same conditions that would facilitate the release of P (Duan et al., 2016), and could influence N:P ratios in SWMPs. Although we are beginning to understand internal biogeochemical processes in SWMPs, there are still many research gaps about how stoichiometric ratios and nutrient dynamics may affect the performance of SWMPs, especially during low flow conditions.

Low flow conditions occur when water is transported through stormwater drains between flow events (Janke et al., 2014). Although most SWMP research does not focus on low flow, some researchers have observed that water regularly flows into these ponds even when there is no rainfall or snow melt (Morales and Oswald, 2020; Strzalkowski, 2023). Currently, there is a prevailing perspective that low flow periods are not as impactful as high flows on water quality. This is because large amounts of water, sediment, and nutrients are typically transported into aquatic ecosystems during high flows (Dang et al., 2018; Rosenberg & Schroth, 2017; Sharpley et al., 2008; Thomas, 1988; Walling & Webb, 1981). However, Janke et al. (2014) found that low flow can contribute significantly to total annual water yields. Moreover, N concentrations and loading during low flow conditions can be comparable to high flow events, although more P tends to flow through urban watersheds during rain events (Frazar et al., 2019; Giraldi, 2014;

Janke et al., 2014). In SWMPs, Van Buren et al. (1997) found that both high flow and low flow contributed to the total pollutant load flowing into a pond; however, the system retained nutrients during high flow conditions and released nutrients during low flow. Similarly, Duan et al. (2016) found that SWMPs retained PP during high flow events but released this P form during low flow conditions. These results indicate that nutrient dynamics in SWMPs may be different under low flows compared to high flows, and we need to further explore how SWMPs perform under the former conditions.

To address this research gap, this dissertation investigates if SWMPs act as nutrient sources or sinks during low flows. Chapter 2 explores the impact of sewershed characteristics and pond properties on nutrient loading into and out of SWMPs. Next, Chapter 3 analyzes the hydrological and limnological factors influencing total dissolved phosphorus and particulate phosphorus concentrations in the water column. Lastly, Chapter 4 examines if stoichiometric ratios differ between influent and effluent of SWMPs under low flow, because if they do, this suggests that there are biogeochemical processes occurring in these ponds.

The research questions guiding this work are:

1. What sewershed characteristics influence nutrient loading into SWMPs during low flows?
2. What pond properties affect nutrient loads out of SWMPs during low flows?
3. What hydrological and limnological factors influence total dissolved phosphorus and particulate phosphorus concentrations in SWMPs during low flows?
4. Do stoichiometric ratios differ between inflow and outflow during low flows?

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Chapter 2: Influence of sewershed characteristics and pond properties on nutrient loading in urban stormwater ponds during low flow conditions.

2.1 Abstract

Stormwater management ponds (SWMPs) are constructed in cities mainly to mitigate flooding, and their secondary purpose is to retain nutrients to protect downstream water quality. However, the treatment efficiency of these systems may be influenced both by sewershed characteristics and pond properties. To analyze the impact of sewershed characteristics and pond properties on nutrient loading during low flow conditions, we selected 10 SWMPs in three municipalities in Ontario, Canada. We identified properties such as maximum depth, length-to-width ratio, volume, and age of the ponds using field measurements, engineering diagrams, and ArcGIS software. We also used ArcGIS software to analyze drainage density and land cover in the study ponds' sewersheds. During October 2010 to 2011, we collected water samples and discharge measurements from the ponds' inlets and outlets to calculate inflowing and outflowing loads of dissolved and particulate carbon, nitrogen, and phosphorus. After, we conducted a correlation analysis between land cover elements, drainage density, and nutrient loads into the ponds. We found that pavement, buildings, fine vegetation (e.g., grasses and herbs), and drainage infrastructure were positively correlated with inflowing particulate organic carbon (POC), dissolved organic carbon (DOC), particulate organic nitrogen (PON), total dissolved nitrogen (TDN), particulate phosphorus (PP), and total dissolved phosphorus (TDP) loads. We also used paired t-tests to determine how selected pond properties would affect inflowing and outflowing nutrient loads. We found that depth, L:W ratio, volume, and age can differentially impact the loading of nutrient species. Specifically, shallower and older ponds had significantly higher DOC loads out of the ponds. Ponds with shorter length-to-width ratios had significantly higher

outflowing DOC and PP loads. Conversely, ponds with larger length-to-width ratios had significantly lower outflowing PP and TDN loads. Ponds that were considered to have a normal volume based on the Ontario Ministry of the Environment SWMP guidelines, had significantly higher outflowing loads of DOC, whereas the enhanced ponds had significantly lower outflowing TDN. Together, the results of the paired t-tests suggest that internal biogeochemical processing of nutrients can affect the chemical composition of SWMP outflow, and that we need to take this into consideration when making decisions about SWMP design and maintenance.

Key words: stormwater management ponds, pond morphometry, dissolved and particulate carbon, nitrogen, phosphorus

2.2 Introduction

Stormwater management ponds (SWMPs) are small water bodies commonly constructed in cities to reduce flooding by slowly releasing stormwater during high flows (Drake & Guo, 2008). A secondary function of SWMPs is to protect downstream water quality by retaining nutrients such as dissolved and particulate forms of carbon (C), nitrogen (N), and phosphorus (P) as stormwater flows through these systems (Kalev et al., 2021; Ontario Ministry of the Environment [OMOE], 2003; Yang & Lusk, 2018). Although both dissolved and particulate nutrient forms are transported into SWMPs, performance guidelines usually focus on reducing total suspended solids (TSS) with the assumption that sediment-bound nutrients will settle in the ponds (Bradford & Gharabaghi, 2004). However, TSS may not be the best predictor of pond performance (Williams et al., 2013) and the efficiency of SWMPs to treat nutrients is inconsistent, particularly for dissolved fractions (Arias et al., 2003; Collins et al., 2010; Comings et al., 2000; Gold et al., 2017; Ivanovsky et al., 2018; Kolath et al., 2021; Mallin et al., 2002;

Sønderup et al., 2016). Although there can be numerous factors influencing the efficiency of SWMPs, one of the most significant factors is pond design (Chiandet and Xenopoulos, 2016).

Pond design can be variable but is generally based on engineering guidelines and regulations set by municipal authorities (Chiandet & Xenopoulos, 2016). Most ponds are designed to optimize the water retention time of inflowing stormwater using the pond's surface area, volume, and length-to-width ratio (OMOE, 2003). A longer water retention time will give more opportunity for processes such as sedimentation or biological uptake to occur (Wong et al., 1999). Ponds should also be deep enough to prevent the resuspension of sediments (OMOE, 2003; Walker, 1987), yet sufficiently shallow that thermal stratification will not occur (McEnroe et al., 2013; Song et al., 2013). Stratification could potentially lead to hypoxic conditions at the bottom of the water column which in turn may increase the potential for P release from pond sediments (McEnroe et al., 2013; Song et al., 2013; Taguchi et al., 2020).

Stratification can occur frequently in shallow ponds during low flows (Holgerson et al., 2022), and generally low flow periods may create conditions that are conducive for biogeochemical activities to occur. For example, Song et al. (2015) indicated that high primary productivity during low flow conditions resulted in the conversion of dissolved P forms into particulate P. Similarly, Duan et al. (2016) found that their study SWMPs and wetlands were sources of PP during low flows but sinks during high flows. During low flows, these researchers suggest that dissolved P was released from anaerobic sediments and converted to particulate P by biological and chemical processes. Although studies such as Duan et al. (2016) highlight the importance of biogeochemical activities during low flow conditions on the overall treatment efficiency of SWMPs, there is still little information on the combined impact of low flow conditions and pond design on nutrient dynamics in SWMPs. To address this research gap, this study assessed what pond properties and sewershed characteristics are influential on dissolved and particulate nutrient loading into and out of the ponds during low flow conditions.

2.3 Methods

2.3.1 Study sites

We selected 10 SWMPs in Richmond Hill, Whitby, and Peterborough, Ontario, Canada for this study (Figure 2.1). The municipalities had assumed the study sites and were responsible for pond monitoring and maintenance activities. We collected data about the ponds on a monthly basis during October 2010 to 2011. However, data for January, February, and April 2011 were not available due to unsafe ice conditions on the ponds, malfunctioning pipes, and/or the measurements for specific conductivity and dissolved oxygen were not within the detection limits of the sampling probes.

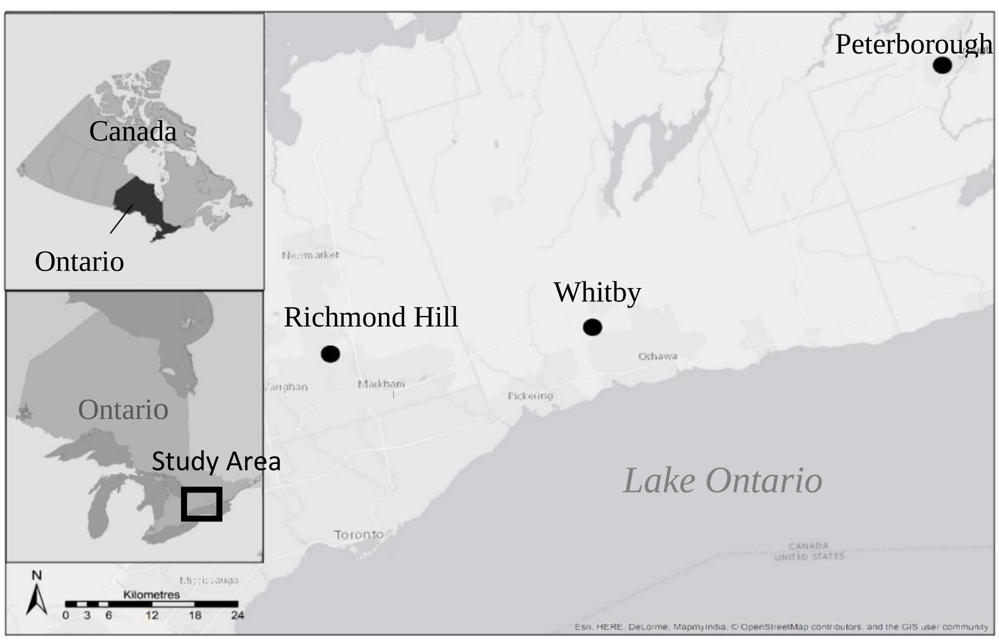

Figure 2.1: Location of the study sites

We analyzed air temperature and precipitation data from the most proximal Environment Canada's meteorological stations to the study sites to determine how the conditions during the study period compared to the 30-year normal (1981-2010). The annual average air temperature in Peterborough was 6.6 ^{o}C, Whitby was 8.3 ^{o}C, and Richmond Hill was 8.0 ^{o}C, which was close to the 30-year normal of 6.9 ^{o}C, 8.1 ^{o}C, and 7.7 ^{o}C, respectively. The study period was slightly drier compared to the 30-year normal in Peterborough by 5.8 mm. However, it was wetter in Whitby by 73.8 mm and in Richmond Hill by 66.1 mm. Potential evapotranspiration (PET) was calculated using the Hamon model (Hamon, 1961) for each municipality.

2.3.2 Sewershed characteristics and pond properties

Geographical Information System (GIS) specialists from the municipalities supplied graphical data (e.g., high-resolution orthophotos and sewer lines) and associated attribute data. Using spatial analyst and data management tools available in ArcGIS 10.8, the sewersheds were delineated. The sewershed area of the ponds ranged in size from 83,000 to 1,323,890 m^2 (Table 2.1). After identifying the sewershed area, the total length of drainage pipe connected to each pond was calculated. Then, the total length of drainage pipe connected to each pond was divided by the sewershed area to estimate the drainage density of the pipes in m/m^2 (Lee et al., 2018). Drainage density in the sewersheds varied from 0.007 to 0.018 m/m^2 (Table 2.1). Additionally, five land cover features in the sewersheds were measured based on Cadenasso et al.'s (2007) High Ecological Resolution Classification for Urban Landscapes and Environmental Systems (HERCULES) method. These biophysical features included buildings, pavement, bare soil, coarse vegetation, and fine vegetation. Coarse vegetation refers to shrubs and trees and fine vegetation refers to grasses and herbs (Cadenasso et al., 2007). Figure 2.2 indicates that impervious surface coverage varied from 30 to 69%, and most sewersheds contained more pavement than buildings. However, a few sewersheds had similar amounts of these surfaces (Pond E and I), and the sewershed for Pond F had slightly more buildings than pavement (Figure 2.2). The dominant type of pervious surface in all the sewersheds was fine vegetation, and coverage ranged from 31 to 47%. In contrast, there was less coarse vegetation and coverage varied from 0.04 to 27% (Figure 2.2). Generally, the sewersheds did not contain bare soil, except for Pond A and B (Figure 2.2). To help identify if sewersheds could be grouped based on their biophysical features, drainage area, and the total length of drainage pipe connected to each pond, a cluster analysis using the hclust function in base R (R Core Team, 2022) was performed. The results of this analysis is displayed in Appendix 1.

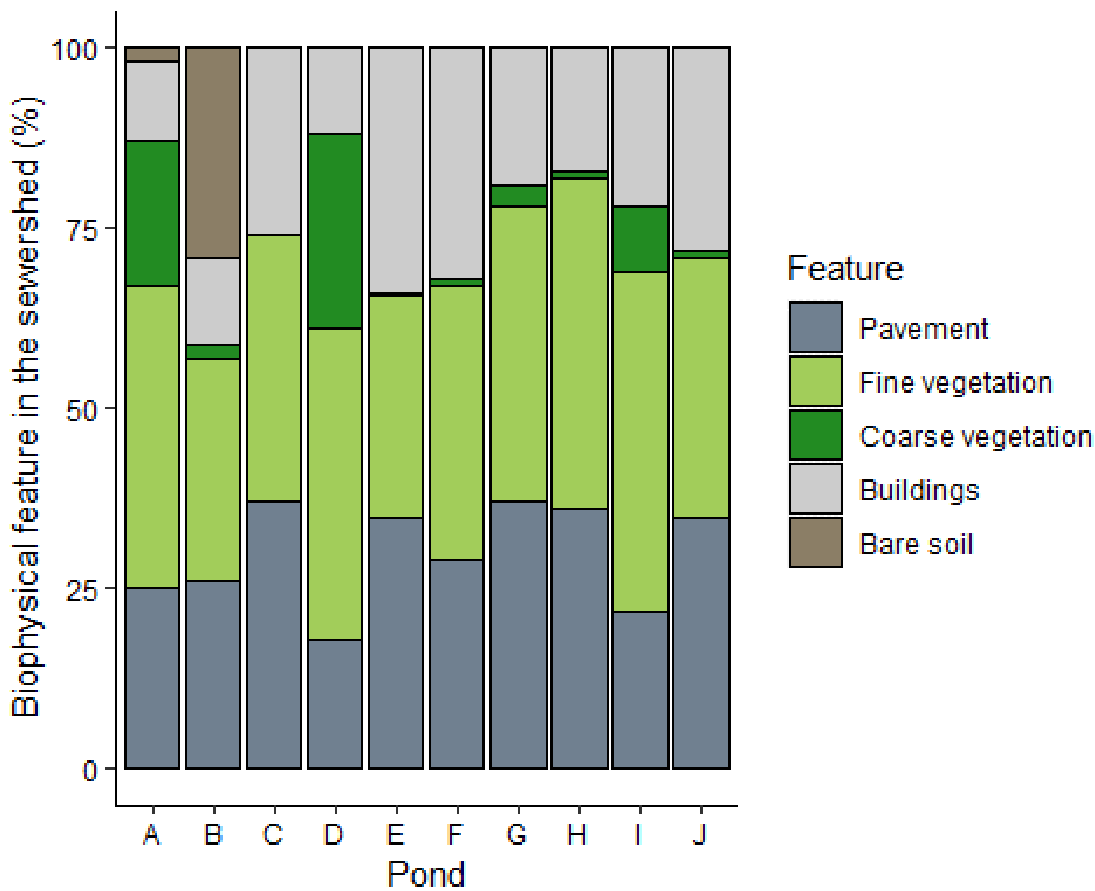

Figure 2.2: Biophysical features in the sewersheds

After analyzing the sewershed characteristics, the graphical data were also used to determine pond properties listed in Table 2.1 such as the design surface area (ranging from 972 to 10,035 m^2) and length-to-width ratio (ranging from 1.3 to 4.8). Data regarding the construction year of the ponds and time elapsed since the ponds were dredged were provided by municipal staff. Based on the engineering diagrams and maintenance records, the ponds varied in age from 1 to 10 years (Table 2.1). The engineering diagrams also indicated that the design volume of the ponds ranged from 780 to 54,783 m^3 (Table 2.1). In the field, monthly pond depth measurements were taken in the middle of the permanent pool using a weighted rope. We determined that the maximum depth of the ponds ranged from 1.2 to 3.6 m (Table 2.1). A cluster analysis was also performed to determine if ponds could be grouped based on surface area, length-to-width ratio, volume, and maximum depth. The results of this cluster analysis are depicted in Appendix 2.

