Evaluating the form and mobility of phosphorus in urban streambed sediment

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Phosphorus (P) enrichment remains a primary driver of eutrophication in freshwater systems, yet the processes governing its storage, transformation, and mobility in urban watersheds are not well documented. Sediment is the dominant vector for P transport in aquatic systems, and its fate is governed by interacting physical and biogeochemical processes. Once deposited, streambed sediments act as both sinks and sources of P, regulating downstream P transport during environmentally sensitive summer baseflow conditions through sediment-water dissolved P exchange. This study investigates the distribution, speciation, and mobility of sediment-associated P in a small (76 km^2), predominantly urban watershed (Laurel Creek, Ontario, Canada), with an emphasis on fine-grained streambed sediments and longitudinal variability along the river continuum. Sequential extraction was used to quantify PP fractions (NAIP, AP, OP), while the major element composition of streambed sediment (Fe, Al, Mn, Mg, Ca, Na) was measured to assess geochemical controls on PP partitioning. Phosphorus mobility was evaluated using the equilibrium phosphate concentration (EPC_0) and phosphate exchange potential (PEP) to determine the potential of stream sediments to function as sources or sinks of soluble reactive P (SRP). Results demonstrate that both PP form and mobility are strongly influenced by land use and impoundments. Total particulate phosphorus (TPP) ranged from 424 to 1220 $\mu g\ g^{-1}$, indicating substantial P storage within streambed sediments. Bioavailable PP (NAIP) was significantly enriched in agricultural headwaters ($U = 0$, $p < 0.01$) and was strongly correlated with Fe, Al, Mn, and organic matter. Downstream trends in sediment geochemistry, characterized by decreasing Fe, Al, and Mn and increasing Ca and Mg, were associated with reduced bioavailable P fractions. Similarly, higher EPC_0 values and positive PEP were observed at agricultural sites, indicating a greater potential for SRP release during baseflow. In contrast, urban sites displayed lower and more variable EPC_0 and PEP values, showing both potential source and sink behavior. Impoundments appear to play a key role in attenuating P transport in Laurel Creek, with reduced PP concentrations and lower EPC_0 observed downstream, suggesting retention of P-rich sediments within upstream reaches. Overall, sediment P dynamics in Laurel Creek watershed are controlled by interactions among land use, geochemistry, and urban impoundments. Fine sediments function as both legacy P reservoirs and regulators of SRP, varying along the river continuum. These findings highlight the importance of integrating P speciation and mobility assessments to improve understanding of in-stream P cycling and to inform management strategies aimed at reducing downstream eutrophication in urbanizing watersheds.

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List of Abbreviations

AP – Apatite Phosphorus

EPC_0 – Equilibrium Phosphate Concentration at net zero sorption

LCW – Laurel Creek Watershed

NAIP – Non-Apatite Inorganic Phosphorus

OM – Organic Matter

OP – Organic Phosphorus

P – Phosphorus

PP – Particulate Phosphorus

PEP – Phosphate Exchange Potential

TPP – Total Particulate Phosphorus

SRP – Soluble Reactive Phosphorus

WWTP – Wastewater Treatment Plant

Chapter 1
Problem statement and thesis organization

1.1 Problem statement

Anthropogenic phosphorus (P) enrichment is a primary driver of eutrophication in freshwater ecosystems globally (Schindler, 1977; Vollenweider, 1968). Excessive P loading stimulates algal and plant growth, leading to biodiversity declines, elevated water treatment costs, and human health risks (Burkholder, 2009; Hilton et al., 2006; Yan et al., 2022). In the Laurentian Great Lakes, eutrophication remains a persistent challenge despite decades of management efforts (Watson et al., 2016), with Lake Erie representing the combined effects of external P inputs from agricultural and urban sources (Michalak et al., 2013; Steffen et al., 2014; Zhou et al., 2015) and internal loading from legacy sediment-bound P (Nurnberg, 2009). Understanding P dynamics in tributary streams is therefore critical, as these systems both transport P from the landscape and regulate its form and bioavailability before delivery to downstream water bodies.

Agricultural and urban land use can alter the physical and biogeochemical processes that govern P dynamics in streams (Withers & Jarvie, 2008). These anthropogenic landscape disturbances often result in increased delivery of fine sediment, altered baseflow regimes, and modified water chemistry (Elliott et al., 2024; Walsh et al., 2005), which collectively degrade aquatic habitat and modify nutrient cycling (Meyer et al., 2005). Excessive P inputs to streams from agricultural and urban land uses are well documented (Blount et al., 2022; Ekka et al., 2006; Macrae et al., 2007; Plach et al., 2019), arising from fertilizer applications (Mainstone & Parr, 2002), wastewater treatment plant (WWTP) effluents (Vianini et al., 2026), and stormwater runoff (B. Zhou et al., 2026). As urban development continues to expand into previously forested and agricultural land, P fluxes and transformations may become increasingly complex given the substantially modified ecohydrological regimes in urbanized areas (Kaushal & Belt, 2012). Consequently, there is a growing need to understand the biogeochemical cycling of P in urban streams to inform effective watershed management (Kaushal et al., 2014).

Fine sediment is a primary driver of P transport in surface waters (House, 2003; Kronvang et al., 1997; Stone & English, 1993). In the Great Lakes basin, approximately 75% of P loading is associated with suspended sediment (Logan, 1987), with the majority bound to particles smaller than 63 μm (Stone & Saunderson, 1992). Although dissolved reactive P, referred to hereafter as soluble reactive phosphorus (SRP), is the most bioavailable P form (Biggs, 2000; Stone et al., 1995), characterization of sediment-bound P is equally vital, as this fraction can rapidly exchange with the overlying water column (House & Denison, 2002a; Withers & Jarvie, 2008). The form and mobility of particulate P (PP) are influenced by both the physical properties of the sediment (e.g., particle size) and its geochemical characteristics, including

coatings of Fe, Al, Mn, and organic matter (OM) (Evans et al., 2004; Stone & Mudroch, 1989). Ambient stream conditions including temperature, pH, and redox potential, further modulate P storage and transformation (House, 2003). Importantly, PP stored within streambeds can represent a legacy P pool that continues to contribute to downstream P loads long after external inputs have been reduced (Jarvie et al., 2005; Sharpley et al., 2013). Identifying the form and concentration of this stored P is therefore essential for accurately estimating water quality trajectories in receiving water bodies.

The forms of PP in streambed sediments can be characterized using sequential extraction procedures (Pettersson et al., 1988), which partition P into fractions of differing ecological significance (Boström & Pettersson, 1982). Non-apatite inorganic phosphorus (NAIP) represents the most bioavailable fraction and includes phosphate sorbed to metal hydroxide surfaces that can be released as SRP. Apatite phosphorus (AP) is considered biologically unavailable due to its geochemical stability (Pettersson et al., 1988). Organic phosphorus (OP) is generally considered biologically unavailable, though it may become accessible through mineralization or hydrolysis (Hupfer & Lewandowski, 2008; Golterman, 2004). Enrichments of total PP and NAIP in streambed sediments have been observed across both agricultural and urban settings (Noll et al., 2009; Stone & English, 1993; Wang & Pant, 2010; Xuan et al., 2014), reflecting the legacy of elevated P inputs from surrounding land use. However, given the hydrological and geomorphological complexity of urban stream systems, knowledge of how PP form and concentration vary along the longitudinal continuum of an urban channel remains limited.