Table 2.1: Sewershed characteristics and pond properties

Pond	Sewershed area (m^2)	Drainage density (m/m^2)	Surface area of the pond (m^2)	Design Volume (m^3)	Max. depth (m)	Length-to-width ratio	Age since construction or last dredging (years)
A	547,929	0.008	8,894	16,009	1.8	4.1	1
B	83,000	0.008	972	780	1.9	1.4	8
C	240,497	0.017	3,414	4,055	2.2	2.9	6
D	450,480	0.007	5,995	5,761	2.5	2.8	2
E	586,214	0.013	9,811	6,740	1.2	3.9	5
F	142,935	0.012	1,549	2,110	1.9	1.3	3
G	1,323,890	0.013	10,035	54,783	3.6	4.8	4
H	998,292	0.010	8,501	1,809	2.2	3.2	10
I	420,000	0.012	3,001	9,715	3	3.6	10
J	669,690	0.018	7,820	29,000	1.9	2.5	9

2.3.3 Hydrological data collection and analysis

Initially, we tried to convert continuous records of water depths to discharge by developing a stage-discharge rating curve for each pond. We measured inflowing and outflowing water levels every 15 minutes using non-vented Solinst Model 3001 Level Loggers. Measurements were corrected for atmospheric pressure fluctuations using a Solinst Barologger. However, the level loggers malfunctioned on numerous occasions and there were large gaps in the dataset. This was likely due to the placement of the level loggers in the manholes upstream of the inlets and below the outlets. Consequently, we relied on the manual measurements we collected every sampling period for our analysis.

During each sampling period, instantaneous discharge (Q in m^3/s) into and out of the ponds were calculated by multiplying the cross-sectional area of flow by the mean flow velocity. The cross-sectional area was determined by measuring the width of the wetted perimeter in the inlets and outlets and taking depth measurements across this area. Velocity (v in m/s) was measured by timing a float moving over a 1 m distance in the pipe, and eight measurements were taken to determine mean flow velocity. For each study pond, water budgets were calculated with the following equation every sampling period:

$$\sum(P + R_{in}) - \sum(PET + R_{out}) = S \qquad (1)$$

where P = precipitation (m^3), R_{in} = runoff into the pond (m^3), PET = potential evapotranspiration (m^3), R_{out} = runoff out of the pond (m^3), and S = storage (m^3). The average amount of storage per pond is available in Appendix 3.

Afterwards, for the study sites that had one inlet and outlet, the concentration of C, N, and P (mg/L) in a sample was multiplied by discharge (L/day) to determine load in mg per day.

These values were converted to obtain load in grams per day. For study sites that had multiple inlets and outlets, the inflowing or outflowing discharge in litres per day was multiplied by the concentration in mg per litre for each inlet or outlet to calculate the nutrient mass in mg per day. The nutrient mass for each inlet or outlet (mg/d) was then added together.

2.3.4 Water sampling and analysis

Ninety samples each from the inlets and outlets were collected during low flow conditions, with a total of 180 samples. We defined low flow as the water flowing into the SWMPs when there was less than 5 mm of precipitation 24 hours prior to sampling (Chiandet & Xenopoulos, 2011). During the study period there was less than 5 mm of precipitation in 24 hours 61%, 67%, and 68% of the time in Richmond Hill, Peterborough, and Whitby, respectively.

Dissolved oxygen (mg/L), specific conductivity (uS/cm), and temperature (^{o}C) profiles in the middle of the permanent pool were created by taking measurements every 10 cm down the water column using handheld meters (YSI Models 54 and 63; Yellow Springs Instrument Co., Yellow Springs, Ohio, USA). Secchi disk depth was also measured at the same location. Water samples were collected in the centre of flow in the inlet and outlet pipes of the SWMPs. The samples were processed within 24 hours of collection by vacuum filtering them through 0.7 µm pre-weighed and pre-combusted GF/F filters (Whatman, Mississauga, Ontario, Canada) and then through 0.2 µm polycarbonate filters (Millipore, Billerica, Massachusetts, USA). The filtered water was analyzed for DOC and TDN by combustion with an O.I. Analytical Aurora Model 1030 TOC analyzer, College Station, Texas, and TDP with the persulfate digestion and molybdate blue-ascorbic acid spectrophotometric method (Clesceri et al., 1998).

The material collected on the GF/F filters was used to determine the amount of POC and PON by combustion with a CN elemental analyzer (Elementar Vario El III, Mt Laurel, NJ, USA). Particulate P was measured by the persulfate digestion and molybdate blue-ascorbic acid spectrophotometric method (Clesceri et al., 1998). Total suspended solids were analyzed by calculating the difference between the initial and final weight of the filter divided by the volume of water that passed through the filter (Clesceri et al., 1998).

2.3.5 Data analysis

R version 4.2.2 (R Core Team, 2022) was used for all statistical analyses. Prior to any parametric analyses, assumptions were tested using the *car* package (Fox & Weisberg, 2019) and base R. The relationships between sewershed characteristics and average nutrient loads into the ponds were analyzed with a correlation matrix. The Pearson correlation coefficients were significant when their p-value ≤ 0.05 and the relationships between variables were visualized in a heatmap using *ggplot2* (Wickham, 2016) and *reshape2* (Wickham, 2007).

To test if there were significant differences of nutrient loads into and out of the ponds, the ponds were first grouped together based on selected features such as depth, length-to-width ratio, volume, and how many years had passed since the pond was constructed or last dredged. The OMOE (2003) guidelines indicate that the minimum criteria for maximum depth in the permanent pool is 3 m and 2.5 m is the preferred depth to avoid hypoxic and anoxic conditions in SWMPs. However, some studies have found that ponds that are approximately 2 m deep still stratify (Song et al., 2013; Taguchi et al., 2020). Accordingly, the ponds were grouped if their maximum depth was equal to or less than 2 m (i.e., shallower ponds) or greater than 2 m (i.e., deeper ponds). The OMOE (2003) guidelines also suggest that the overall length-to-width (L:W) ratio of a pond should be at minimum 3:1 and preferably from 4.1 to 5.1. Thus, ponds in this study were grouped based on a L:W ratio equal to or less than 3.1 (i.e., shorter L:W) or greater than 3.1 (i.e., longer L:W). In addition, OMOE (2003) guidelines outline the volumetric water quality criteria based on the size of the sewershed, impervious coverage, and the protection level for suspended solids removal. The enhanced protection level aims for 80% TSS removal long-term and the normal protection level aims for 70% TSS removal long-term (OMOE, 2003). Ponds in this study were categorized if they fit the enhanced or normal levels of protection. Lastly, Sønderup et al. (2016) found in a SWMP field study that the nutrient retention performance of a pond declines after 5 years. Accordingly, the ponds were grouped if they were equal to or less than 5-years-old (i.e., younger) or older than this. Once the ponds had been categorized, the data were log transformed and a paired t-test was applied to the data to determine if there were significant differences in POC, PON, PP, DOC, TDN, and TDP loads into and out of the ponds. The t-test results were generated using the *report* package (Makowski et al., 2023), and the p-values were adjusted using the Benjamini-Hochberg method (1995). Boxplots visualizing the results were created with the *ggplot2* package (Wickham, 2016).

2.4 Results

2.4.1 Relationship between sewershed characteristics and nutrient loads into the ponds

Residential sewersheds in this study were composed of various biophysical features, but predominately pavement, buildings, and fine vegetation. There was less coarse vegetation and very little bare soil. Figure 2.3 outlines the relationship between sewershed characteristics and nutrient loads into the study ponds. We found that sewershed area, pavement, drainage density, and fine vegetation had strong positive correlations with each other (Figure 2.3). Sewershed area, pavement, and drainage density were also positively correlated with buildings (Figure 2.3). In contrast, coarse vegetation was weakly correlated with all the other biophysical features in the sewersheds (Figure 2.3). However, coarse vegetation did have a significant positive relationship with TDN loads into the ponds (Figure 2.3). Fine vegetation was moderately correlated with TDN, but had strong positive correlations with POC, DOC, and PP (Figure 2.3). Sewershed area, drainage density, pavement, and buildings also had strong positive correlations with POC, DOC, and PP and positive correlations with TDP and PON (Figure 2.3).

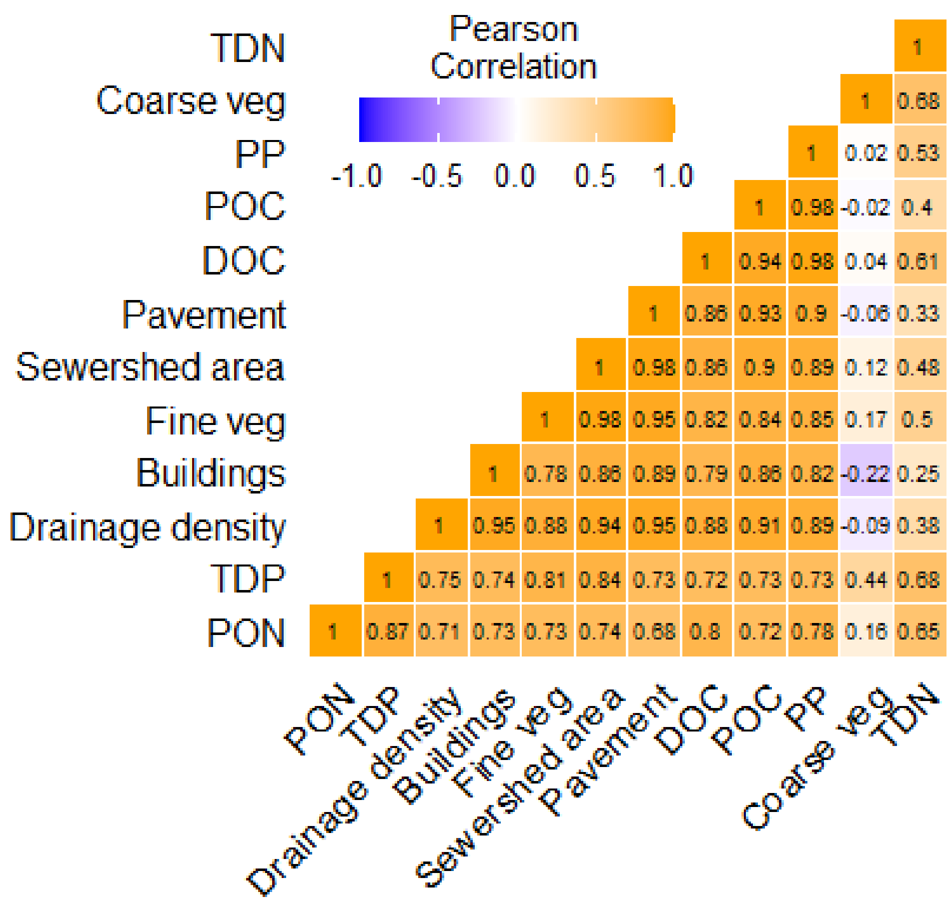

Figure 2.3: Pearson correlation coefficients indicating the relationship between sewershed characteristics and nutrient loads into the study ponds.

2.4.2 Pond properties - Depth

Design guidelines for SWMPs indicate that shallower ponds are preferred to minimize thermal stratification and the re-suspension of sediments (OMOE, 2003). The shallower ponds in our study ranged in depth from 1.2 to 1.9 m and the deeper ponds ranged from 2.2 to 3.6 m. The deeper ponds were stratified 14% of the sampling periods and the shallower ponds were stratified for 17% of the sampling periods. In addition, the shallower ponds were slightly less transparent and warmer than the deeper ponds. For example, the average Secchi disk depth was 0.7 m for the former and 1 m for the latter. Also, the average temperature was 15^{o}C at the top of the water column and 13.8^{o}C near the sediments for shallower ponds. It was 14.4^{o}C at the top and 13^{o}C at the bottom for deeper ponds.

In both shallower and deeper ponds, the nutrient species with the largest loads flowing into and out of the ponds was DOC, followed by POC, TDN, PON, PP, and TDP (Figure 2.4). Although the shallower ponds had greater outflowing loads for all nutrient forms (Figure 2.4), only DOC had statistically higher loads exiting the ponds with a medium effect size $t(44) = -3.61$, $p < 0.001$; Cohen's $d = -0.54$, 95% CI [-0.85, -0.22]. In contrast, the deeper ponds had smaller loads out of the ponds for all nutrient forms compared to inflowing loads, but these were not statistically different (Figure 2.4).

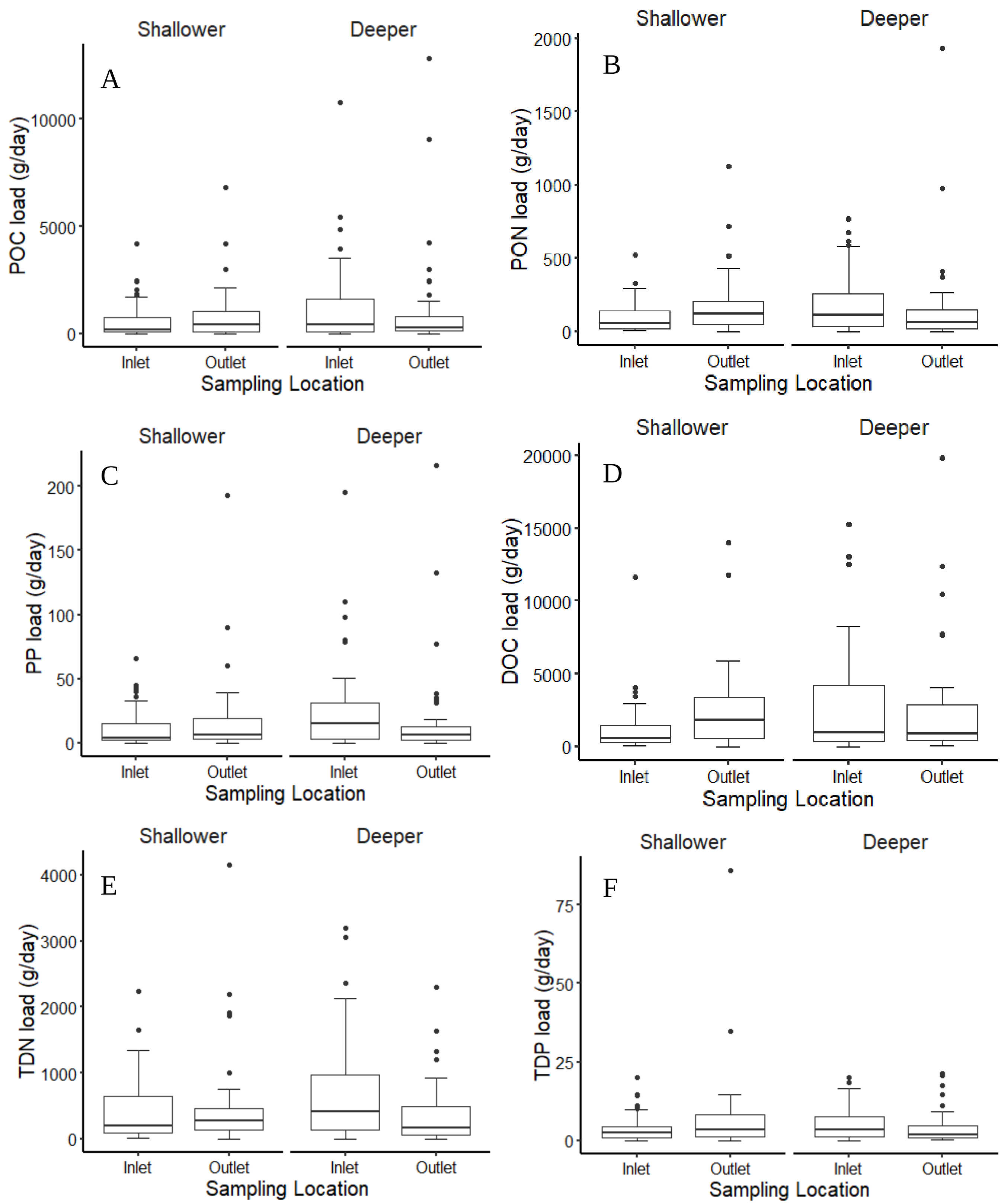

Figure 2.4: Differences in (A) POC, (B) PON, (C) PP, (D) DOC, (E) TDN, and (F) TDP loads into and out of the ponds that were shallower (≤ 2 m) or deeper (> 2 m). Note: The y-axes vary.

2.4.3 Pond properties - Length-to-width (L:W) ratio

Field studies and computer models indicate that longer L:W ratios can help enhance the efficiency of a SWMP by extending water retention time and increasing the potential for sedimentation to occur (Gharabaghi et al., 2006; Persson, 2000; Walker, 1998). In this study, we used MOE (2003) guidelines to classify ponds as having a shorter or longer L:W ratio. The ponds with shorter L:W ratios ranged from 1.3 to 2.9 and the ponds with longer L:W ratios ranged from 3.2 to 4.8. The highest inflowing and outflowing nutrient form was DOC followed by POC, TDN, PON, PP, and TDP (Figure 2.5). The ponds with shorter L:W ratios were acting as sources for all nutrient forms; however, only DOC and PP had significant differences between inflowing and outflowing loads. Specifically, there were greater DOC loads out of the ponds and this difference had a medium effect size $t(44) = -3.52$, $p = 0.001$; Cohen's $d = -0.53$, 95% CI [-0.83, -0.21]. There were also greater PP loads out with a small effect size $t(44) = -2.10$, $p = 0.042$; Cohen's $d = -0.31$, 95% CI [-0.61, -0.01].

In contrast, ponds that had longer L:W ratios generally acted as nutrient sinks, except for DOC and POC (Figure 2.5). These nutrient forms had higher loads out of the ponds, although there were not any significant differences. There were statistically significant lower loads out of the ponds for PP with a small effect size $t(44) = 2.06$, $p = 0.046$; Cohen's $d = 0.31$, 95% CI [-0.006, 0.60] and TDN with a small effect size $t(44) = 2.45$, $p = 0.018$; Cohen's $d = 0.36$, 95% CI [0.06, 0.66].

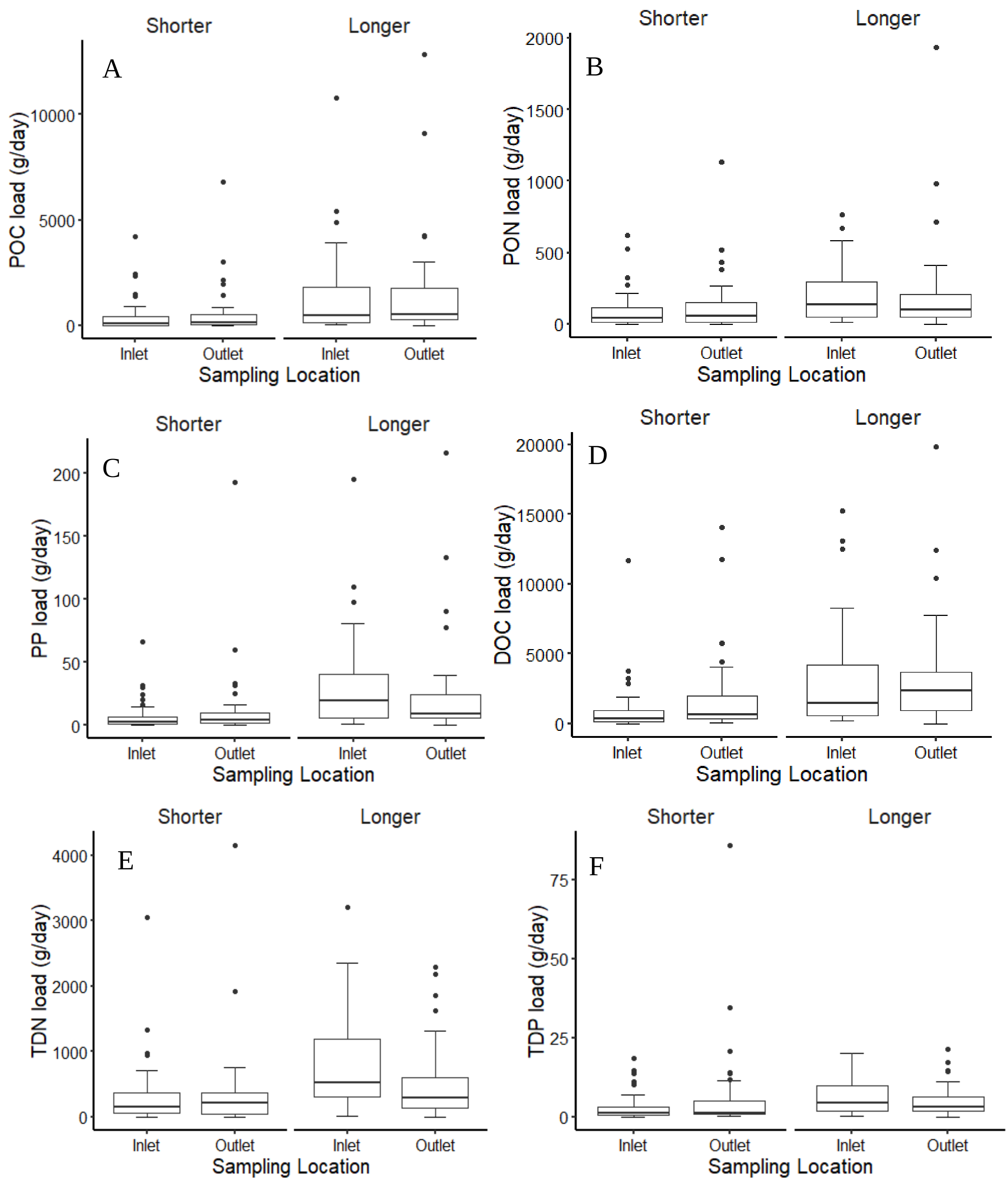

Figure 2.5: Differences in (A) POC, (B) PON, (C) PP, (D) DOC, (E) TDN, and (F) TDP loads into and out of the ponds that had a shorter (≤ 3.1) or longer (> 3.1) length-to-width ratio. Note: The y-axes vary.

2.4.4 Pond properties - Volume

To protect downstream aquatic habitat from suspended sediment loading, SWMPs are designed based on specific volumetric criteria (OMOE, 2003). Enhanced protection aims to remove on average 80% of suspended solids over the long-term, whereas normal protection aims to remove 70% (OMOE, 2003). In normal and enhanced ponds, DOC had the highest inflowing and outflowing nutrient loads followed by POC, TDN, PON, PP, and TDP (Figure 2.6). All the ponds in the normal grouping had higher loads out of the ponds compared to the inflowing loads, but these were not statistically significant differences, except for DOC. There was higher outflowing DOC loads with a small effect size $t(44) = -2.58$, $p = 0.013$; Cohen's $d = -0.38$, 95% CI [-0.69, -0.08].

In comparison, the ponds that met the enhanced criteria had lower loads out of the ponds compared to inflowing loads for POC, PON, PP, and TDN; however, TDN was the only statistically significant difference (Figure 2.6). There was less outflowing TDN with a small effect size $t(44) = 3.04$, $p = 0.004$; Cohen's $d = 0.45$, 95% CI [0.14, 0.76]. Although there was more outflowing DOC and TDP, these were not statistically significant.

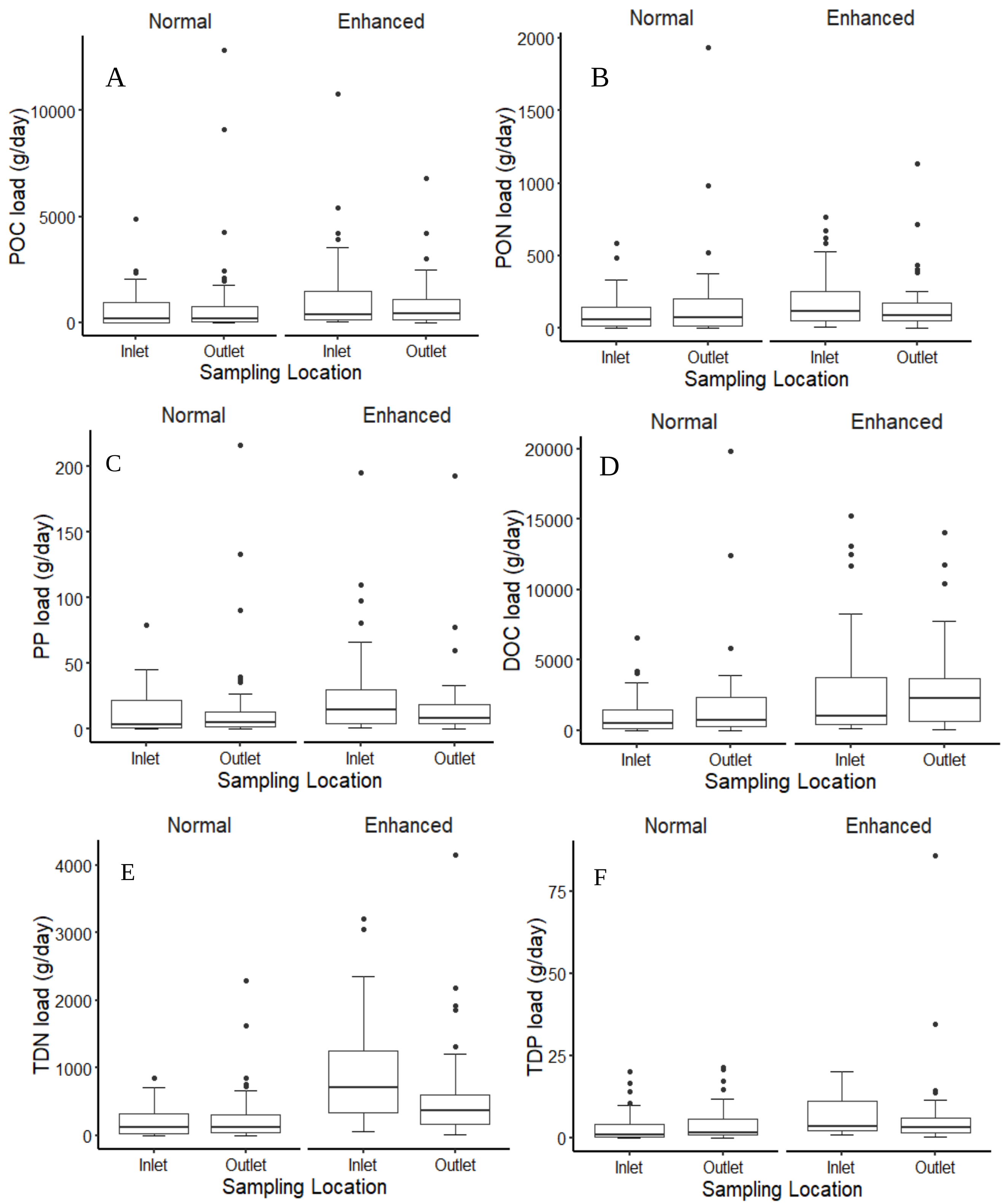

Figure 2.6: Differences in (A) POC, (B) PON, (C) PP, (D) DOC, (E) TDN, and (F) TDP loads into and out of the ponds that had a normal or enhanced volumetric water quality control. Note: The y-axes vary.

2.4.5 Pond properties – Age

Generally, younger ponds have more space in their permanent pool to allow particulate material to settle and have less sediment build up that could release nutrients to the water column (Sønderup et al., 2016). Based on Sønderup et al.'s (2016) observations that indicate the efficiency of SWMPs decreases after 5 years, our younger ponds ranged in age from 1 to 5 years and the older ponds ranged from 6 to 10 years. Overall, DOC had the highest inflowing and outflowing nutrient loads followed by POC, TDN, PON, PP, and TDP (Figure 2.7). The younger ponds were nutrient sinks for all nutrient forms except DOC; however, these were not statistically significant differences (Figure 2.7).

Older ponds were nutrient sources for all forms, but these were also not statistically significant differences, except for DOC (Figure 2.5). There were statistically significant higher DOC loads out of the older ponds with a small effect size $t(44) = -2.14$, $p = 0.038$; Cohen's $d = -0.32$, 95% CI [-0.62, -0.02].

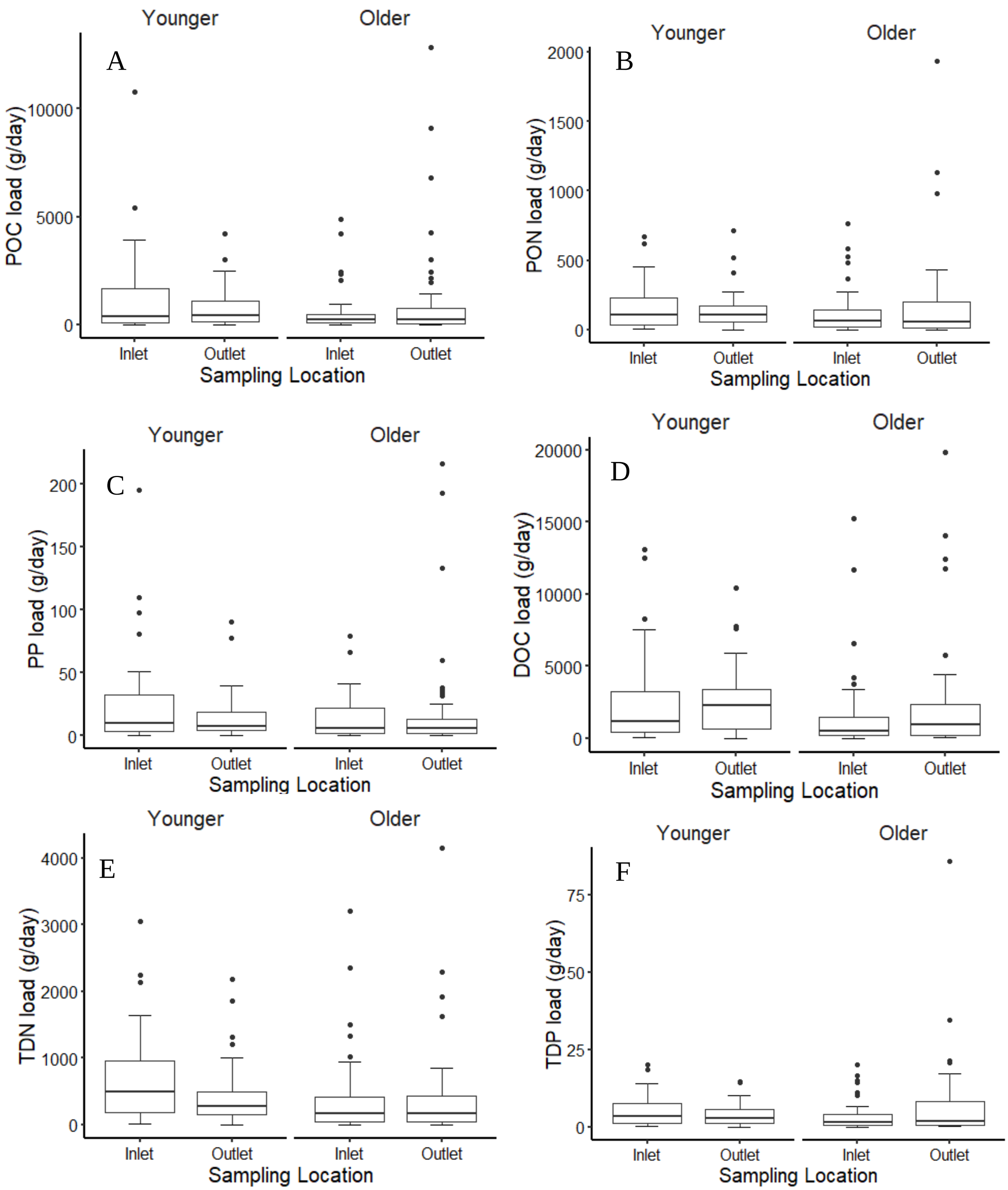

Figure 2.7: Differences in (A) POC, (B) PON, (C) PP, (D) DOC, (E) TDN, and (F) TDP loads into and out of the ponds that are younger or older. Note: The y-axes vary.

2.5 Discussion

2.5.1 Relationship between sewershed characteristics and nutrient loads into the ponds

Since urbanized sewersheds contain a mix of impervious and pervious surfaces, there is potential for specific biophysical features to disproportionately impact the speciation and amount of C, N, and P flowing into SWMPs. Our results indicate that pavement, buildings, and fine vegetation are positively correlated with POC, DOC, PON, TDN, PP, and TDP. This is similar to findings from Puczko and Jekatierynczuk-Rudczyk (2020), who used the HERCULES framework to analyze the impact of land cover on water quality in an urbanized catchment in Poland. These researchers determined that buildings and fine vegetation were the most influential biophysical features on nutrient concentrations flowing into shallow groundwater and surface water in their study area.

In our study, the relationship between impervious surfaces and C, N, and P forms may be due to organic matter such as lawn clippings, leaves, sediment, and atmospheric deposition accumulating on pavement and buildings (Hobbie et al., 2017) and being transported into the SWMPs. Additionally, the relationship between fine vegetation and nutrients may be related to lawn care practices occurring in the sewershed. Turfgrass lawns usually cover a large proportion of urban areas in the USA and Canada (Robbins & Birkenholtz, 2003). Maintaining a socially acceptable lawn aesthetic generally results in increased nutrient concentrations in residential areas, particularly from chemical fertilizer use (Hobbie et al., 2017; Robbins & Birkenholtz, 2003). Often, chemical fertilizers are misused by miscalculating fertilizer application rates, applying fertilizer at sub-optimal times, and incorrectly placing the fertilizer on a lawn (Carey et al., 2012). In a study that analyzed N and P mass balances for seven urban watersheds in Minnesota, USA, 24% of households in the area were overapplying chemical fertilizer, and fertilizer comprised 37 to 59% of the total N inputs (Hobbie et al., 2017). Aside from fertilizer use, lawns can increase nutrients in the urban environment through grass clippings (Newcomer et al., 2012), particularly by contributing relatively significant amounts of PON (Lusk et al., 2020). Furthermore, lawn irrigation by homeowners can cause surface runoff that transports particulate and dissolved N and P in residential areas (Toor et al., 2017). Over-irrigation can frequently occur in residential areas as homeowners strive to have well-manicured lawns or if they do not know the watering requirements for turfgrass (Bremer et al., 2013).

Although fine vegetation had strong relationships with both particulate and dissolved C, N, and P forms, coarse vegetation was positively correlated only with TDN. This may be due to urban trees planted on private properties and lining the street. Trees can contribute nutrients to the urban environment in a couple of ways. First, the tree canopy can deposit N, P, C on surfaces in urban areas by throughfall inputs (Decima et al., 2018). Second, in regions that experience seasonal changes in temperature, leaves can fall of the trees and decompose thereby releasing nutrients that can be transported into storm drains (Duan et al., 2014). One of the most prevalent forms of nitrogen from decomposing leaf litter is dissolved organic nitrogen (Lusk et al., 2020), which may explain why our results indicate a relationship between coarse vegetation and TDN.

Aside from our results showing that biophysical features in a sewershed have relationships with specific nutrient species, we also demonstrate that drainage infrastructure is positively correlated with POC, DOC, PON, TDN, PP, and TDP. This is consistent with findings from McConaghie and Cadenasso (2016) who observed that drainage infrastructure density was a strong predictor of N export in urbanized catchments during high flow events. These researchers suggested that this is due to the engineered drainage network not allowing the nutrients to interact with the soil matrix and vegetation. Interestingly, these researchers did not find any significant relationship between HERCULES-classified biophysical features in their study catchment and N export during wet weather (McConaghie & Cadenasso, 2016). However, McConaghie and Cadenasso (2016) indicated that their unpublished data shows relationships between land cover and nutrient export during low flow conditions and suggests this is related to irrigation practices during the dry season. This difference in how land cover influences nutrient releases during high flow and low flow conditions emphasizes the importance of understanding how nutrients are transported in urban catchments under both hydrologic regimes, since the chemical composition of inflowing water into SWMPs may affect how nutrients are initially processed in the pond. Overall, the results of our study demonstrate that under low flow conditions both land cover and drainage infrastructure impact the particulate and dissolved C, N, and P forms flowing into SWMPs. This suggests that minimizing non-point sources of nutrients in the sewershed would help to reduce the amount of inflowing nutrients into SWMPs.