Streambed sediment plays an important role in regulating the dissolved P concentration of the water column via sorption and desorption of SRP (House, 2003), a process that may become environmentally significant during baseflow conditions when dilution is low (Jarvie et al., 2005). Baseflow periods in summer represent an ecologically sensitive window, as elevated SRP concentrations, temperatures, and increased sunlight increase the likelihood of eutrophication (Rosemond et al., 2011). The equilibrium phosphorus concentration at net zero sorption (EPC_0) is a widely used metric for quantifying this exchange (Froelich, 1988; Simpson et al., 2021). The EPC_0 represents the SRP concentration at which adsorption and desorption are equal and has been shown to correlate with ambient stream SRP in a range of catchment types (Haggard et al., 2007; Machesky et al., 2010; McDaniel et al., 2009), making it a useful indicator of P loading potential (McDowell, 2015). Sediment can buffer diffuse P inputs from agricultural and urban runoff, temporarily attenuating P fluxes to downstream environments; however, this stored P may be remobilized under altered hydrological or geochemical conditions (Evans et al., 2004; Withers & Jarvie, 2008). Most EPC_0 research to date has focused on agricultural catchments and streams (Agudelo et al., 2011; Haggard et al., 2007; Hoffman et al., 2009; McDowell et al., 2020; Reddy et al., 1996; Simpson et al., 2021), or on larger urbanized watersheds where WWTP effluents represent the dominant P source (Ekka

et al., 2006; Jarvie et al., 2005; McDaniel et al., 2009; Roberts & Cooper, 2018; Zhang et al., 2019). As a result, P mobility in small urban catchments driven primarily by diffuse, non-point sources remain poorly understood.

Small first- and second-order channels constitute a disproportionately large fraction of total stream length in most watersheds (Wohl, 2017) and are particularly sensitive to surrounding land use and engineered modifications to channel geometry and hydrology (Fernández et al., 2014; Graf et al., 2016; Mishra et al., 2025). Despite their vulnerability, these systems play a critical role in delivering sediment and nutrients to larger receiving waters, and in supporting aquatic habitat (Ferreira et al., 2023; Verdonschot & Verdonschot, 2023). Understanding how P form and mobility vary along the urban stream continuum, from headwater sources to downstream receiving waters, is important not only for identifying spatial hotspots of P input and transformation (Kaushal et al., 2014), but also for evaluating how urban stream features such as impoundments and stormwater management infrastructure modify P dynamics at the watershed scale (Xuan et al., 2014). As urban areas continue to expand, a continuum-based understanding of P storage and transformations in small urban catchments is essential for developing targeted management strategies to protect downstream water quality.

1.2 Research objectives

The primary goal of the present research is to quantify P form and mobility of fine streambed sediment in a small urban watershed during summer baseflow conditions in Laurel Creek watershed, Ontario. Sediment P fractions (NAIP, AP, OP) were determined and compared to sediment major element composition (Fe, Al, Mg, Mn, Ca, Na and organic matter). Sediment EPC_0 was used to examine P mobility. It was hypothesized that changes to the form, concentration, and mobility of fine Laurel Creek streambed sediment reflect surrounding land use influences, sediment geochemistry, and in-stream impoundments.

The overall objectives of this research are to

1. evaluate downstream variability of PP forms and geochemical composition of fine bed sediment in an urban stream,
2. determine P-sorption characteristics of fine streambed sediment along the Laurel Creek continuum during environmentally sensitive low flow conditions; and,
3. examine the effect of sediment geochemistry, riverine impoundments, and upstream land use on P form and mobility in fine streambed sediment.

1.3 Thesis organization

Chapter 1 presents the problem statement, research objectives, and overall organization of the thesis. Chapter 2 provides a review of relevant literature. Chapter 3, *"Controls on the source and variability of phosphorus forms in bed sediment of an urban stream,"* examines particulate phosphorus forms and sediment geochemistry in fine streambed sediments of Laurel Creek. Chapter 4, *"Sediment phosphorus buffering in an urban stream during baseflow,"* focuses on phosphorus mobility along the stream continuum. Finally, Chapter 5 synthesizes the findings and presents the overall conclusions regarding particulate phosphorus form, sediment geochemistry, and phosphorus mobility in Laurel Creek.

Chapter 2
Literature review

2.1 Introduction

The following review presents literature on land-use controls on sediment-P dynamics in streams. Phosphorus as a contaminant of concern and cycling in streams is briefly discussed. Emphasis is placed on abiotic controls on P form and mobility, and how agricultural and urban land disturbances influence factors dictating P cycling, both directly and indirectly. The goal of this literature review is to identify knowledge gaps and to highlight the importance of understanding streambed P dynamics in small urban catchments.

2.2 Phosphorus in aquatic environments

Phosphorus plays a key role in the degradation of water quality in freshwater systems (Vollenweider, 1968). Excess levels of P in surface waters can lead to eutrophication, causing harmful algae blooms (HABs) and hypoxia (Heisler et al., 2008; Schindler, 1977). Notably, nutrient enrichment of aquatic systems can have direct impacts on human and ecosystem health, as well as social and economic implications by challenging water treatment operations (Burkholder, 2009). Algal blooms reduce light penetration, limiting photosynthesis for deeper-dwelling organisms (Havens, 2008), while the decay of algal biomass depletes oxygen, potentially causing fish kills and disrupting food webs (Breitburg et al., 2018; Hale et al., 2016; Yan et al., 2022). Eutrophication has been an increasing global concern in recent decades (Anderson, 2009; Gobler, 2020), with water bodies such as Lake Erie experiencing significant water quality issues in recent years (Watson et al., 2016). The eutrophication of Lake Erie is caused by both excess external P loading (Michalak et al., 2013; Steffen et al., 2014; Zhou et al., 2015) from surrounding urban and agricultural land use (Watson et al., 2016), and internal release of sediment-P from legacy sources (Nurnberg, 2009), which emphasizes the need for comprehensive understanding of P sources and transport dynamics in Lake Erie tributaries.

Phosphorus in stream water consists of particulate phosphorus (PP), associated with sediment or organic matter, or as dissolved forms (Records et al., 2016). Soluble reactive P (SRP) is a fraction of dissolved P that receives particular attention in water quality assessments because it is the most bioavailable form of P (Biggs, 2000; Muscarella et al., 2014). However, PP forms can also contribute significantly to nutrient cycling in aquatic systems due to their potential to exchange between particulate and dissolved forms (Withers & Jarvie, 2008). Notably, during stream baseflow conditions, when eutrophication risk is highest, streambed sediment plays a key role in regulating water column SRP concentrations (Biggs, 2000; Dodds, 2006; House, 2003; McDowell, 2015; Simpson et al., 2021). This abiotic regulatory function is referred to

as the sediment phosphorus (P) buffer mechanism, in which benthic sediments adsorb or release SRP depending on environmental conditions (Froelich, 1988; Haggard et al., 1999; Klotz, 1988). These environmental factors include complex abiotic and biotic processes which can be influenced by watershed characteristics such as hydrology, geology, and surrounding land-use (Ballantine et al., 2009; Evans et al., 2004; House, 2003; House & Denison, 2002a; Reddy et al., 1999; Stutter & Lumsdon, 2008; Withers & Jarvie, 2008).