To help minimize non-point sources of nutrients from both the landscape and through the stormwater drainage network, future research should explore what socio-political factors help reduce excess nutrients in the sewershed and how these factors may impact the performance of SWMPs. For example, Souto et al. (2019) found that counties in Florida, USA with strong fertilizer ordinances for residential lawncare helped homeowners become aware of the impacts of their practices and used more effective management strategies. Moreover, Beckingham et al. (2019) indicate that using a multi-disciplinary framework is valuable to evaluate the effectiveness of a SWMP and to determine the most appropriate design and management strategies, since the performance of a pond is influenced not only by hydrological and biogeochemical processes, but also local policies, practices, and social factors.

2.5.2 Pond properties and nutrients loads

Pond properties such as depth, L:W ratio, volume, and age can differentially affect the dynamics of nutrient species. For example, some researchers have observed that ponds deeper than 1 m did not perform as well as shallower ponds to retain ammonium (Koch et al., 2014), while others have found that deeper ponds retain TN more efficiently (Sønderup et al., 2016). Additionally, Chiandet and Xenopoulos (2016) indicate that deeper ponds can have lower suspended solids and temperature near the sediments but tend to stratify which may induce internal P releases from sediments. However, stratification can occur in even shallow ponds and recent research indicates ponds only 0.8 m deep can stratify for prolonged periods (Ahmed et al., 2023). In our study, shallower and deeper ponds were stratified for a similar proportion of the sampling period; however, we did not have continuous measurements that could elucidate trends on a finer temporal scale.

On average, the water was slightly warmer in the shallower ponds at the top and bottom of the water column. Perhaps the warmer water in the shallower ponds influenced the amount of DOC, as there was more outflowing than inflowing DOC. Some studies suggest that warmer water temperatures are associated with higher DOC concentrations in freshwater systems (Abarike et al., 2021). In addition, the shallower study ponds had lower transparency based on the average Secchi disk depth, which could indicate that there was increased suspended solids in the water column. This may align with findings from Williams et al. (2013) who suggest that suspended solids in their study SWMPs were likely produced autochthonously.

Since SWMPs with shorter L:W ratios tend to have more short-circuiting and quicker water retention times which results in less settling of particles (Matthews et al., 1997; Persson, 2000; Persson et al., 1999), perhaps the autochthonous DOC in combination with allochthonous material flowing into the ponds were transported through the pond with less time to settle. This may align with findings from Schroer et al. (2018) who found that terrestrial biomass contributed to sediment build up in SWMPs located in South Carolina, USA. Together, the terrestrial and algal biomass may have resulted in statistically higher outflowing loads of DOC for ponds with shorter L:W ratios. In addition, since settling and sedimentation are the main removal processes for PP (Troitsky et al., 2019), perhaps ponds with shorter L:W ratios had shorter water retention times and consequently there was not enough time to for these processes to occur effectively. As a result, there were statistically higher PP loads out of the ponds with shorter L:W ratios.

Conversely, ponds with longer L:W ratios had statistically lower PP loads out of the ponds. This was likely due to longer water retention times allowing settling and sedimentation to take place as well as for transformation processes like uptake and assimilation to occur. This is consistent with Song et al. (2015), who found that primary productivity converts P flowing through SWMPs into more algal derived PP. Similarly, ponds with longer L:W ratios and consequently longer water retention times would have sufficient time for sedimentation and the assimilation of TDN by phytoplankton and macrophytes. This may explain why there was significantly less TDN loads out of the ponds with longer L:W ratios.

In addition, there were significantly less loads of TDN out of enhanced ponds. This is perhaps due to sedimentation; however, other processes such as plant uptake and denitrification (Jansson et al., 1994) could have transformed and removed N as well. Hohman et al. (2021) suggest that vegetative matter, significant amounts of nitrate, and low oxygen near the sediments can create ideal conditions in SWMPs to facilitate denitrification. Overall, the combination of denitrification, assimilation, and sedimentation may have helped reduce TDN loads out of the study ponds.

We also observed in normal ponds that there were significantly higher DOC loads exiting the study sites and this could be related to the internally derived DOC that can be generated in SWMPs (Williams et al., 2013). Furthermore, the autochthonous DOC could explain why we found significantly more DOC loads out of older SWMPs. However, this contradicts findings from Goeckner et al. (2022) who indicate that C burial increased for older ponds and suggests this could be due to increasing sediment layers and anaerobic conditions under the new layers could be slowing the breakdown of organic matter. The difference between Goeckner et al.'s (2022) results and ours could be related to the age of the study ponds. Our older ponds ranged in age from 6 to 10 years while the study ponds for Goeckner et al.'s (2022) were between 14 to 34 years. These conflicting results suggest that there is much to explore about C cycling in SWMPs, especially regarding the transformation mechanisms and removal pathways in the ponds. Overall, these results indicate that internal processes in SWMPs can greatly impact the amount and species of nutrients that are flowing out of stormwater ponds during low flow conditions and this needs to be considered when designing SWMPs and selecting maintenance strategies.

To help increase the treatment efficiency of SWMPs, future research should identify how specific design features impact the removal pathways of C, N, and P in the water column, in the sediments, and at the sediment-water interface. Future research should also explore how aging infrastructure can be retrofitted to effectively address internal releases of nutrients. Lastly, we need identify maintenance practices that can support biogeochemical processes that will retain nutrients. Since SWMPs have become common features in urban areas, we need to design and maintain these systems in a manner that optimizes the physical, chemical, and biological processes that retain nutrients in order to protect downstream water quality during both high flows and low flows.

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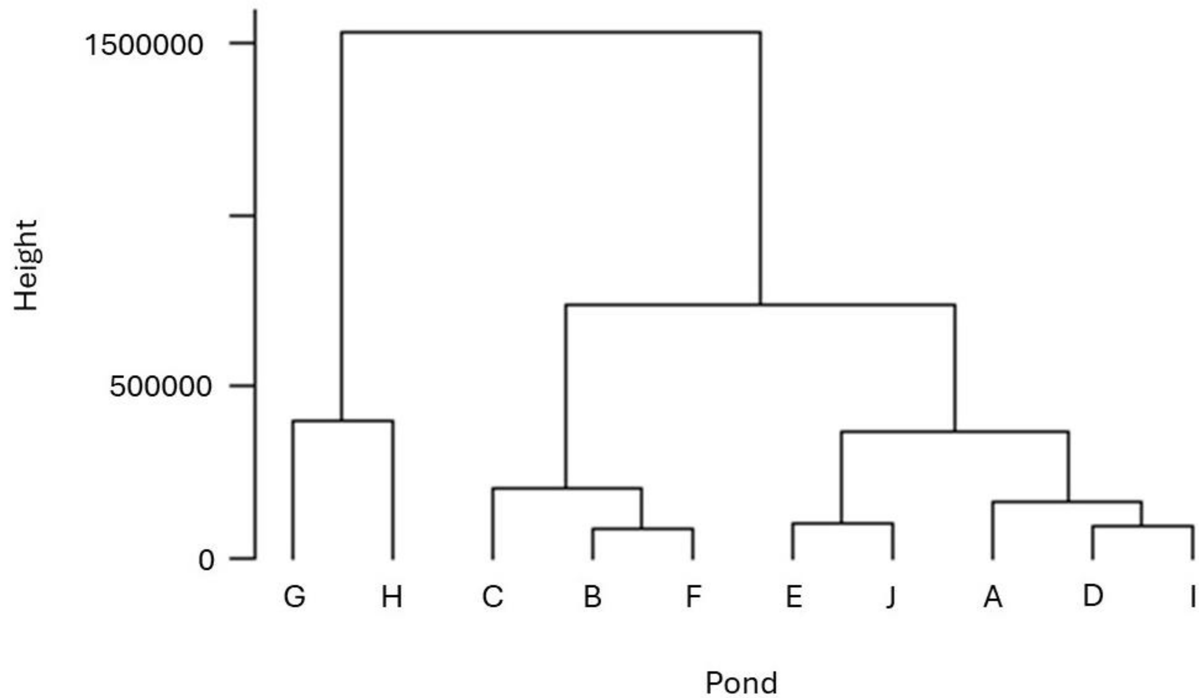
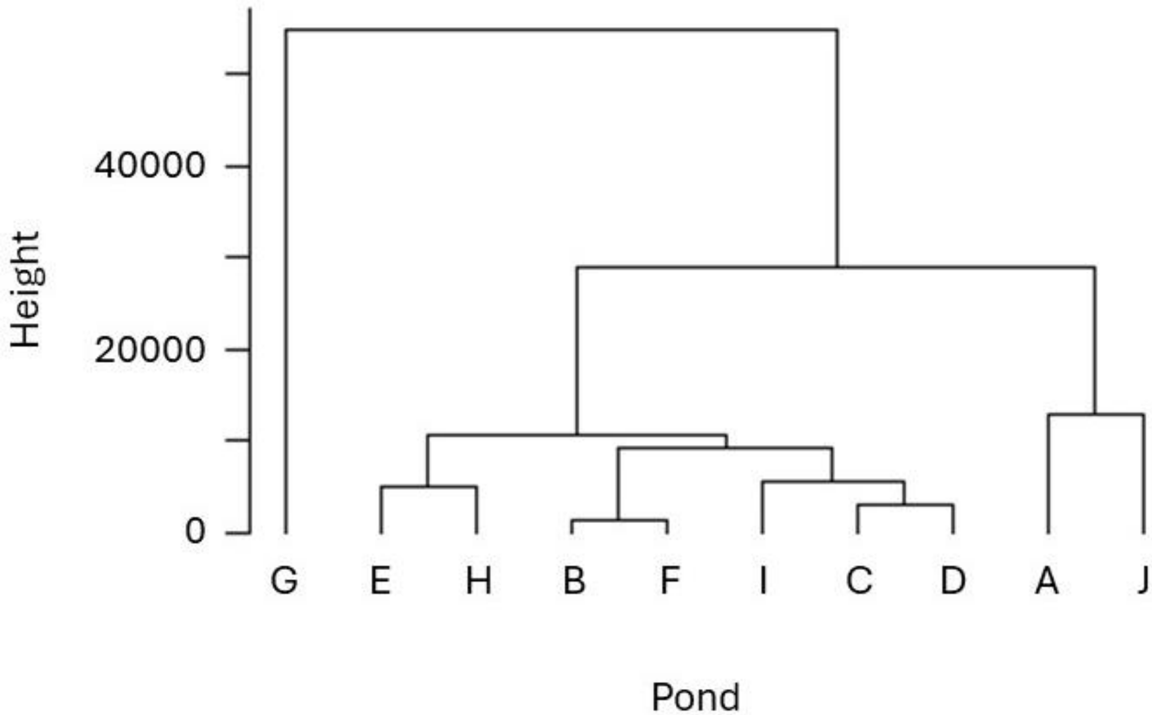
2.7 Appendix 1 – Cluster analysis based on sewershed characteristics



2.8 Appendix 2 – Cluster analysis based on pond properties



2.9 Appendix 3 – Average amount of storage per pond (m^3). Note: Storage was calculated based on monthly measurements taken in the field. Consequently, more measurements should be taken on a finer time scale to develop appropriate recommendations about pond design and maintenance.

Pond	Average storage (m^3)
A	-604
B	-126
C	-174
D	-73
E	-530
F	-170
G	-3
H	-994
I	178
J	-1004

Chapter 3: Influential hydrological and limnological factors on phosphorus concentrations in urban stormwater ponds.

3.1 Abstract

To date, most stormwater management pond (SWMP) research addresses their ability to retain nutrients during high flows. However, little is known about phosphorus (P) dynamics in these systems during low flows. Our study identifies key limnological and hydrological factors influencing particulate phosphorus (PP) and total dissolved phosphorus (TDP) concentrations in the water column during low flows. To assess this, we measured monthly PP and TDP concentrations at the surface and near the sediment-water interface in 10 SWMPs during October 2010 to 2011. The study sites were located in Richmond Hill, Whitby, and Peterborough, Ontario, Canada. At the time of sampling, we also measured water temperature, specific conductivity, Secchi disk depth, dissolved oxygen, salinity, and total suspended solids (TSS). Based on these measurements, we calculated water retention time, resistance to thermal mixing (RTRM), and the antecedent precipitation index (API) at the time of sampling. We found that season, thermal stratification, and antecedent moisture conditions were the most influential factors on P concentrations in SWMPs. We also found that there were higher PP concentrations at the bottom of the water column during the ice-free season, when there were drier antecedent moisture conditions, and when the ponds were thermally stratified. By developing a better understanding of the hydrological and limnological factors influencing P cycling in SWMPs, we can refine our design, monitoring, and maintenance strategies to enhance P retention.

Key words: stormwater management ponds, seasonality, antecedent moisture conditions thermal stratification, low flow

3.2 Introduction

Stormwater management ponds (SWMPs) are an end-of-pipe Best Management Practice that are principally used to reduce flooding and are also intended to protect water quality in cities (Ontario Ministry of the Environment [OMOE], 2003). Although the morphometry of SWMPs varies, they are usually small water bodies that are widely constructed in urban areas, with estimates indicating that these systems occur at densities of 0.14 to 0.99 pond/km^2 (Williams et al., 2013 based on calculations by Downing et al., 2006). Small water bodies can intensively process nutrients such as carbon (Downing et al., 2010), and microbial activity in SWMPs has been found to transform nutrients (Song et al., 2017; Williams et al., 2013) before they flow out of these facilities.

Generally, SWMPs contain both organic and inorganic phosphorus (P) that may occur in a dissolved or particulate form (Frost et al., 2019; Song et al., 2015; Song et al., 2017). The P flowing into SWMPs is derived from various sources in urban areas such as atmospheric deposition, pet waste, eroded soil, decomposing organic matter like leaves and grass clippings, and fertilizer (Bratt et al., 2018; Hobbie et al., 2017; Janke et al., 2017; Yang and Toor, 2017; Yang & Toor, 2018). The dominant form and amount of P available in a sewershed may change due to land cover and hydrologic conditions (L. Li et al., 2017; Yang et al., 2021). For instance, particulate-bound P can accumulate on impervious surfaces and get washed off during high flow events (Berretta & Sansalone, 2012; Yang et al., 2021). A longer period without precipitation prior to a high flow event may allow greater amounts of particulate matter to build up on surfaces and enter SWMPs during the first flush of a storm (Arias et al., 2013; L. Q. Li et al., 2007; Sartor & Boyd, 1972). Thus, antecedent moisture conditions can affect the quality of stormwater runoff. In turn, the quality of inflowing stormwater in combination with design and maintenance practices can influence the treatment efficiency of a SWMP (Chiandet & Xenopoulos, 2016; Wong et al., 1999).

Once stormwater flows into SWMPs, the process of sedimentation primarily helps to retain P but assimilation may also occur (Troitsky et al., 2019). In temperate regions, the assimilation process can be affected by winter conditions. During the winter, some aquatic vegetation in freshwater systems may go dormant depending on the species (Haag, 1979) and some biological processes can decrease in colder temperatures (Kadlec & Reddy, 2001). Generally, the combination of cold-water temperatures, de-icing salts, and ice cover can reduce the overall removal efficiency of SWMPs in the winter (Semadeni-Davies, 2006).

However, in the ice-free season, the efficiency of SWMPs may also be variable due to internal releases of P. Internal releases of P may occur due to the mineralization of organic matter (Søndergaard et al., 2003). Alternatively, P can be released from sediments because of changes in pH, redox conditions, and temperature (Søndergaard et al., 2003). For example, thermal stratification occurs in SWMPs both diurnally and for prolonged periods (Ahmed et al., 2022; Ahmed et al., 2023; He et al., 2015; McEnroe et al., 2013; Song et al., 2013). This can be problematic as stratification can cause hypoxia or anoxia near the sediments bed which in turn alters redox conditions and leads to increased P release (Forsberg, 1989; Song et al., 2013; Taguchi et al., 2021).

Although there is evidence that indicates thermal stratification, seasonality, and antecedent moisture conditions may contribute to the variable performance of SWMPs, we need to deepen our understanding about the effects of these factors on P speciation and dynamics. With this knowledge, we can refine SWMP design and management practices to help minimize internal P releases. In addition, since SWMP monitoring programs rely mostly on total phosphorus (TP) and total suspended solids (TSS) measurements to assess the water quality of a pond, we need to increase our knowledge about different P forms in the ponds to improve our predictions regarding P cycling between the water column and sediments. To help better understand P cycling in SWMPs, the objective of this research was to examine how hydrological and limnological factors can impact different P forms in the water column.

3.3 Methods

3.3.1 Study sites and meteorological conditions

Water samples were collected from 10 SWMPs in urbanized municipalities (Peterborough, Whitby, and Richmond Hill) in Ontario, Canada (Figure 1). Sampling was conducted from October 2010 to 2011, with 90 samples taken from the top and bottom of the water column, resulting in a total of 180 samples. Data for January, February, and April 2011 were not available due to unsafe ice conditions on the ponds and/or the measurements for specific conductivity and dissolved oxygen were not within the detection limits of the sampling probes.