2.3 Phosphorus cycling in rivers

Phosphorus cycling in streams is governed by the interaction of physical, chemical, and biological processes that collectively control P mobility (Withers & Jarvie, 2008). Particulate forms of P are strongly influenced by sediment grain size, with fine sediments exhibiting higher PP concentrations and playing a key role in P transport and storage (Owens & Walling, 2002; Stone & Droppo, 1994; Stone & English, 1993; Stone & Mudroch, 1989; Vervier et al., 2009). Sediment geochemistry further regulates PP availability, as fine particles enriched in Fe, Al, Mn, and organic matter have high P sorption capacity, whereas Ca and Mg-dominated minerals typically bind P less strongly (Evans et al., 2004; Stone & English, 1993; Stone & Mudroch, 1989). Biotic factors include P uptake by periphyton (Dodds, 2003) or microorganisms (Gächter & Meyer, 1993), as well as biologically mediated changes to redox and pH conditions (Gächter & Meyer, 1993; Jarvie et al., 2002), and altering sediment-water interactions (Carpenter & Lodge, 1986; Dodds, 1991; Mulholland et al., 1994). While biological processes can play an important role in in-stream phosphorus cycling (Withers & Jarvie, 2008), abiotic processes largely determine P form, fate, and mobility within watersheds (Froelich, 1988; Stone & Droppo, 1994; Stone & English, 1993; Svendsen et al., 1995).

High-flow events and changes in sediment sources can alter streambed sediment composition, thereby influencing P storage and mobility within streams (Emelko et al., 2016; McDowell et al., 2019). Increases in sediment transport and associated contaminates into streams are often associated with surrounding land disturbances (McDowell & Wilcock, 2004; Owens & Rutherford, 2023; Poirier et al., 2012; Russell et al., 2017; Walling et al., 2001). Changes to dissolved P concentrations in the water column are also strongly impacted by anthropogenetic land use (Ekka et al., 2006; Foy et al., 1995; Li et al., 2017; Neal et al., 2010; Roy & Bickerton, 2014; Smith et al., 1995), which can determine sediment sink/source behavior (Withers & Jarvie, 2008). Notably, streambed sediments can strongly regulate water column P concentrations during baseflow through the release of sediment-bound P to the water column (Jarvie et al., 2005; McDowell, 2015; Simpson et al., 2021). The direction of P exchange between streambed sediments and the overlying water column depends on both sediment saturation and ambient P concentrations (Simpson et al., 2021), with potential uptake occurring under high concentrations and potential release occurring when dissolved P concentrations are low. The capacity of sediments to buffer P in aquatic environments is well documented

(Froelich, 1988; McDowell, 2015; Simpson et al., 2021; Taylor & Kunishi, 1971; Withers & Jarvie, 2008); however, the influence of multiple land-use disturbances on P storage, form, and mobility along a stream continuum remains poorly understood.

2.4 Land use impacts on sediment and phosphorus dynamics

Land use change within watersheds alters the physical, chemical, and ecological functioning of stream systems. Extensive research has shown that modifications associated with agricultural and urban development can change hydrologic regimes, increase sediment fluxes, disrupt aquatic ecosystems, and degrade water quality (Elliott et al., 2024; Paul & Meyer, 2001; Russell et al., 2019; Schmidt et al., 2018; Sharpley & Tunney, 2000; Walsh et al., 2005). In many agricultural watersheds, a reduction in riparian buffers, increased soil exposure, and enhanced runoff often result in elevated sediment and nutrient loading to streams (Elliott et al., 2024; Montgomery, 2007; Skaggs et al., 1994). In contrast, urbanization increases impervious surface cover and drainage density, producing streams characterized by erosive flow regimes, reduced baseflow, and enhanced transport of sediment-bound contaminants (Meyer et al., 2005; Walsh et al., 2005). Therefore, careful consideration of watershed-scale land use influences on in-stream sediment and P dynamics is required.

Agricultural land use is a dominant driver of sediment and P loading to streams, exerting strong controls on in-stream P transport and storage (King et al., 2015; McDowell & Wilcock, 2004; Poirier et al., 2012; Schmidt et al., 2018; Sharpley & Syers, 1979), and contributing to widespread surface water quality degradation due to the intensive use of fertilizers (Mainstone & Parr, 2002; McDowell et al., 2001; Ouyang et al., 2005). Specifically, the use of P-rich fertilizers can enrich P in agricultural soils because P inputs often greatly exceed outputs (Reid & Schneider, 2019; Sharpley et al., 2013). Notably, this sediment-associated P form can be transported to receiving streams via surface runoff or subsurface drainage, and the magnitude of export is influenced by hydro-climatic conditions, tillage practices, slope, and both crop and soil types (Lam et al., 2016; Macrae et al., 2007). Consequently, streams draining agricultural watersheds often exhibit elevated concentrations of bioavailable P and reduced sediment-P buffering capacity, including higher water-column SRP concentrations and greater accumulation of inorganic particulate P in streambed sediments compared to forested landscapes (Falk et al., 2021; McDowell et al., 2002). While numerous studies have examined sediment-P dynamics in agricultural systems (Ballantine et al., 2009; Hoffman et al., 2009; Jarvie et al., 2008; Machesky et al., 2010; McDowell et al., 2019), comparatively little is known about P speciation, and mobility in urban streams, even as urban landscapes become increasingly dominant sources of contaminants to riverine and downstream aquatic environments (Kaushal et al., 2014).

Urbanization is a major land use disturbance type that can influence stream hydrology, sediment character and transport as well as P dynamics in the water column. The well-documented degradation of stream structure and function associated with urbanization, commonly referred to as the urban stream syndrome, is characterized by flashy high flows, elevated stream temperatures, increased erosion, pH, and contaminant transport, and reductions in channel complexity, dissolved oxygen, and biodiversity (Meyer et al., 2005; Paul & Meyer, 2001; Walsh et al., 2005). The changes to the physical processes within these streams can influence sediment-P dynamics (McDowell et al., 2002). For example, increased scour and fine-sediment transport can lead to increased downstream fluxes of PP transport (Kerr et al., 2011; Mihiranga et al., 2021; Pulley et al., 2016). Additionally, fine sediment and associated PP can ingress into the urban streambed armor layer during high flows (Beschta & Jackson, 1979; Karna et al., 2015), which can result in legacy P impacts such as P exchange with the water column during baseflow, or remobilization of PP during high discharge events (Evans et al., 2004; Jarvie et al., 2005; Svendsen et al., 1995). Furthermore, changes to stream chemistry of urban streams can influence P mobility in the water column. These changes include shifts in stream pH, which can change SRP concentrations through enhanced sorption to sediment metal oxides at low pH (Evans et al., 2004) or increased sorption and co-precipitation with Mg or Ca minerals at higher pH (Corman et al., 2016; House, 2003; Records et al., 2016; Strauss et al., 1997; Zhou et al., 2005). Additionally, increased stream temperatures and associated anoxia commonly observed in urban streams (Walsh et al., 2005), can lead to increased release of sediment bound P into the water column (Cai & Sayles, 1996; House & Denison, 2002a), due to the dissolution of Fe-P phases (Baldwin et al., 2002; Boström et al., 1988).