We collected the samples during low flow conditions. Low flow was characterized as less than 5 mm of precipitation 24 hours prior to sampling (Chiandet & Xenopoulos, 2011). We used precipitation data from the closest Environment Canada weather stations to the study sites to determine low flow conditions during the study period. There were 244, 250, and 224 low flow days in Peterborough, Whitby, and Richmond Hill, respectively. Overall, the study period was marginally drier in Peterborough and wetter in Whitby and Richmond Hill compared to the 30-year normal (1981-2010), with 876.3 mm of precipitation in Peterborough, 945.7 mm in Whitby, and 919.0 mm in Richmond Hill.

Precipitation data from Environment Canada were also used to calculate an Antecedent Precipitation Index (API) for each sampling period using Kohler and Linsley's (1951) method. The time-step used was a 7-day antecedent period. A decay constant of 0.84 was used as this value is incorporated into the Ontario Ministry of Natural Resources' flood forecasting (Cheng et al., 2012). Based on the median API value for this study, values above the median were considered a higher API and values below the median were considered a lower API.

We selected our study ponds from residential sewersheds and they all had design features that adhered to the OMOE's (2003) construction guidelines. Specifically, the ponds ranged in surface area from 972 to 10,035 m^2, volume from 780 to 54,783 m^3, and depth from 1.1 to 3.6 m (Table 1).

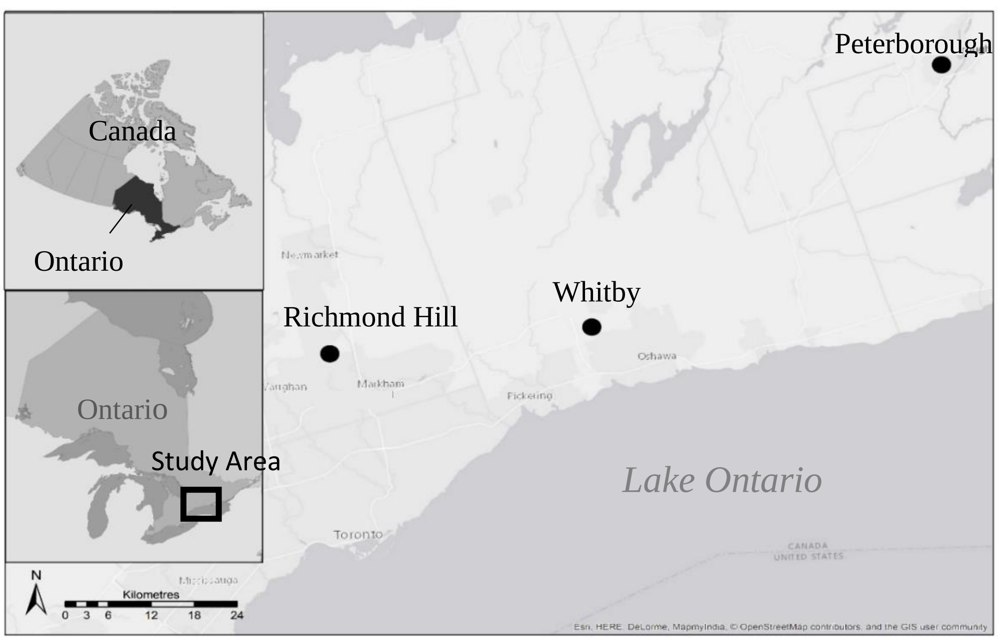


Figure 3.1: Location of the study sites

Table 3.1: Sewershed characteristics and pond properties

Pond	Sewershed area (m^2)	Impervious surfaces (%)	Pervious surfaces (%)	Surface area of the pond (m^2)	Volume (m^3)	Depth (m)	Length-to-width ratio	Age since construction or last dredging (years)
A	547,929	35	65	8,894	16,009	1.8	4.1	1
B	83,000	38	62	972	780	1.9	1.4	8
C	240,497	63	37	3,414	4,055	2.2	2.9	6
D	450,480	30	70	5,995	5,761	2.5	2.8	2
E	586,214	69	31	9,811	6,740	1.2	3.9	5
F	142,935	61	39	1,549	2,110	1.9	1.3	3
G	1,323,890	55	45	10,035	54,783	3.6	4.8	4
H	998,292	54	46	8,501	1,809	2.2	3.2	10
I	420,000	44	56	3,001	9,715	3	3.6	10
J	669,690	64	36	7,820	29,000	1.9	2.5	9

3.3.2 Water sampling and analysis

Samples were collected in 1-L polypropylene bottles from the middle of the permanent pond 10-20 cm below the surface and 10-20 cm above the sediment using a Van Dorn grab sampler. At the same location, water transparency was measured using Secchi disk depth and pond depth was measured using a weighted rope. Based on these depth measurements and engineering diagrams for the study ponds, we also calculated the volume at the time of sampling. The volume of a pond (m^3) was divided by the inflow volume per day (m^3/day) to calculate the water retention time (WRT) in days for each sampling period.

In situ measurements for specific conductivity (uS/cm) and temperature (^oC) were also taken using handheld meters (YSI Models 54 and 63; Yellow Springs Instrument Co., Yellow Springs, Ohio, USA). Temperature data were used to calculate the relative thermal resistance to mixing (RTRM), by converting temperature measurements at the top and bottom of the ponds to density and then calculating the difference between them divided by the difference in water density at 4^oC and 5^oC (Vallentyne, 1957; Wetzel, 2001). Similar to Song et al. (2013), the SWMPs were categorized as thermally stratified if the RTRM value at the time of sampling was more than 50. Temperature data and observations in the field were also used to distinguish between two general seasons. The first season was when the ponds were ice-covered (December 2010 to March 2011), and the second season was when the ponds were ice-free.

The water samples were vacuum filtered through 0.7 µm pre-weighed and pre-combusted GF/F filters (Whatman, Mississauga, Ontario, Canada) and then through 0.2 µm polycarbonate filters (Millipore, Billerica, Massachusetts, USA) within 24 hours after they were collected in the field. The filtered water and the material collected on the GF/F filters were used to analyze TDP and PP, respectively, with the persulfate digestion and molybdate blue-ascorbic acid spectrophotometric method (Clesceri et al., 1998). Total suspended solids were analyzed by calculating the difference between the initial and final weight of the filter divided by the volume of water that passed through the filter (Clesceri et al., 1998).

3.3.3 Data analysis

All statistical analyses were performed in R version 4.2.2 (R Core Team, 2022). To explore the relationship between P concentrations and hydrological and limnological variables, a principal components analysis (PCA) was applied to the data and visualized using multiple packages such as *ggplot2* (Wickham, 2016), *corrr* (Kuhn et al., 2022), *ggcorrplot* (Kassambara, 2022), *FactoMineR* (Lê et al., 2008), and *factoextra* (Kassambara & Mundt, 2020). The variables in the analysis included PP and TDP concentrations at the top and bottom of the water column, season (i.e., ice-covered or ice-free), API, WRT, RTRM, Secchi disk depth, and the difference between TSS concentrations (dTSS) and specific conductivity (dSC) at the top and bottom of the column. Prior to conducting the PCA, the data were standardized.

Based on the results of the PCA, differences between P concentrations at the top and bottom of the water column were analyzed with paired t-tests under three conditions. First, we examined PP and TDP concentrations when the ponds were ice-covered and when they were ice-free. Second, we evaluated the P concentrations when there was a higher API or lower API based on the median of the dataset. Lastly, we compared P concentrations when the ponds were thermally mixed and stratified. Prior to testing, the data were log transformed and the t-test result reports were generated using the *report* package (Makowski et al., 2023). The p-values were adjusted using the Benjamini-Hochberg method (1995).

In addition, a redundancy analysis (RDA) using the *vegan* package (Okasanen et al., 2022) was applied the data. The RDA was used to determine what combination of limnological and hydrological factors explain the most variation in top-bottom differences for PP and TDP concentrations based on the API, thermal conditions, and season. The ordination plots were developed using R code modified from Block and Meave (2015). Prior to analysis, the hydrological and limnological data were centered and scaled and only variables with a variance inflation factor less than five were included in the models to avoid multicollinearity (Akinwande et al., 2015).

3.4 Results

The PCA results indicate that PP concentrations at the top and bottom of the water column were positively correlated with each other (Figure 3.2). In addition, PP concentration were also positively correlated with RTRM and to a lesser extent with season (Figure 3.2). Similarly, TDP concentrations at the top and bottom of the water column were positively correlated with each other (Figure 3.2). However, TDP concentrations were negatively correlated with the API (Figure 3.2). Secchi disk depth, WRT, difference between TSS concentrations at the top and bottom of the water column, and difference between specific conductivity at the top and bottom of the water column did not have significant relationships with PP and TDP concentrations (Figure 3.2). Based on the results of the PCA, an RDA was applied to the data; however, the models did not yield highly significant results (Appendix 1).

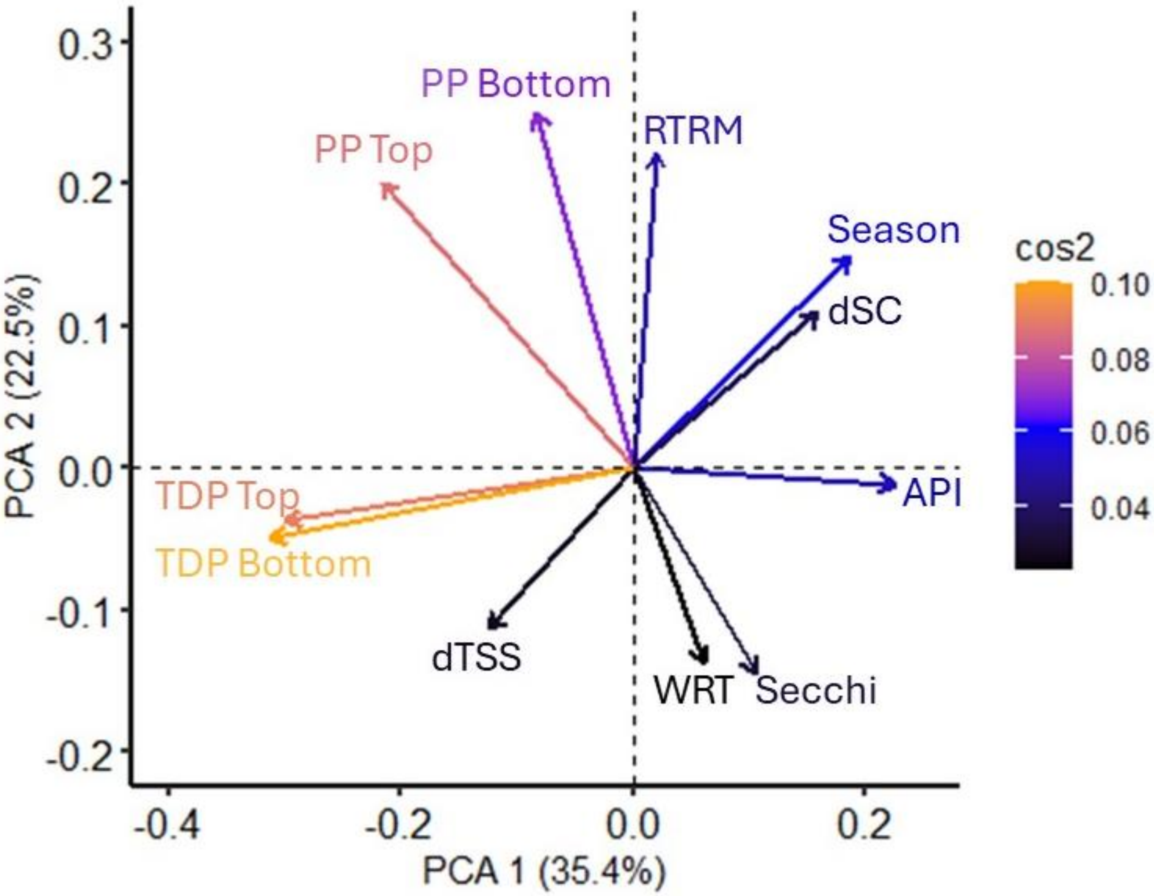


Figure 3.2: Ordination plot with the first two components and the square cosine value for each variable with respect to the two components. A high square cosine value indicates that the variable is well represented by a component and a low value indicates the opposite. The label dSC refers to the difference in specific conductivity measurements (uS/cm) at the top and bottom of the water column, dTSS indicates the difference in total suspended solids (mg/L) at the top and bottom of the water column, WRT is water retention time (days), Secchi is Secchi disk depth (m), API is the antecedent precipitation index, Season indicates ice-free or ice-covered ponds, RTRM is resistance to thermal mixing, PP is particulate phosphorus, and TDP is total dissolved phosphorus.

3.4.1 Antecedent Precipitation Index

There were 48 sampling periods that had a lower antecedent precipitation index (API) and 42 sampling periods that had a higher API. Within both the API groupings, PP concentrations at the top and bottom of the ponds were higher and more variable than TDP concentrations. In addition, there were not any statistically significant top-bottom differences between TDP concentrations. However, when there was a lower API, there was significantly higher concentrations of PP at the bottom of the water column with a small effect size $t(47) = -2.95$, $p = 0.005$; Cohen's $d = -0.43$, 95% CI [-0.72, -0.13]. This trend did not occur when there was a higher API.

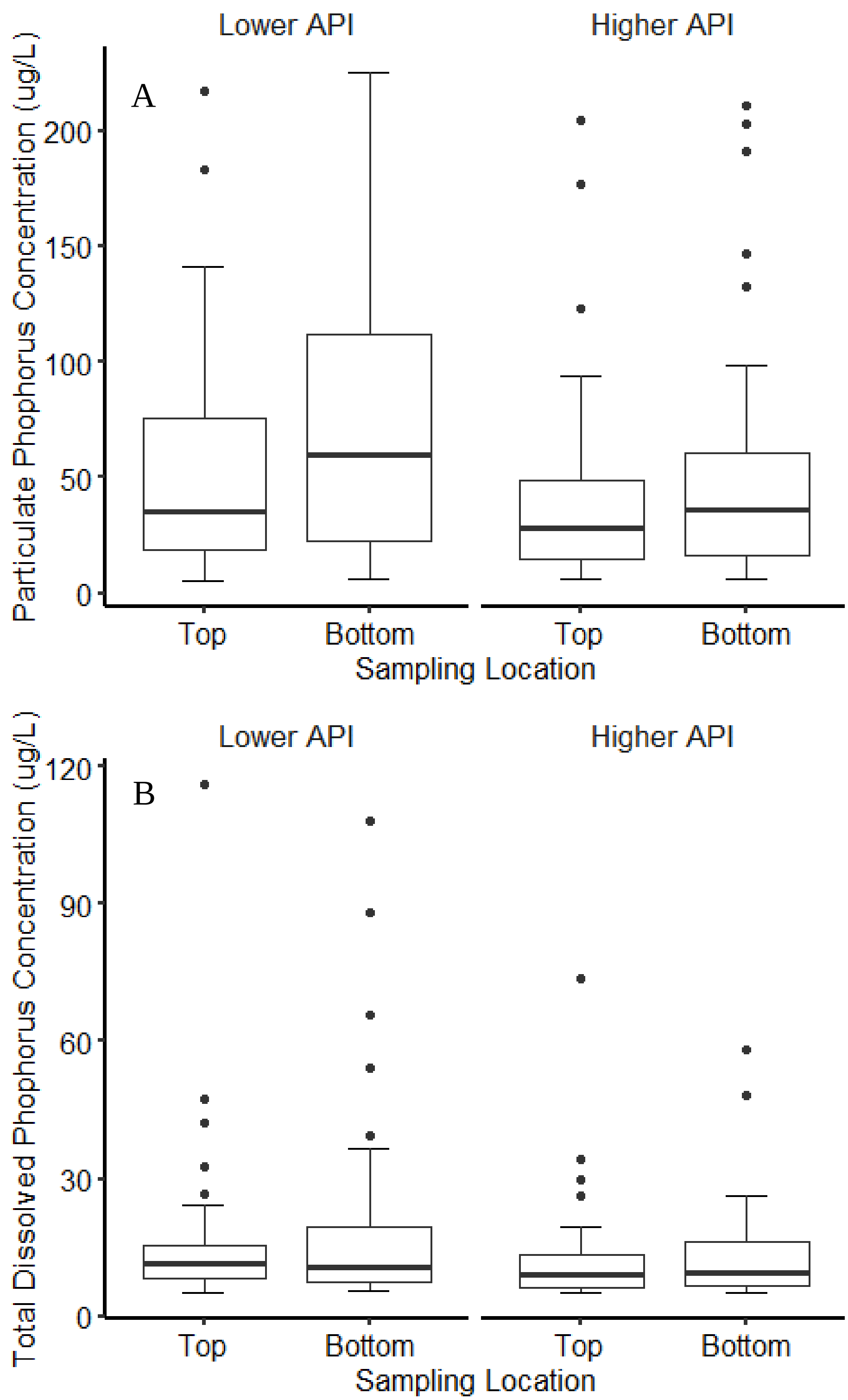


Figure 3.3: (A) Particulate P concentrations at the top and bottom of the permanent pool when the sewersheds have a lower API and a higher API. (B) Total dissolved P concentrations at the top and bottom of the permanent pool when the sewersheds have a lower API and a higher API.

3.4.2 Thermal condition

There were 62 sampling periods within mixed conditions and 28 sampling periods during stratified conditions. Similar to the API groupings, PP concentrations at the top and bottom of the ponds were higher and more variable than TDP concentrations. During mixed conditions, there were significant differences for PP concentrations at the top and bottom of the water column with a small effect size $t(61) = -2.34$, $p=0.022$; Cohen's $d = -0.30$, 95% CI [-0.55, -0.04]. However, there were no significant differences for TDP.

Similarly, during stratified conditions there were no significant differences for TDP, but there were significantly higher PP concentrations at the bottom of the SWMPs with a medium effect size $t(27) = -2.95$, $p = 0.006$; Cohen's $d = -0.56$, 95% CI [-0.95, -0.15].

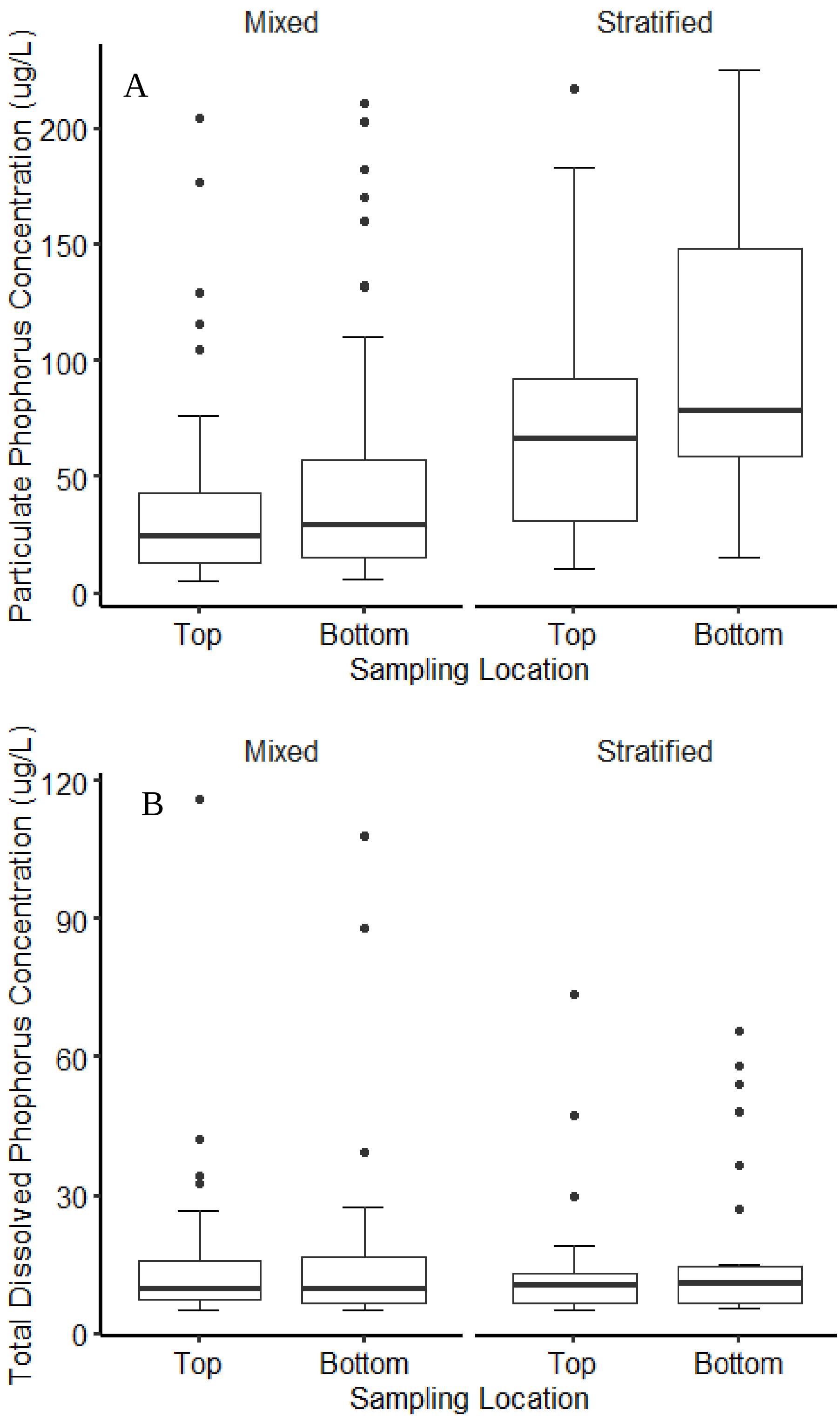


Figure 3.4: (A) Particulate P concentrations at the top and bottom of the permanent pool under mixed and stratified conditions. (B) Total dissolved P concentrations at the top and bottom of the permanent pool under mixed and stratified conditions.

3.4.3 Season

There were 20 sampling periods during the ice-covered season and 70 sampling periods during ice-free conditions. Within both the ice-covered and ice-free seasons, PP concentrations at the top and bottom of the ponds were higher and more variable than TDP concentrations. Within the ice-covered season, there were not any significant differences for PP and TDP concentrations at the top and bottom of the water column. However, within the ice-free season there were statistically higher PP concentrations at the bottom of the ponds with a small effect size $t(69) = -3.68$, $p < 0.001$; Cohen's $d = -0.44$, 95% CI [-0.68, -0.19].

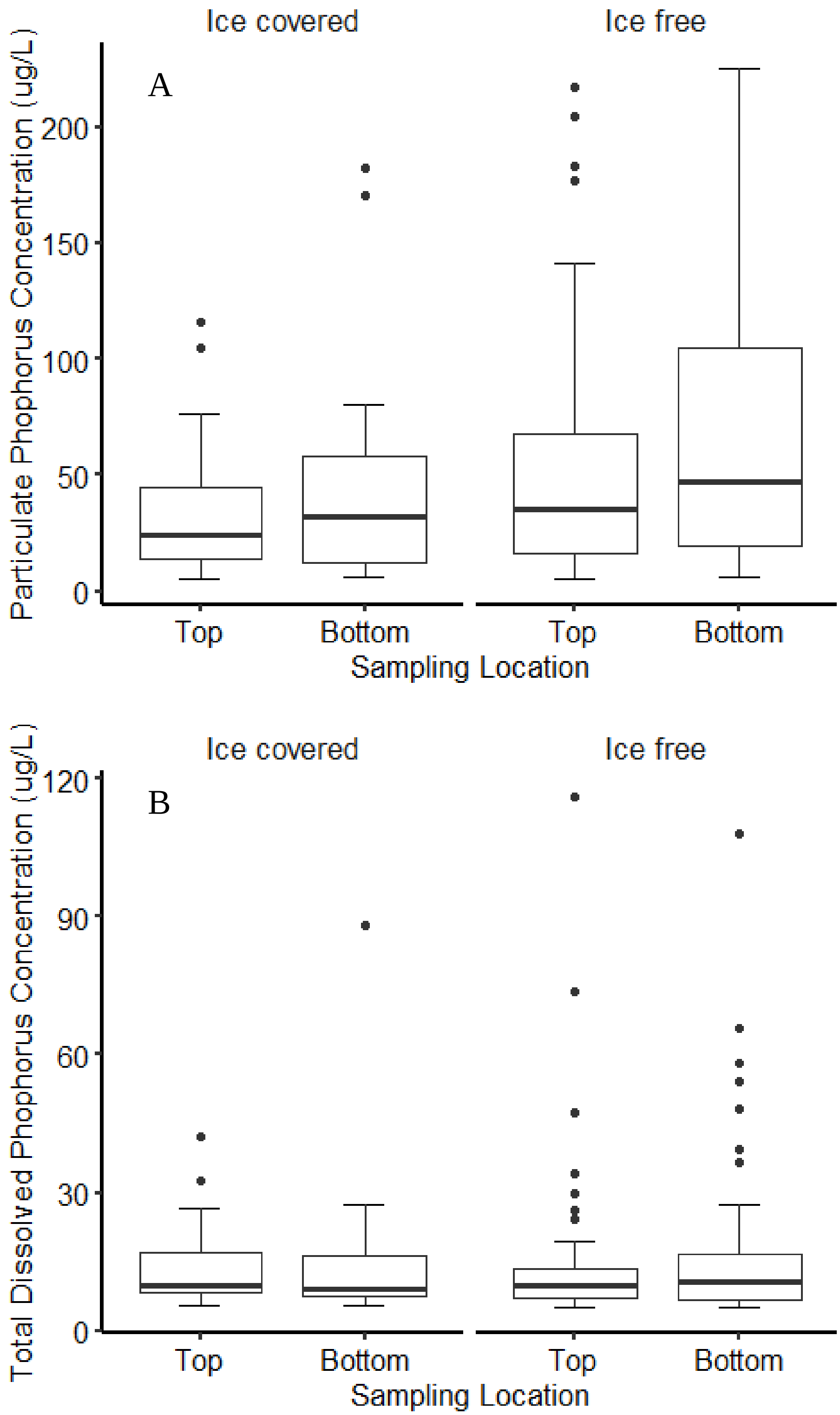


Figure 3.5: (A) Particulate P concentrations at the top and bottom of the permanent pool during the ice covered and ice-free season. (B) Total dissolved P concentrations at the top and bottom of the permanent pool during the ice covered and ice-free season.

3.5 Discussion

Our findings indicate that antecedent moisture conditions influence P concentrations. This may be linked to the effects antecedent moisture conditions have on the amount and size of particles flowing into SWMPs. Prolonged dry periods allow particles to build up on surfaces in a sewershed which increases the amount of nutrients transported in stormwater when they are washed off (Chow et al., 2013). In addition, the length of time between rain events can influence the size of particles that are accumulating, and due to vehicular traffic and other factors breaking down particulate matter on roads, particles can become finer during longer periods of dry weather (Chow et al., 2015; Vaze & Chiew, 2002). Although particle size is just one of many variables that can influence the settling process in SWMPs, it is a significant factor (Gu et al., 2017; Rommel et al., 2020), and finer particles are not as effectively retained as larger ones (Greb & Bannerman, 1997). Research indicates that inflowing TP is attached to particles between 11 and 150 µm in diameter, and SWMPs need to be able to retain material at the lower end of this range to be effective (Miguntanna et al., 2010; Vaze & Chiew, 2004). Perhaps we observed statistically higher and more variable PP concentrations in the water overlying the sediments during drier antecedent periods due to finer material not settling out or being resuspended due to wind action.

According to analytical modelling and field measurements by Andradóttir (2017), wind can vertically mix sediments in SMWPs and may restrict the settling of finer particulates. Shaw et al. (1997) found velocities of 33 mm/s at the bottom of a SWMP during low flow conditions, which indicates there is also potential for the wind to be strong enough to resuspend sediments. Wind-induced releases of P from the sediments may also partly explain why we observed statistically higher PP concentrations at the bottom of the water column when the ponds were mixed and during the ice-free season. However, we did not find any statistical differences between top-bottom TDP and PP concentrations during the ice-covered period. This may be due to seasonal variations in physical, chemical, and biological factors affecting P cycling in SWMPs.

For instance, during the ice-free season, one of the factors affecting P release from the sediments could have been bioturbation. Bioturbation occurs when benthic organisms feed, secrete, excrete, and burrow in the sediment *(*Adámek & Maršálek, 2013; Chakraborty et al., 2022*)*. Bioturbation can release dissolved P at the sediment-water interface through mineralization *(*Mermillod-Blondin et al., 2005*)*. Bioturbation can also add PP to overlying water through nutrient excretion (Persson & Svensson, 2006) or mixing the sediment through feeding activities *(*Lake Simcoe Region Conservation Authority [LSRCA], 2020*)*. Similar to LSRCA (2020), we observed the presence of introduced goldfish (*Carassius auratus*) in many of our study sites. Since goldfish are benthic feeders, they could have stirred up the sediment and released P. Bioturbation may be more impactful in the ice-free season compared to the ice-covered season, as higher temperatures increase the intensity of some activities (Baranov et al., 2016). Higher temperatures can also increase microbial activity (Forsberg, 1989) and in turn this would influence biogeochemical processes.

For example, uptake and assimilation are processes that occur in SWMPs (Troitsky et al., 2019), especially during the ice-free season. However, the retention of P in phytoplankton and macrophytes may only be temporary, because when they die and decay their debris could contribute to internal organic P releases (Feng et al., 2016). Song et al. (2017) observed that SWMP sediments can contain significant amounts of organic P. When organic P in the sediments is mineralized, TDP concentrations can increase in the overlying water (Song et al., 2017). We did not find that that TDP concentrations at the bottom of the water column were significantly different than the top during the ice-free season. However, Song et al. (2015) proposed that PP concentrations increased in the water column of their study SWMPs due to primary productivity. Since we studied some of the same ponds as Song et al. (2015), perhaps dissolved P that had been mineralized was converted into particulate P due to the presence of algae and bacteria near the sediments.

Additionally, the PP we found at the bottom of the water column could have formed by P adsorbing or coprecipitating with calcium (Ca) or iron (Fe) from the sediment. In SWMP sediment from the same region as our study, Frost et al. (2019) and Song et al. (2017) found a relatively high proportion of Ca-P and smaller amounts of Fe-P. This is consistent with findings from Lusk and Chapman (2021) in Florida who found that Ca and magnesium (Mg) bound P were the largest inorganic fractions of P in SWMP sediment. Although we do not have pH measurements for every sampling period, our measurements at the bottom of the water column during the ice-free season indicate that pH varied between 7.59 to 9.84. These pH measurements fall within the optimal range for adsorption to occur (Peng et al., 2007; Z. Li et al., 2017). However, changes in pH and redox conditions can cause releases of P from the sediment to the water column (Orihel et al., 2017). For example, desorption of P from Fe can occur in low oxygen conditions, and one explanation for this is that $Fe3^{+}$ is reduced to $Fe2^{+}$ and then the P from the Fe oxides and hydroxides in sediment detaches and moves into the overlying water (Amirbahman et al., 2003).

Low oxygen conditions can occur in SWMPs due to thermal stratification (Ahmed et al., 2022; Ahmed et al., 2023; He et al., 2015; McEnroe et al., 2013; Song et al., 2013). The main effect of thermal stratification is that warmer, less dense air floats over cooler, denser water and resists mixing which causes lower dissolved oxygen levels near the bottom of a water body (Kalff, 2002). Even though most SWMPs are small and shallow, thermal stratification can occur for prolonged periods, especially in the ice-free period between May to August (Ahmed et al., 2022; Song et al., 2013). Diurnal stratification can also occur, and He et al. (2015) found that temperature differences in the water column of a SWMP that occurred during the day disappeared after sunset due to cooler air temperatures and wind. Both short-term and prolonged thermal stratification can impact the water quality in SWMPs (He et al., 2015; Song et al., 2013; Taguchi et al., 2020).

Similar to Song et al. (2013) and Taguchi et al. (2020), we found that thermal stratification was a significant factor influencing P concentrations in our study ponds. During the ice-free period, we observed statistically higher PP concentrations at the bottom of the water column when the ponds were thermally stratified. Thermal stratification may have induced low oxygen conditions near the sediment-water interface which may have stimulated the internal release of dissolved P. As dissolved P moved into the water column it could have been subsequently adsorbed to suspended sediment or taken up by phytoplankton.

Aside from thermal stratification, chemical stratification can also occur in SWMPs likely due to high concentrations of de-icing salts applied to roads (Ahmed et al., 2022; Litmanovitch, 2021; Marsalek et al., 2000; Marsalek, 2003; Marsalek et al., 2003; McEnroe et al., 2013; Semadeni-Davies, 2006). These de-icing salts can induce chemical stratification in the winter that lasts until the salts are flushed out in the spring or summer (Lam et al., 2020). Litmanovitch (2021) indicates they found that chemical stratification lasted for longer periods in their study sites in the ice-covered period compared to thermal stratification in the ice-free season and postulated that this may cause more internal releases of nutrients during the winter. However, more research is needed to understand how chemical and thermal stratification impact specific P forms and cycling in SWMPs. Furthermore, it would be beneficial to study the effects of seasonality on biogeochemical processes in SWMPs and the specific mechanisms influencing P cycling at the sediment-water interface during the ice-free and ice-covered seasons.

Overall, we found that season, thermal stratification, and antecedent moisture conditions were influential factors on P concentrations in SWMPs. We also found that there were higher PP concentrations at the bottom of the water column during the ice-free season, when there were drier antecedent moisture conditions, and when the ponds were thermally stratified. As we learn more about the hydrological and limnological factors influencing P inputs and internal releases, we can move away from the traditional mindset that assumes sedimentation will remove most nutrients in SWMPs, and focus on developing strategies to optimize pond design, monitoring, and maintenance activities to ensure these systems perform effectively and consistently.