In many urban river systems, effluent from wastewater treatment plants (WWTPs) and industrial activities represents a major source of P, resulting in elevated P concentrations in receiving waters that can substantially degrade in-stream water quality (Carey & Migliaccio, 2009; Vianini et al., 2026; Zhang et al., 2015). Because of the magnitude of these inputs, research on urban P dynamics has historically focused on P fluxes in larger rivers receiving WWTP effluent (Arfania et al., 2025; Ekka et al., 2006; Roberts & Cooper, 2018; Zhang et al., 2019). However, improvements in wastewater treatment have increasingly highlighted the importance of non-point urban P loading as a key driver of in-stream P dynamics (Duan et al., 2012; Ghane et al., 2016; Macintosh et al., 2018; Schliemann et al., 2021). Diffuse P inputs in urban systems arise from multiple and often interacting sources, which complicate effective management (Kaushal & Belt, 2012; Schliemann et al., 2021). These sources may include residential fertilizer application, road runoff, leaking sewer infrastructure, stormwater ponds, and streambed sediments (Ghane et al., 2016; Kaushal & Belt, 2012; Taguchi et al., 2020; Withers & Jarvie, 2008). Additionally, because urban watersheds are characterized by highly altered surface and subsurface ecohydrological processes, a more integrated understanding of urban systems is needed (Kaushal & Belt, 2012). As urban areas continue

to expand, evaluating P dynamics along the urban continuum, beyond traditional point sources such as WWTPs, is increasingly important for understanding and managing downstream water quality impacts at the watershed scale.

Phosphorus dynamics in urban watersheds may be further influenced by reservoirs, dams, and impoundments, which modify nutrient retention and transport within fluvial networks and affect downstream water quality (Dixit et al., 2000; Maavara et al., 2015; Miranda et al., 2008; Van Cappellen & Maavara, 2016). Numerous studies have demonstrated the capacity of reservoirs to retain P, thereby influencing nutrient availability and export to downstream systems (Kõiv et al., 2011; Paul et al., 1998; Powers et al., 2014; Tiessen et al., 2011), with estimates that ~17% of global river P may be retained by river impoundments by 2030 (Maavara et al., 2015). However, higher percentages of P storage may be observed at the watershed scale. For example, a study by Donald et al. (2015) on nutrient sequestration in Canada found that twelve reservoirs in the Saskatchewan River watershed captured 92% of incoming TP before draining into Lake Winnipeg. Substantial research has focused on P retention in large reservoirs (Tang et al., 2018; Varol, 2020; Yin et al., 2022; Zhou et al., 2013), yet the role of small reservoirs and impoundments in regulating P dynamics within urban stream networks, particularly those influenced by multiple impoundments, has received far less attention (Bao et al., 2018; Xuan et al., 2014; Yin et al., 2025). Recent studies of impoundments in urban streams have demonstrated that these small structures can capture both dissolved and particulate P, as well as reduce the downstream transport of bioavailable PP (Bao et al., 2018; Xuan et al., 2014). Therefore, when evaluating P dynamics in urban streams, it is important to consider the influence of reservoirs and impoundments on the transport and fate of sediment associated P in river systems.

2.5 Particulate phosphorus and sediment geochemistry

Particulate phosphorus constitutes the dominant fraction of P (Brunet & Astin, 1998; Kronvang & Laubel, 1997; McDowell & Wilcock, 2004), and understanding its form is critical for assessing P mobility, sediment–water interactions, and downstream loading (DePinto et al., 1981; Stone & Droppo, 1994; Stone & English, 1993; Withers & Jarvie, 2008). Various operationally defined forms of particulate P can be characterized based on their relative physical, chemical, and biological (i.e. bioavailability) properties using chemical extraction schemes (Katsaounos et al., 2007; Pettersson et al., 1988; Psenner, 1984) developed based on the early work of Chang & Jackson (1957). These forms include non-apatite inorganic phosphorus (NAIP), the most bioavailable form, which includes phosphate sorbed to metal hydroxide surfaces that can be released as SRP. The degree to which this occurs in the environment depends upon several factors including temperature, competitor ions, pH and redox (DePinto et al., 1981; Emelko et al., 2016; Wang et al., 2006). In the Pettersson et al. (1988) fractionation scheme, NAIP is determined by the sum of NH_4Cl

(1.0M), BD (0.11M, 40°C) and NaOH (1.0M) leaches, that remove easily desorbable P forms, Fe-bound, and Ca and Mg metal oxide P forms, respectively. NH_4Cl extractable P is also referred to as 'labile P' in some instances (Pettersson et al., 1988) and NaOH P has been described as 'algal available P' (DePinto et al., 1981; Lottig & Stanley, 2007). Apatite phosphorus (AP), sometimes referred to as Ca-bound P, is extracted using a HCl (0.5M) leach and is considered to be biologically unavailable given its geochemical stability (Pettersson et al., 1988). Lastly, organic phosphorus (OP) is extracted using a NaOH (1.0M, 85°C) leach. Some components of organic P may become bioavailable through mineralization or hydrolysis (Hupfer & Lewandowski, 2008); however, it is generally considered to be biologically unavailable (Golterman, 2004).

Geochemical controls play a key role in determining P availability in aquatic environments (Boström et al., 1988; Stone & English, 1993). The direction and magnitude of P exchange between sediments and the water column are controlled by in-stream physical and biogeochemical conditions that mediate P sorption and desorption (Withers & Jarvie, 2008). The capacity of fine particles to adsorb P is closely linked to coatings of Fe, Mn, Al, and organic matter, with higher oxyhydroxide abundance corresponding to stronger phosphorus binding (Evans et al., 2004; Stone & Mudroch, 1989). Phosphorus binding to sediment oxyhydroxides is strongly redox sensitive, with effective sorption of negatively charged phosphate ions to Fe and Mn oxyhydroxides occurring under oxic conditions (Borch et al., 2010; Lijklema, 1993). Under anoxic conditions, the reductive dissolution of Fe phases promotes P release from sediments to the overlying water (Amirbahman et al., 2003; Boström & Pettersson, 1982), which is a key mechanism driving internal P loading in aquatic ecosystems (Boström et al., 1988; Søndergaard et al., 2003; Welch & Cooke, 2005). Anoxia may also enhance the hydrolysis of organic P, further increasing the pool of biologically available P (Golterman, 2004). Stream pH also exerts a strong control on P adsorption and desorption processes (Li et al., 2013; Wang et al., 2005; Zhou et al., 2005). Under low pH conditions, P adsorption to Fe and Al oxyhydroxides is enhanced, whereas increasing pH reduces this binding capacity and promotes P association with Ca through co-precipitation or mineral formation (Froelich, 1988; House, 2003). Generally, changes in metal oxyhydroxide availability regulate the extent to which labile P is retained on sediment coatings, with lower oxide availability resulting in diminished P sorption (Golterman, 2004). Additionally, high ionic strength and presence of organic matter can have strong influences on P sorption processes (Wang et al., 2006). High ionic strength in solution can inhibit P sorption due to presence of competitor ions such as Cl^- (Karthikeyan et al., 2004). Alternatively, increasing amounts of sediment organic matter result in greater P sorption (House & Denison, 2002b; Wang et al., 2006).

Geochemical controls stated above are dependent on in-stream conditions, which can be strongly influenced by surrounding land use. For example, intensive agriculture practices are known to cause

increased soil erosion and transport of fine sediment and clays into nearby streams either from overland flow or in tile drain effluent (Chichester & Richardson, 1992; Collins et al., 2009; Deasy et al., 2009; Tapia-Vargas et al., 2001). These fine particles may be enriched in Fe, Al, and Mn oxyhydroxides, thereby increasing P sorption and PP storage in streambed sediment (Evans et al., 2004; Stone & Mudroch, 1989). Urban-impacted streams are commonly characterized by lower dissolved oxygen, elevated pH, and reduced in-stream organic matter relative to natural systems (Meyer et al., 2005; Walsh et al., 2005; Webster et al., 1990), conditions that can influence the transformation and bioavailability of P forms. Additionally, in regions where road salt is commonly applied in the winter months, streams may have increased ionic strength due to increased loading of Na^+ and Cl^- ions (Kaushal et al., 2005), potentially reducing P sorption to urban sediments. Sediment geochemistry is also heavily impacted by urbanization, with increases to Ca, Na and Mg in urban sediment attributed to concrete weathering, vehicular traffic and emissions (Poňavič et al., 2018; Rate, 2018; Vieira et al., 2019). The enrichment of Ca in urban areas has been well documented (Bain et al., 2012; Chambers et al., 2016; Kaushal et al., 2014), and a recent study by Wu et al. (2018) determined that the precipitation of Ca with P may be an important factor governing P dynamics in urban streams. Consequently, land-use driven changes in in-stream conditions and geochemistry can substantially alter P dynamics and bioavailability in urban streams (Khan et al., 2025; Owens & Rutherford, 2023; Xuan et al., 2014). Improved understanding of urban geochemical controls on P fluxes, transformations, and storage is therefore essential for informing effective watershed management strategies.

Particulate phosphorus fractions have been widely examined in marine and lentic environments (Aminot & Andrieux, 1996; Boström et al., 1988; Purushothaman & Chakrapani, 2015) whereas comparatively fewer studies have focused on lotic systems (Lannergård et al., 2020; van der Grift et al., 2018). Within rivers, PP composition exhibits substantial spatial and temporal variability, reflecting differences in sediment sources, surrounding geology, stream order, hydrologic conditions, and downstream transformation processes (De Pinto et al., 1981; Fogal et al., 1995; Barral et al., 2012; Stone & Mudroch, 1989; Records et al., 2016). Although natural and anthropogenic controls on PP form and fate have been investigated in agricultural (Lannergård et al., 2020; Stone, 2004; Falk et al., 2021), and more recently, in fire-affected watersheds (Allin et al., 2012; Emelko et al., 2016; Watt et al., 2021), comparatively little is known about how multiple landscape disturbance types in urban watersheds influence the distribution of PP fractions in urban streambed sediments (Owens & Walling, 2002).

2.6 Phosphorus mobility

Streambed sediment can strongly influence P dynamics during baseflow conditions in streams, primarily through an abiotic (e.g. sorption and desorption) process referred to as the phosphate buffer mechanism (Froelich, 1988). Biotic processes (e.g. assimilation of P by algae) may also play an important role (Dodds,

2003; Withers & Jarvie, 2008). Abiotic sorption/desorption of P to/from sediments occurs as a rapid initial sorption (or desorption), followed by a slower 'solid-state diffusion' (Froelich, 1988). P isotherms are commonly used to evaluate the sediment P buffer (Haggard et al., 1999; Klotz, 1988; McDaniel et al., 2009; McDowell & Sharpley, 2003). These can be used to determine the equilibrium phosphate concentration at net zero sorption (EPC_0, mg P L^{-1}) (Froelich, 1988). The EPC_0 is the concentration of SRP in the water column at which sorption and desorption of P from the sediment is equal (Froelich, 1988; Taylor & Kunishi, 1971). When water column SRP concentrations are below the EPC_0, benthic sediment has the potential to release P into the water column. If EPC_0 is below the ambient SRP concentration, the streambed sediment may act as a sink for P (Froelich, 1988). Bench scale experiments are commonly used to determine the EPC_0, by combining a series of solutions with known SRP concentrations with a standard amount of sediment and mixing until equilibrium between the two can be assumed (Golterman, 2004). The data are plotted using the equation 1 below,

$$P_{ads} = \frac{[(P_{initial} - P_{final}) * 0.025L]}{wt_{sed}} \quad (1)$$

where initial SRP concentration (x-axis) is plotted against P adsorbed/desorbed (y- axis). This is referred to as a buffer diagram, which describes the ability of the sediment to buffer SRP (Froelich, 1988). The EPC_0 is identified as the x-intercept of the isotherm and the slope of the line represents the adsorption coefficient; steeper slopes are associated with a greater P buffering ability (Froelich, 1988). However, sorption experiments, and consequently EPC_0 measurements, can be influenced by solution pH, ionic strength, Ca concentration, competitor ions and temperature (Bhadha et al., 2012; Li et al., 2013; Lucci et al., 2010; Wang et al., 2006). Therefore, sorption characteristics determined under laboratory conditions only represent a proxy for in-stream P mobility and should not be considered a complete representation of environmental conditions (Barrow, 1983). Furthermore, a lack of standardized methodology for determining EPC_0 may hinder accurate representation and comparison between P sorption studies (Simpson et al., 2021).

Comparison of P mobility between studies is also hindered by the range of reported data, as the relative capacity of streambed sediment to buffer P may be similar across watersheds, despite vastly different magnitudes of P in the system (i.e. comparing watersheds with P differences of ±1 µg L^{-1} to ones with ±1000 µg L^{-1}). To account for this, Simpson et al. (2021) proposed the phosphate exchange potential (PEP) as a metric to estimate the sediment phosphorus buffer potential, which allows for a relative comparison of sediment-P buffer capacity between studies. The PEP is the difference in magnitudes between EPC_0 and SRP in the river water and is determined using the following equation:

$$PEP = log_{10}\left(\frac{EPC_0}{SRP}\right) = log_{10}(EPC_0) - log_{10}(SRP) \quad (2)$$

A negative PEP represents potential P adsorption by sediments, whereas a positive value indicates potential P release. Apart from the meta-analysis by Simpson et al. (2021) PEP has been applied only rarely to quantify sediment-water P exchange. To date, PEP has been used in agricultural catchments in the United States (Kreiling et al., 2023; Pawlowski, 2022), and Ireland (Li et al., 2023), whereas applications in urban stream systems remain scarce (Kreiling et al., 2025).

The ability of streambed sediment to buffer SRP has been studied across a wide variety of environments, land disturbances, and scales. Streambed sediment EPC_0 measurements vary considerably in the literature, from values ranging from <10 μg L^{-1} (Falk et al., 2021; Hoffman et al., 2009; McDowell, 2015) to 7000 μg L^{-1} (Ekka et al., 2006). Substantial variability has been observed for catchments influenced by similar disturbances and within the same study (Table 2.1). For example, Machesky et al. (2010) found streambed EPC_0 in an agricultural watershed in Illinios, USA to be 13 – 87 μg L^{-1}, whereas Weigelhofer (2017) measured streambed EPC_0 >1500 μg L^{-1} within agricultural headwaters in Northeastern Austria. Similarly, an EPC_0 range of 20 – 730 μg L^{-1} was found in the urban Bronx River, New York (Wang & Pant, 2010). Son et al. (2015) found that EPC_0 varied between 300 to 1200 μg L^{-1} in the Cache la Poudre River, Colorado after a wildfire. These differences emphasize the complexity of P sorption processes and may result from factors such as differing sediment sources (Stutter & Lumsdon, 2008), sediment physiochemical properties (Stone & English, 1993), and land use (Haggard et al., 2007), but may also stem from differences in EPC_0 methodology and interpretation (Simpson et al., 2021).