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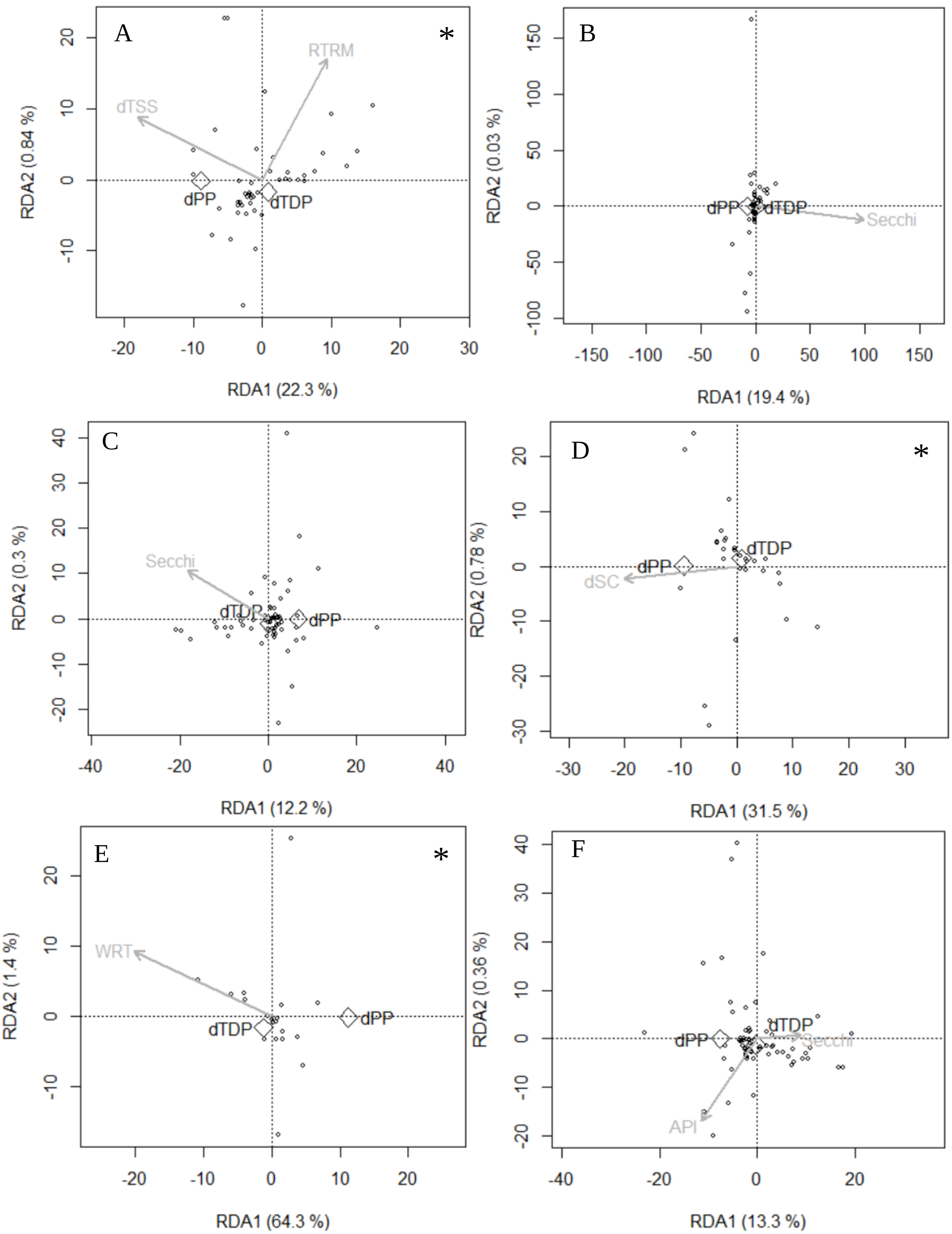
3.7 Appendix 1 – Redundancy analysis based on significant hydrological and limnological variables.



Ordination plots visualizing the results of the RDA when there was a (A) lower API, (B) higher API, (C) mixed conditions, (D) stratified conditions, (E) ice-covered season, and (F) ice-free season. Significant models are indicated by an asterix and only the significant explanatory variables are shown.

Chapter 4: Stoichiometric ratios in urban stormwater ponds during low flow conditions.

4.1 Abstract

Traditionally, we have assumed that nutrient retention in stormwater management ponds (SWMPs) occurs through physical processes. However, we are starting to understand that biogeochemical activities may impact the treatment efficiencies of these systems by influencing how single and coupled elements cycle through these facilities. To assess if stoichiometric ratios differ between the inflowing and outflowing water from SWMPs, we took monthly water samples during October 2010 to 2011 from the inlets and outlets of 10 study ponds. We measured dissolved organic carbon (DOC), particulate organic carbon (POC), total dissolved nitrogen (TDN), particulate organic nitrogen (PON), total dissolved phosphorus (TDP), and particulate phosphorus (PP) concentrations to calculate C:N:P stoichiometric ratios. Our results indicate there were not any significant differences between particulate stoichiometric ratios inflowing and outflowing from the ponds. However, in the effluent there was an enrichment of DOC compared to TDN and TDP. Although most SWMP design and maintenance considerations focus on high flow events, biogeochemical processing during low flow conditions may influence how single and coupled elements cycle through the ponds and we need to account for this to minimize nutrient imbalances downstream.

Key words: stormwater management ponds, C:N:P ratios, biogeochemical processes

4.2 Introduction

Land use changes and human activities in urban areas have drastically altered natural hydrological and biogeochemical cycles (Kaye et al., 2006; Kennedy et al., 2007; Lin et al., 2014; McGrane, 2016). One of the most pronounced impacts of urbanization has been an increase in stormwater runoff that occurs when infiltration and evapotranspiration are reduced due to impervious surfaces (Arnold & Gibbons, 1996). As stormwater flows across impervious and pervious surfaces, it can concentrate and convey nutrients like carbon (C), nitrogen (N), and phosphorus (P) from various natural and anthropogenic sources to downstream water bodies (Paul & Meyer, 2001). Excessive nutrients can degrade water quality by promoting eutrophication, which results in numerous other negative effects on aquatic ecosystems (Carpenter et al., 1998).

To mitigate both water quality and quantity concerns associated with increased stormwater runoff, a variety of stormwater management practices are used either alone or in tandem (Jefferson et al. 2017; Ontario Ministry of the Environment [OMOE], 2003). One practice that started in the 1970's but became increasingly more commonplace over time, is the construction of stormwater management ponds (Bradford & Gharabaghi, 2004; Drake and Guo, 2008). The main goal of these first-generation stormwater management ponds (SWMPs) was to reduce flooding and erosion during storm events (Bradford & Gharabaghi, 2004; Drake and Guo, 2008). However, ponds constructed during and after the 1990s, have a secondary function and are intended not only to mitigate flooding, but to also decrease downstream transport of sediments, nutrients, and other contaminants (Bradford & Gharabaghi, 2004; Drake and Guo, 2008).

Although the performance objectives of SWMPs have expanded, design and maintenance practices have not changed dramatically over the past few decades. The current water quality design guidelines are still geared primarily towards treating total suspended solids (TSS) with the expectation that pollutants will be removed from the water column by sedimentation (OMOE, 2003; Bradford & Gharabaghi, 2004). However, we now know that biogeochemical activity can occur in SWMPs and the treatment of TSS is masked by the abundant microbial activity taking place in these facilities (Williams et al. 2013). Furthermore, although SWMPs are generally designed to be small and shallow, research indicates that they can stratify for long periods which can lead to hypoxic or anoxic conditions at the bottom of water column (Ahmed et al., 2022; Ahmed et al., 2023; He et al., 2015; McEnroe et al., 2013a, Song et al., 2013). In turn, low-oxygen conditions can lead to internal releases of solutes such as P (Song et al., 2013; Taguchi et al., 2020) and less net retention of this nutrient. In addition, SWMPs can also contain high levels of bioavailable N (Jani et al., 2020) and dissolved organic material that appears to be internally derived (Williams et al., 2013). Consequently, internal processes occurring in SWMPs that transform and potentially release nutrients may compromise the treatment efficiency of these systems (Duan et al., 2016).

Although we are starting to understand how some nutrients are transformed in SWMPs (Gold et al., 2017; Gold et al., 2021; Song et al., 2013; Song et al., 2017), there is still little known about how these transformations impact the cycling of coupled elements in SWMPs. Moreover, some research indicates that stoichiometry can be affected by hydrological conditions, and that low flow periods may be periods of higher biogeochemical activity in SWMPs (Chiandet & Xenopoulos, 2011). To build on our understanding of how coupled elements are cycling through SWMPs, the objective of this research is to determine if C:N:P stoichiometric ratios change between the influent and effluent during low flow conditions.

4.3 Methods

4.3.1 Description of study sites

Sampling took place in 3 municipalities (Peterborough, Whitby, and Richmond Hill) in southern Ontario, Canada (Figure 4.1) during October 2010 to 2011. The meteorological conditions in these municipalities were analyzed with precipitation and air temperature data from Environment Canada stations closest to the study sites. The average monthly temperature and precipitation during the study period is generally comparable to monthly 30-year average (1981-2010) data. However, there was less than average precipitation in Peterborough by 5.8 mm and above average precipitation in Whitby and Richmond Hill by 73.8 mm and 66.1 mm, respectively. Precipitation data from Environment Canada were also used to calculate an Antecedent Precipitation Index (API) for each sampling period using Kohler and Linsley's (1951) method with a time-step of 7-days and a decay constant of 0.84 (Cheng et al., 2012).

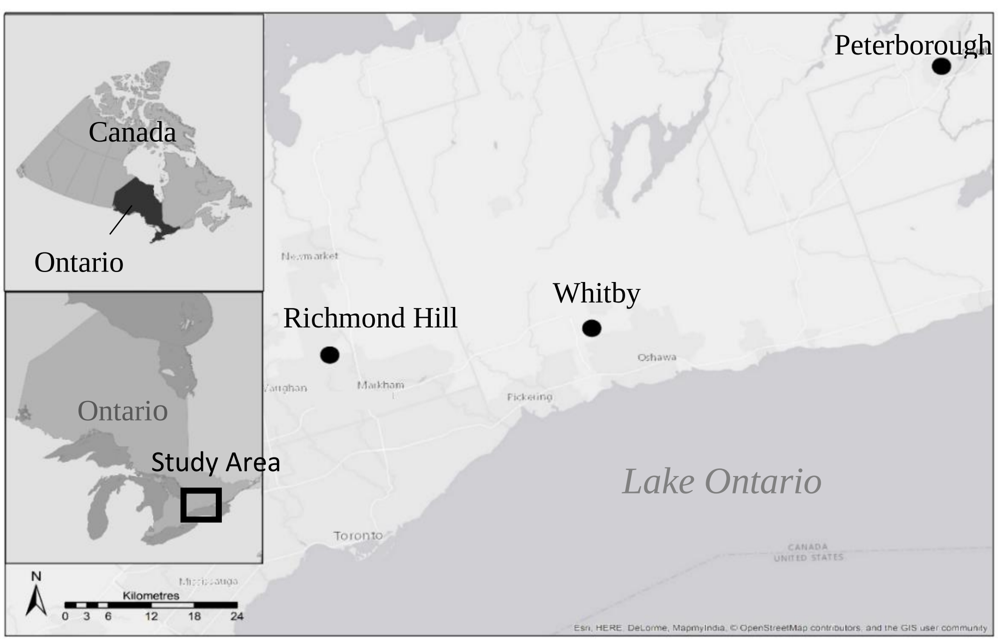


Figure 4.1: Location of the study sites

The morphometric characteristics of the ponds varied, but their designs are representative of SWMPs in the region (Table 4.1). Design characteristics such as sewershed area (m^2), surface area of the pond (m^2), length-to-width ratio were calculated using spatial analyst and data management tools in ArcMap 10.8. The municipalities provided data about pond age (i.e., time elapsed since the pond was constructed or dredged) and engineering diagrams which indicated the design volume of the ponds. In the field, monthly pond depth measurements were taken from the center of the permanent pool using an inflatable raft. Global Positioning System (GPS) coordinates were used to maintain consistency of the sampling location. Pond depth was measured by dropping a weighted roped marked with 10-centimeter increments from the raft until it connected with the sediment. Based on these depth measurements and engineering diagrams for the study ponds, we also calculated the volume at the time of sampling.

Table 4.1: Sewershed characteristics and pond properties

Pond	Sewershed area (m^2)	Surface area of the pond (m^2)	Design Volume (m^3)	Depth (m)	Length-to-width ratio	Age since construction or last dredging (years)
A	547,929	8,894	16,009	1.8	4.1	1
B	83,000	972	780	1.9	1.4	8
C	240,497	3,414	4,055	2.2	2.9	6
D	450,480	5,995	5,761	2.5	2.8	2
E	586,214	9,811	6,740	1.2	3.9	5
F	142,935	1,549	2,110	1.9	1.3	3
G	1,323,890	10,035	54,783	3.6	4.8	4
H	998,292	8,501	1,809	2.2	3.2	10
I	420,000	3,001	9,715	3	3.6	10
J	669,690	7,820	29,000	1.9	2.5	9

4.3.2 Sampling and physiochemical analysis

During the study period, each SWMP was sampled once a month during low flow periods, except in January, February, and April 2011. Data were not available during these periods due to unsafe ice conditions on the ponds, malfunctioning pipes and/or the measurements for specific conductivity and dissolved oxygen were not within the detection limits of the sampling probes. Our definition of low flow was based on Chiandet and Xenopoulos (2011) who indicate that this condition happens when there is less than 5 mm of precipitation 24 hours prior to sampling. According to this definition, low flow conditions occurred 61%, 67%, and 68% of the time during the study period in Richmond Hill, Peterborough, and Whitby, respectively.

We took 90 samples in the inlets and outlets using acid washed 1-L polypropylene bottles and collected a total of 180 samples. Prior to taking a sample, the bottles were rinsed three times with the influent or effluent. The samples were stored in coolers on ice during transport to the laboratory. While in field, measurements for dissolved oxygen (mg/L), specific conductivity (uS/cm), and temperature (^{o}C) were taken in the inlet and in the outlet using handheld meters (YSI Models 54 and 63; Yellow Springs Instrument Co., Yellow Springs, Ohio, USA). Temperature data were used to calculate relative thermal resistance to mixing (Vallentyne, 1957; Wetzel, 2001). Also in the field, Secchi disk depth (m) and maximum depth measurements were taken. The depth measurements (m) were used in conjunction with the engineering diagrams for the study ponds, to calculate the volume at the time of sampling. The volume of a pond (m^3) was divided by the inflow volume per day (m^3/day) to calculate the water retention time in days for each sampling period.

Water samples were transported from the field and stored at 4^{o}C until they were analyzed. Within 24 hours of sampling, we vacuum filtered the water samples through 0.7 µm pre-weighed and pre-combusted GF/F filters (Whatman, Mississauga, Ontario, Canada) and then through 0.2 µm polycarbonate filters (Millipore, Billerica, Massachusetts, USA) into acid washed, pre-combusted (500°C) amber glass bottles. The filtrate was analyzed for DOC in mg/L and TDN in µg/L by combustion with an O.I. Analytical Aurora Model 1030 TOC analyzer, College Station, Texas. The filtrate was also analyzed for TDP in µg/L with the persulfate digestion and molybdate blue-ascorbic acid spectrophotometric method (Clesceri et al., 1998).

The GF/F filters were used to analyze TSS, POC, PON, and PP. The amount of TSS in mg/L was calculated by subtracting the initial mass of the filter from the final mass of the filter plus the residue, and then dividing this value by the volume of water that was filtered (Clesceri et al., 1998). The particulate matter collected on the GF/F was analyzed for POC and PON by wrapping the filters in tin foil and then compressing them using a manual pressing tool into a pellet. The tin pellets were placed in a CN elemental analyzer (Elementar Vario El III, Mt Laurel, NJ, USA) to measure the POC and PON on the filters by combustion. Lastly, the GF/F filters were used to analyze PP with the persulfate digestion and molybdate blue-ascorbic acid spectrophotometric method (Clesceri et al., 1998).

4.3.3 Data analysis

Concentration data for all the ponds were aggregated into one dataset to increase statistical power. Using nutrient concentration data, molar stoichiometric ratios for POC:PON, POC:PP, PON:PP, DOC:TDN, DOC: TDP, and TDN:TDP were calculated. The molar stoichiometric ratios were natural log transformed and since they had non-normal distributions, a paired Mann-Whitney U test was used to compare stoichiometry into and out of the ponds in R version 4.2.2 (R Core Team, 2022). The p-values were adjusted using the Benjamini-Hochberg method (Benjamini & Hochberg,1995).

In addition, we performed a redundancy analysis (RDA) using the *vegan* package (Okasanen et al., 2022). This analysis was completed to determine what combination of factors including antecedent precipitation index (API), water retention time (WRT), resistance to thermal mixing (RTRM), outflowing total suspended solids (TSS), and Secchi disk depth explain the most variation in outflowing stoichiometric ratios. The ordination plots were developed using R code modified from Block and Meave (2015). Prior to analysis, the hydrological and limnological data were centered and scaled.

4.4 Results

The dominant inflowing and outflowing nutrient concentration was DOC, followed by POC, TDN, PON, PP, and then TDP (Table 4.2). The most variable inflowing stoichiometric ratios were PON:PP, DOC:TDN, and POC:PP, and the most variable outflowing stoichiometric ratios were PON:PP and POC:PON (Table 4.2). Generally, there was less variability in outflowing stoichiometric ratios compared to the inflow (Table 4.2).

Table 4.2: Mean (± standard deviation) nutrient concentrations and stoichiometric ratios in the inflow and outflow.

	N	Inflow (Mean ± SD)	N	Outflow (Mean ± SD)
Concentration				
POC (mg/L)	90	2.0 ± 1.7	90	1.6 ± 1.3
PON (µg/L)	90	407.8 ± 240.7	90	346.5 ± 226.2
PP (µg/L)	90	43.8 ± 32.4	90	32.7 ± 21.0
DOC (mg/L)	90	4.3 ± 2.2	90	4.8 ± 1.3
TDN (µg/L)	90	1482.2 ± 1004.1	90	918.7 ± 595.3
TDP (µg/L)	90	14.1 ± 14.3	90	11.4 ± 6.5
Stoichiometric Ratios				
POC:PON (moles)	90	7 ± 5	90	7 ± 6
POC:PP (moles)	90	148 ± 147	90	151 ± 104
PON:PP (moles)	90	36 ± 40	90	35 ± 41
DOC:TDN (moles)	90	6 ± 6	90	10 ± 7
DOC:TDP (moles)	90	1177 ± 926	90	1396 ± 792
TDN:TDP (moles)	90	329 ± 268	90	224 ± 178

The paired Mann-Whitney U test indicated there were not any significant differences between inflowing and outflowing stoichiometry for POC:PON, POC:PP, and PON:PP (Figure 4.2). However, DOC:TDN and DOC:TDP ratios increased significantly out of the ponds with a $p < 0.001$ (Figure 4.2). In contrast, there were significant decreases in TDN:TDP ratios out of the ponds, with a $p < 0.001$ (Figure 4.2). The RDA model did not yield significant results and is shown in Appendix 1.