Most studies on EPC_0 have focused on agricultural catchments (Agudelo et al., 2011; Haggard et al., 2007; Hoffman et al., 2009; McDowell et al., 2020; McDowell & Sharpley, 2003; Reddy et al., 1996; Simpson et al., 2021) including small ditches and streams (Ezzati et al., 2020; Kröger & Moore, 2011; Weigelhofer, 2017), and large rivers (Jarvie et al., 2005; McDaniel et al., 2009; McDowell, 2015). Alternatively, research on the impacts of urban land disturbance on P mobility often involve large watersheds influenced by point-source P loading from WWTPs (Ekka et al., 2006; Jarvie et al., 2005; McDaniel et al., 2009; Roberts & Cooper, 2018; Zhang et al., 2019), as P from point sources is often the largest contributor to urban P. Consequently, P mobility in small urban catchments dominated by diffuse P sources remains poorly characterized. As urban centers continue to expand, improving our understanding of the factors controlling phosphorus exchange in these systems is critical for protecting in-stream processes, downstream water quality, and aquatic habitat.

Table 2.1- EPC_0 and SRP concentrations ($\mu g\ L^{-1}$) for different riverbed sediments across a variety of landscapes and land use.

Authors	Location	Land use/Impacts	Site/ River	EPC_0	SRP	Sediment P buffering
Hoffman et al., 2009	Wisconsin, USA	Agricultural	Dorn Creek	6.2 - 710	80	Source
Arfania et al., 2025	Iran	Urban	Shahar Chai	230	250	Sink
Arfania et al., 2025	Iran	Agricultural - Urban	Lake Urmia watershed	360 - 700	130 - 320	Source
Reddy et al., 1996	Florida, USA	Dairy farms/pasture	Otter Creek	120 - 150	590 - 1900	Sink
Jarvie et al., 2005	SW, UK	Agricultural/pasture/sewage	Avon	2 - 230	3 - 573	Sink
Wang and Pant, 2015	New York, USA	Urban, WWTP	Bronx River	20 - 730		
Falk et al., 2021	Ontario, Canada	Agricultural	Big Creek	5	71	Sink
Zhang et al., 2019	Eastern China	Urban	Shiwuli River	325	1030	Sink
Zhang et al., 2019	Eastern China	Rural	Hangbu River	143	18	Source
Agudelo et al., 2011	Kansas, USA	Agricultural	Upper West Emma Creek	125	140	Sink
Machesky et al., 2010	Illinois, USA	Agricultural	Spoon River	13 - 87	23 - 33	Source
McDaniel et al., 2010	Illinois, USA	WWTP	Vermilion watershed (SF)	251 - 347	238 - 1670	Sink
McDaniel et al., 2010	Illinois, USA	Agricultural	Emarras watershed (BLS)	56	51	Source
Haggard et al., 2007	Arkansas, USA	Urban	Ozark streams (various)	100	38	Source
Haggard et al., 2007	Arkansas, USA	Pasture	Ozark streams (various)	125	36	Source

Chapter 3
Controls on the source and variability of phosphorus forms in bed sediment of an urban stream

3.1 Overview

The accumulation of sediment-associated phosphorus (P) in streambeds contributes to legacy P effects and can exert long-term controls on downstream water quality and aquatic ecosystem function. Land use can influence the source, transport, and fate of P in watersheds. While agricultural impacts on water quality in surface waters are widely reported, much less is known about the fate and form of particulate phosphorus (PP) in urban impacted streams, particularly that which is stored in stream bed sediment. This study examines the spatial distribution of particulate P forms and geochemical composition of fine streambed sediment during environmentally sensitive low flow conditions in an urban impacted stream in southern Ontario. Study sites were selected to examine the effects of land use and stream impoundments on the spatial distribution of PP form and geochemical composition of fine streambed sediment. Particulate P was fractionated using sequential extraction into three operationally defined forms (NAIP, AP, & OP). Results show form and concentration of PP reflect watershed-scale land use gradients with bioavailable PP (NAIP) up to 7 times greater at agricultural sites compared to urban sites. Total particulate phosphorus (TPP) concentrations ranged from 424 to 1220 $\mu g\ g^{-1}$ in Laurel Creek sediment, demonstrating considerable streambed P storage. Bioavailable PP (NAIP) and TPP were significantly greater ($U = 0$, $p < 0.01$) at agriculture headwater sites compared to urban downstream sites. Enrichment of NAIP in fine streambed sediment was lowest within highly urban tributaries (average enrichment of 37%) of Laurel Creek, and highest at the agricultural sites (average enrichment of 58%). Major elements (i.e. Fe, Al, Mn, Mg, Ca, Na) showed increasing (Mg, Ca, Na) and decreasing (Fe, Al, Mn) downstream trends and significant differences between land use types. Concentrations of NAIP were highly correlated with Al, Mn, Fe and organic matter concentrations. Impoundments attenuate P transport from the headwaters into the urban sections of the watershed. TPP and NAIP concentrations were greater at sites upstream of impoundments compared to those downstream. Overall, streambed PP patterns were correlated with sediment geochemistry, indicating watershed-scale landscape disturbances can control PP form in urban streams.

3.2 Introduction

Cultural eutrophication is driven primarily by phosphorus (P) enrichment in surface waters due to anthropogenic landscape disturbances (Schindler, 1974). In rivers, this may cause excessive algae and plant growth, leading to economic and ecological concerns and decreasing biodiversity (Hilton et al., 2006;

Mainstone & Parr, 2002). Excess P in rivers can propagate downstream to receiving water bodies causing disruptions to tourism and fishing industries, increasing costs of drinking water treatment, and human health concerns (Burkholder, 2009; Hilton et al., 2006; Yan et al., 2022). Despite improvements to understanding and management practices to control excess P inputs (Schindler, 2006; Smith & Schindler, 2009), cultural eutrophication remains a global problem (Glibert & Burford, 2017; Watson et al., 2016; Wurtsbaugh et al., 2019), in part due to "legacy P" stored within the watershed (Kleinman et al., 2011; Sharpley et al., 2013).

Streambed sediments represent a major reservoir of legacy P in fluvial environments, where particulate phosphorus (PP) accumulates, transforms, and exchanges with the overlying water column (Sharpley et al., 2013; Withers & Jarvie, 2008). Because much of watershed-scale P transport is sediment-associated (Hatch et al., 2001; Kronvang et al., 1997; Uusitalo et al., 2000; Walling et al., 1997), the storage and remobilization of PP exert strong control over downstream P fluxes (Kronvang et al., 1997; Owens & Walling, 2002). Importantly, PP can be characterized by multiple geochemically distinct fractions, including non-apatite inorganic P (NAIP), apatite P (AP), and organic P (OP), that differ in stability and bioavailability (Katsaounos et al., 2007; Pettersson et al., 1988). The distribution of these fractions governs sediment-water P interactions and determines the potential for internal P loading under changing environmental conditions, making their characterization critical for assessing P dynamics to inform effective management strategies (DePinto et al., 1981; Stone & Droppo, 1994; Stone & English, 1993; Withers & Jarvie, 2008).

The abiotic control of sediment plays a key role in P dynamics within a watershed (House, 2003), as the form and bioavailability of PP are dependent on environmental conditions, the physical and biogeochemical properties of sediment, and ambient water quality (Golterman, 2004; Records et al., 2016). Fine sediments (<63 μm) are particularly important in in-stream P cycling (Stone & English, 1993; Zhang & Huang, 2007), due to their high surface area and adsorption capacity (Evans et al., 2004; Stone & Mudroch, 1989). Additionally, bioavailable forms of inorganic PP are often associated with Fe, Al, Mn and organic matter coatings on fine particles (Emelko et al., 2016; Evans et al., 2004; Stone, 2004; Stone & Droppo, 1994; Watt et al., 2021), where binding strength and stability are influenced by geochemical factors such as redox-driven dissolution of Fe/Mn oxides (Ding et al., 2016; Records et al., 2016), pH-dependent sorption to Ca-bearing minerals (House & Donaldson, 1986; Wang et al., 2005), and presence of competitor ions and organic matter (Li et al., 2013; Wang et al., 2007). Consequently, the distribution of major sediment elements (e.g., Fe, Al, Mn, Ca, Mg) provides key insight into PP partitioning and potential reactivity within streambed sediments.

Land use exerts a primary control on sediment and geochemical factors and can in turn have a strong influence on P dynamics in fluvial systems. In agricultural watersheds, long-term fertilizer inputs have

produced substantial legacy P stores in soils and sediments (Sharpley et al., 2013; Falk et al., 2021; McDowell et al., 2002) which can be mobilized by overland flow and tile drain effluent during precipitation events that can contribute high sediment-P loading in agricultural streams (Elliott et al., 2024; Macrae et al., 2007; Montgomery, 2007). Consequently, agricultural land use can contribute to elevated concentrations of bioavailable PP fractions within streambed sediment and increased water-column SRP compared to forested watersheds (Falk et al., 2021; McDowell et al., 2002). Accordingly, research on streambed PP fractions and storage has been conducted extensively in agricultural systems (Audette et al., 2018; Falk et al., 2021; Kerr et al., 2011; Lannergård et al., 2020; Noll et al., 2009; Stone & English, 1993). However, there is a paucity of studies examining PP dynamics in urban streambeds (Barral et al., 2012; Lin et al., 2009; Owens & Walling, 2002), despite the rapid expansion of urban land use globally.

Urbanization alters the ecohydrological and biogeochemical processes that regulate sediment-P interactions. Increased impervious surface cover enhances hydrologic flashiness, sediment mobilization, and channel instability, while engineered drainage networks modify sediment transport and storage pathways (Meyer et al., 2005; Paul & Meyer, 2001; Walsh et al., 2005). These disturbances can promote downstream export of particulate P while simultaneously facilitating the accumulation of fine, P-enriched material within streambed sediments that may act as legacy P reservoirs capable of exchanging phosphorus with the overlying water column under baseflow conditions (Evans et al., 2004; Jarvie et al., 2005; Kerr et al., 2011). Understanding how P is stored and transformed along the river continuum is essential for predicting downstream impacts (Mainstone & Parr, 2002). Urban stream networks commonly include impoundments that disrupt natural sediment transport, creating zones of enhanced deposition and biogeochemical processing (Powers et al., 2014; Tiessen et al., 2011). These features can alter PP composition and retention, generating spatial differences in P forms (Xuan et al., 2014), and may act as critical zones of P accumulation and transformation. However, the influence of impoundments on longitudinal patterns in PP speciation and their relationship to sediment geochemistry in urban systems remains poorly understood (Bao et al., 2018; Xuan et al., 2014).

Small headwater streams are particularly important for stream discharge and represent most of the channel length within a watershed (Wohl, 2017). These streams are strongly influenced by surrounding land use and subject to direct anthropogenic modification, making them highly vulnerable to urban disturbances (Fernández et al., 2014; Mishra et al., 2025; Walsh et al., 2005). Yet these systems play a critical role in regulating sediment and nutrient transport and in shaping downstream water quality. Despite their importance, P dynamics in small urban streams remain poorly documented. In many urban river systems, effluent from wastewater treatment plants (WWTPs) and industrial activities has historically represented a dominant phosphorus (P) source, resulting in elevated in-stream concentrations and

substantial water quality degradation (Carey & Migliaccio, 2009; Zhang et al., 2015; Vianini et al., 2026). Accordingly, research on urban phosphorus dynamics has focused primarily on larger rivers receiving WWTP effluent (Arfania et al., 2025; Ekka et al., 2006; Roberts & Cooper, 2018; Zhang et al., 2019). However, improvements in wastewater treatment have increased the relative importance of non-point urban phosphorus loading (Duan et al., 2012; Ghane et al., 2016; Macintosh et al., 2018; Schliemann et al., 2021), arising from multiple interacting sources including residential fertilizer application, road runoff, leaking sewer infrastructure, stormwater ponds, and streambed sediments (Kaushal & Belt, 2012; Taguchi et al., 2020; Withers & Jarvie, 2008). Because existing urban research has largely focused on large, point-source influenced watersheds, the processes governing streambed PP form, geochemical partitioning, and potential mobility in small urban catchments dominated by diffuse sources remain poorly resolved.

As urbanization of watersheds continue, improved characterization of P storage, transport, and transformation along the urban continuum, from source areas to downstream receiving waters, is needed to inform effective management, as interpretation of larger-scale watershed responses depends on resolving processes operating at smaller spatial scales (Kaushal & Belt, 2012). The present research addresses this gap by examining the spatial distribution of PP forms and their relationships with the geochemical properties of fine streambed sediments in a small, predominantly urban watershed in southern Ontario. The geochemical composition and P forms of fine sediment that ingresses and accumulates within streambeds can reflect stable upstream contributions of particulate matter over time (Lannergård et al., (2020), making streambed sediment a useful integrated proxy of catchment-wide inputs. Accordingly, analysis of sediment-associated P forms in fine streambed sediment can be used to evaluate the cumulative influence of land use on sediment geochemical composition in urban and agricultural streams (Owens & Walling, 2002; Van der Perk et al., 2007). The following two hypotheses are tested in this study.

H_1: Longitudinal variation in PP form and concentration in streambed sediments reflects spatial changes in land use and the presence of impoundments along the river continuum, and

H_2: Concentrations of bioavailable PP (NAIP) are controlled by key physical and geochemical properties of fine streambed sediment, including grain size, metal oxide content, and organic matter, that can vary with land use and river impoundments.

Specific objectives of this research are to

1. quantify downstream variability in PP forms and sediment geochemical composition in an urban stream.
2. evaluate the influence of land use and riverine impoundments on the spatial distribution of PP forms along the river continuum.

3. examine relationships between PP forms and the physical and geochemical properties of fine streambed sediments.

3.3 Methods

3.3.1 Study site

The Laurel Creek watershed (LCW) drains an area of 76.1km^2 within the greater Grand River watershed, in Southern Ontario, Canada (Figure 3.1). The watershed is highly modified by human activities, including agriculture and urbanization. The headwaters of LCW consist primarily of agricultural and rural land use (>60%), with remnant woodlands and wetlands, some of which are classified as Environmentally Sensitive Landscapes (ESLs) (Dougan & Associates, 2016). The ESLs contain critical habitat for native species and serve important ecological/hydrological functions in the watershed, including drinking water source protection and flood control (Dougan & Associates, 2016). The downstream reaches of LCW are dominated by urban land use (>60%), draining extensive residential and industrial areas of the City of Waterloo. The river channel within the city is highly modified, with impoundments, erosion control measures, channelization, culverts, and stormwater drainage systems. The LCW also has three reservoirs (Laurel Creek Reservoir, Columbia Lake, and Silver Lake), all of which are located within the city limits of Waterloo, serving both practical (flood control) and aesthetic purposes.