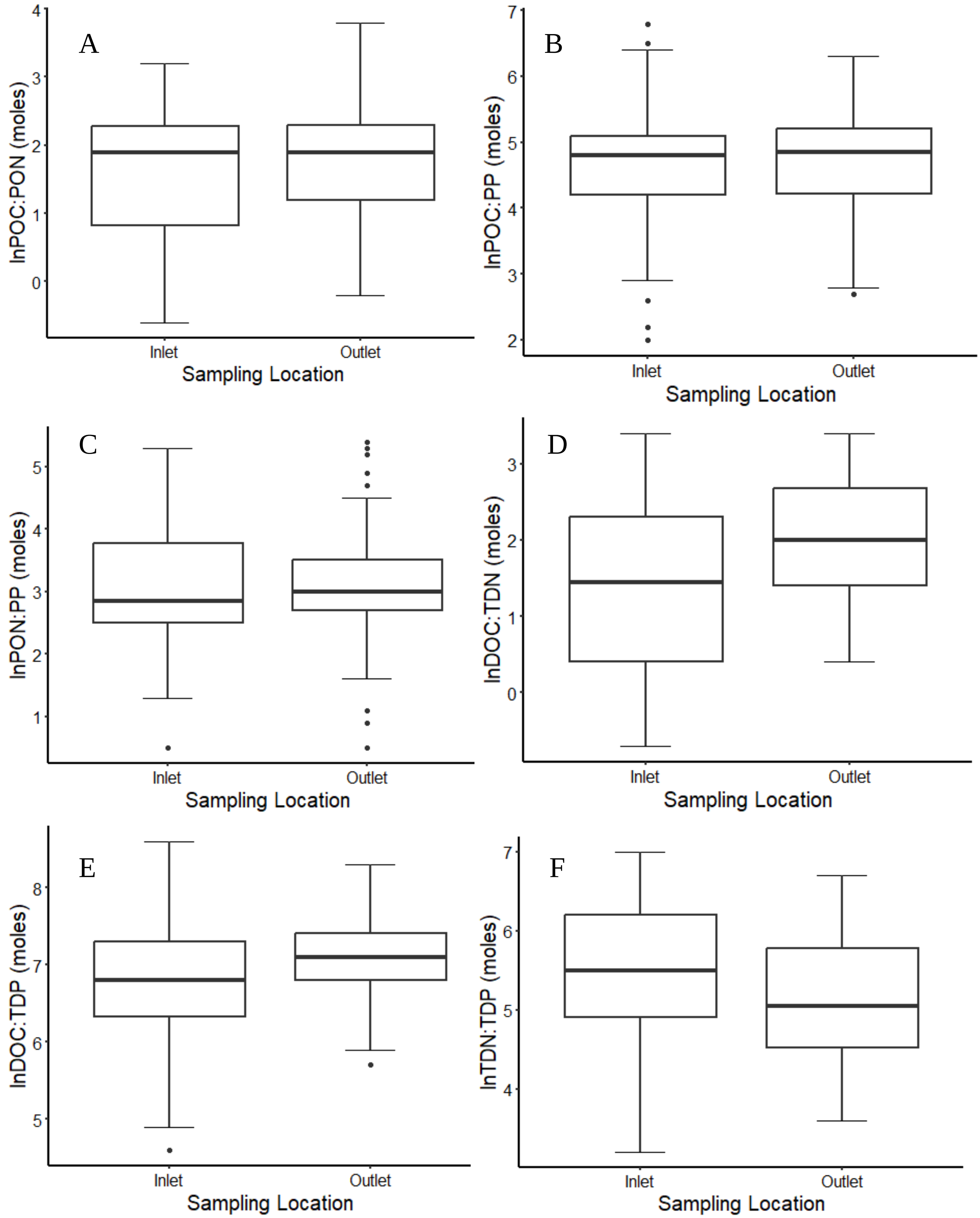


Figure 4.2: Inflowing and outflowing stoichiometric ratios for (A) POC:PON, (B) POC:PP, (C) PON:PP, (D) DOC:TDN, (E) DOC:TDP, and (F) TDN:TDP. Note: The y-axes vary.

4.5 Discussion

The inflowing and outflowing POC:PON, POC:PP, and POC:PP ratios were similar. However, we found that there was significantly higher outflowing DOC:TDN and DOC:TDP ratios compared to the inflow, but significantly lower outflowing TDN:TDP ratios. These results indicate that there is more enrichment of DOC in the ponds compared to TDN and TDP. These results also suggest more TDN is being retained than TDP. These trends may be explained by two factors. First, TDN and TDP seem to cycle through the ponds in a manner that results in more retention of dissolved N forms. Second, the higher outflowing DOC:TDN and DOC:TDP ratios suggest that there was internal production of C in the SWMPs.

The latter finding is similar to observations made by Kalev et al. (2021), who indicate that during some high flow events, the DOC pool in their study SWMPs contained mostly internally derived DOC. Williams et al. (2013) also found that dissolved organic matter (DOM) in Ontarian SWMPs had autochthonous origins, even when precipitation occurred within a week before their samples were collected. Generally, the DOM in SWMPs contains less terrestrial material and has been characterized predominantly as microbial and humic-like through excitation-emission matrix spectroscopy and parallel factor analysis modelling (McEnroe et al., 2013b; Williams et al., 2013). Microbially-derived DOM has been found in freshwater ecosystems near highly populated areas and those impacted by human activities, and this DOM composition is different than what is typically observed in less developed watersheds (Hosen et al., 2014; Lambert et al., 2017; Parr et al., 2015; Williams et al., 2016). Furthermore, human-altered DOM can impact various biogeochemical processes in freshwater ecosystems (Xenopoulos et al., 2021), and in turn this may affect how single and coupled elements are cycled.

For instance, increased amounts of carbon can result in high C:N stoichiometric ratios. The C:N ratio in combination with low light and low oxygen levels can create conditions in SWMPs that may facilitate some N transformation pathways over others (Gold et al., 2019; Valiente et al., 2022). Under these conditions, there is potential for denitrification, dissimilatory nitrate reduction to ammonium (DNRA), and anaerobic ammonium oxidation (annamox) to co-occur (Valiente et al., 2022). Denitrification transforms nitrate (NO_3^-) into N_2 (Collins et al., 2010), and DNRA occurs when microbes reduce NO_3^- to nitrite (NO_2^-) then to ammonium (Thamdrup, 2012). Anaerobic ammonium (NH_4^+) oxidation takes place when bacteria convert NH_4^+ and NO_2^- into N_2 (Van de Graaf, 1995).

In anoxic and low light conditions, Valiente et al. (2022) found that DNRA and to a lesser extent annamox occurred more so than denitrification in a saline lake. Other researchers have indicated that DNRA may occur more frequently than denitrification when there is higher amounts of C in a water body (Kelso et al., 1997). This may be problematic in SWMPs because if DNRA is the dominant transformation pathway compared to denitrification, then there could be internal releases of N, particularly when there are low NO_3^- concentrations in the system (Rahman et al., 2019). Although we did not measure the mechanisms affecting N transformations, our results show that there was less TDN in the outflow than inflow, thus indicating our study ponds are transforming or retaining N through processes potentially including denitrification, DNRA, annamox, sedimentation, or assimilation (Collins et al., 2010; Gold et al., 2019).

Conversely, there is potential for internal P releases in SWMPs that could be induced from chemical and thermal stratification creating hypoxic or anoxic conditions near the sediments (Ahmed et al., 2022; Ahmed et al., 2023; He et al., 2015; McEnroe, 2013a; Song et al., 2013). Low-oxygen conditions can stimulate redox-P releases (Søndergaard et al., 2003). The increase of P in the ponds with the concomitant retention of N, has the potential to affect N:P ratios.

Low N:P ratios can be problematic because they can create favourable conditions for cyanobacteria growth (Smith, 1983). In urban ponds, research indicates that there can be a relatively high occurrence of harmful algal blooms (HABs) that are predominately composed of the cyanobacteria *Microcystis* (de la Cruz et al., 2017; Waajen et al., 2014). Waajen et al. (2014) suggest elevated nutrient levels and stratification may create conditions suitable for HABs. If SWMPs release cyanobacteria, harmful toxins could be transported downstream and drinking water could be adversely impacted (Brooks et al., 2016).

Consequently, it is beneficial to design and maintain SWMPs in a manner that optimizes both physical and biogeochemical processes to mitigate stoichiometric imbalances. To help balance stoichiometric ratios, Gold et al. (2017) suggest constructing shallower facilities to minimize stratification or periodically mixing SWMPs to change oxygen conditions in the water column. To retain a sufficient pond volume and remove some sources of nutrients, both Gold et al. (2017) and Janke et al. (2022) recommend regular maintenance activities like dredging sediments. Floating treatment wetlands may also be beneficial since there may be increased uptake of N and P by plants without reducing the volume of the pond (Winston et al., 2013).

Pond design and maintenance considerations can affect the internal biogeochemical processes that are acting on different solutes, their various forms, and their stochiometric ratios in SWMPs. To help refine design and maintenance practices, more research is required to understand the specific mechanisms affecting the fate of C, N, and P in SWMPs. For example, we are beginning to realize that different forms of P are susceptible to internal releases due to chemical and thermal stratification in the ponds (McEnroe, 2013a; Song et al., 2013; Taguchi et al., 2020); however, we know less about the transformation and removal pathways as well as the speciation of N and C under similar conditions in these systems.

Overall, our research generally characterizes influent and effluent stoichiometric ratios in SWMPs during low flow conditions. We demonstrate that there is greater change between inflowing and outflowing stoichiometric ratios for dissolved compared to particulate forms of nutrients. Specifically, there is more enrichment of DOC compared to TDN and TDP. Based on our results, although high flow periods may contribute disproportionately to the annual nutrient loads, low flow periods are important for design and maintenance considerations as well since biogeochemical processing during these conditions may influence how single and coupled elements cycle through the ponds. Since we are relying on SWMPs to address numerous, complex performance objectives for the protection of urban ecosystems, a deeper understanding about their impact on urban biogeochemical cycling would help us design and maintain these systems as pollution sinks rather than sources.

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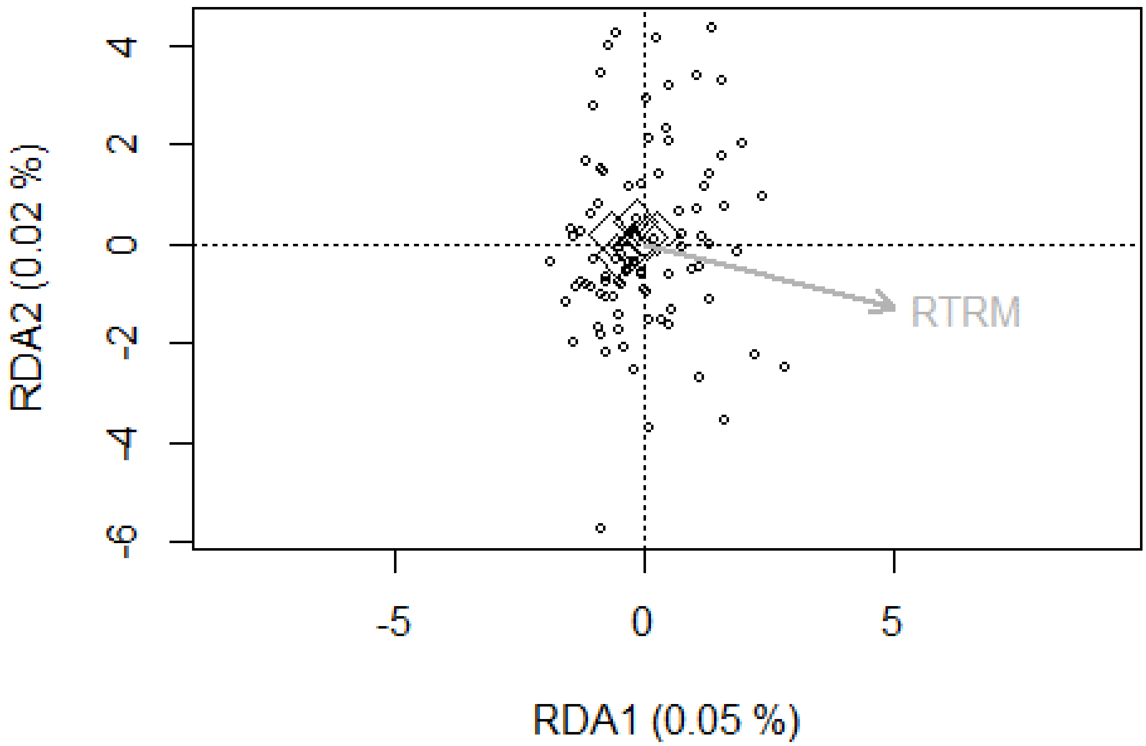
4.7 Appendix 1 – Redundancy analysis with selected hydrological and limnological factors and stoichiometric ratios out of the SWMPs.



Ordination plot visualizing the results of the RDA. Only the significant explanatory variable is shown.

Chapter 5: General Discussion

Generally, our results suggest that biogeochemical processes may affect how single and coupled elements cycle through SWMPs during low flows. This result adds to the literature that demonstrates biogeochemical activities can transform nutrient forms in SWMPs, and some processes may induce internal releases of C, N, and P (Frost et al., 2019; Gold et al., 2017; Gold et al., 2021; Song et al., 2015; Song et al., 2017; Williams et al., 2013). This result also highlights the importance of analyzing nutrient loading during low flows, since these hydrologic conditions can contribute significantly to overall loads in urban areas (Frazar et al., 2019; Janke et al., 2014), may transform and transport different dominant nutrient forms compared to high flow periods (Janke et al., 2014), and may facilitate conditions that stimulate internal loading of nutrients that were retained in SWMPs during high flows (Duan et al., 2016). Overall, SWMPs are complex systems, and when we construct these facilities, we need to consider this complexity at both the pond and sewershed level.

For example, Chapter 2 shows that sewershed characteristics influence nutrient loading into ponds, which means that more urbanized landscapes with higher drainage densities will have higher inflowing nutrient loads that SWMPs need to treat. In addition, Chapter 2 indicates that even though ponds may adhere to OMOE (2003) design guidelines for properties such as depth, volume, and L:W ratio, they can differentially affect the retention of various nutrient forms. However, this gives us the opportunity to try more novel design and maintenance activities that considers their impact on different nutrient forms and keeps biogeochemical processes in mind. For example, Gold et al. (2017) suggest regularly mixing SWMPs to reduce the occurrence of thermal stratification. This would help mitigate internal P releases from the sediments, but managers would need to carefully time this activity so that the oxygenated water would not decrease denitrification (Gold et al., 2017).

Not only can design and maintenance activities impact nutrient dynamics in SWMPs, but Chapter 3 shows that certain hydrological and limnological conditions can be influential. For example, when sewersheds are drier and when ponds are ice-free and/or thermally stratified, biogeochemical processes can influence how P is transformed in the water column. In addition, the results of Chapter 4 suggest that biogeochemical processes may impact how coupled elements cycle in SWMPs. We found higher outflowing stoichiometric ratios for DOC:TDN and DOC:TDP, which indicates an enrichment of DOC compared to TDN and TDP. Together, the findings of Chapter 3 and 4 imply we need to modify the techniques we use to monitor the water quality of SWMPs. Managers currently rely mostly on TSS measurements and assume sedimentation will remove nutrients from the water column (Ontario Ministry of the Environment [OMOE], 2003; Bradford & Gharabaghi, 2004). However, we should consider monitoring for both dissolved and particulate forms of C, N, and P as well as coupled elements to get a more accurate understanding of how SWMPs impact urban water quality in general.

For example, although DOC is not routinely monitored in SWMPs, we found that some of our study ponds acted as DOC sources. Dissolved organic carbon is a component of DOM, and research demonstrates that SWMPs and human activities can produce distinctive anthropogenic DOM (Xenopoulos et al., 2021; Williams et al., 2013; Williams et al., 2016). Consequently, there is potential for SWMPs to create new water quality management issues since they generate what Kaushal et al. (2018) describe as “chemical cocktails” (p. 283), by processing and transporting unique combinations of nutrients downstream. Furthermore, the proportion of DOC to N or P can also impact how the latter nutrients are processed in freshwater systems (Stutter et al., 2018). For example, Stutter et al. (2018) indicates when there are high organic C:N or high organic C:P stoichiometric ratios, heterotrophic microbes sequester N and P, but the opposite trend occurs when there are low organic C:N or C:P ratios (Stutter et al., 2018). If high amounts of N and P are released from SWMPs, there is potential for these nutrients to stimulate eutrophication and adversely impact water quality in surrounding natural water bodies.

In our study, we observed that the stoichiometric ratios between inflows and outflows changed for dissolved nutrients; however, we do not know yet all the mechanisms that are driving this change. Future research should explore specific mechanisms affecting the fate of C, N, and P in SWMPs. There is also more work to do to understand nutrient removal pathways and how this seasonality may impact these pathways, particularly when ponds are covered in ice. We also need to quantify the downstream effects of SWMP outflow and the cumulative impacts of using large numbers of SWMPs in highly populated areas. The latter may help identify the role SWMPs play in urban biogeochemical cycling on a local to global scale. Since SWMPs are proliferating in cities across the world, we need to ensure that these facilities are acting as nutrient sinks, not sources.

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