Laurel Creek flows through a carbonate-rich landscape, as the bedrock geology of the surrounding region is primarily limestone and dolostones. Surficial geology of Laurel Creek watershed is comprised primarily of Quaternary glacial fluvial depositional features, including the Waterloo Moraine which extends in the northwest-southeast direction and is characterized by hummocky morphology and till ridges (Karrow, 1993). The Moraine and associated surficial materials are comprised of a complex mix of stratified ice-contact deposits and various tills (Frind et al., 2014; Ontario Ministry of Northern Development and Mines, 2010). The channel elevation ranges from 395 to 298 msl, with a slope of 3.7 m km^{-1} in the main channel.

Daily average temperature for the area between May and September ranges from 12.6^{o}C (May) to 20.2^{o}C (July), and monthly average precipitation is between ~67 mm (August) and ~96 mm (July) during this time (Environment Canada, 2024a). Discharge at the Environment Canada 02GA024 monitoring station within Laurel Creek ranged from 0.1 m^3/s to 34.1 m^3/s between May and September 2024 (Environment Canada, 2024b).

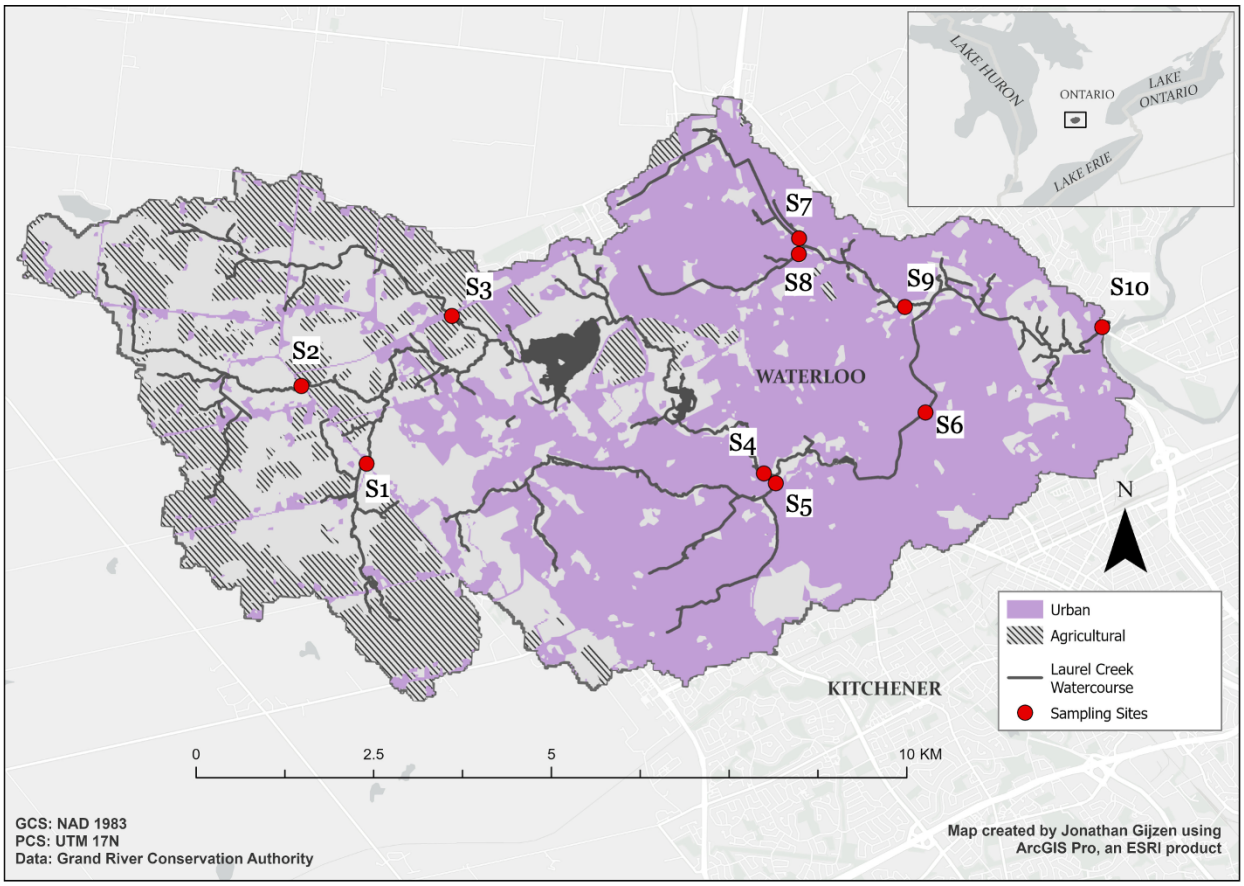

Figure 3.1 - Study site locations and land use in Laurel Creek watershed.

3.3.2 Site selection

Sediment and water samples were collected at ten study sites within the Laurel Creek watershed (Figure 3.1). Study sites were located within every major tributary in the watershed, and the characteristics of bed sediment at these sites reflected the influence of varying degrees and types of land disturbance (Table 3.1). Four sites were located within the main channel (S2, S4, S6, & S10) to examine cumulative downstream effects of landscape disturbance along the river continuum. Headwater sites S1 (Monastery Creek) and S2 (Upper Laurel) are located on the municipal boundary and characterized by relatively small natural channels with stable banks, muddy substrate, and abundant riparian vegetation. Sites S1 and S2 are located within wetland areas, and the upstream watershed areas are impacted by agricultural activities. Site S3 (Beaver Creek) has the highest percentage of upstream agricultural land use (~ 74%) and is entrenched with steep banks. Site S4 (Mid-Laurel) is downstream of both Laurel Creek and Columbia Lake reservoirs and upstream of the confluence of Clair and Laurel Creek. Site S5 (Clair Creek) is located upstream from its confluence with Laurel Creek and drains a primarily urban - residential area (~72%). Both S4 and S5 have incised channels with gravel beds and stream banks are stabilized with riparian vegetation. Site S6 (Mid-

Laurel) is a main channel site located in a highly urbanized section of the watershed, just downstream of the Environment Canada's gauging station (Water Survey of Canada #02GA024). The streambed in this deeply incised section of the stream consists primarily of gravel. The banks of the stream are heavily armored, and storm sewers flowing directly into the stream were observed. Site S7 (Upper Forwell) drains a primarily urban – industrial area (~86% urban land-use upstream). Site S8 (Cedar Creek) has the highest percentage of upstream urban land use (~91%), draining a predominately residential area and located within Cedar Creek shortly before its confluence with Forwell Creek. Both sites S7 and S8 have steep banks with a sandy – gravel bed substrates with some riparian vegetation. Site S9 (Forwell Creek) is in a ravine with a vegetated floodplain and located immediately upstream of the Forwell Creek inflow to Laurel Creek. In this wide and shallow stream reach the stream bed consisting of sand and gravel. Site S10 (Lower Laurel) is the most downstream site, located directly upstream of the mouth of Laurel Creek. This site is located within a highly urban area directly downstream a busy intersection, overpass and storm drain. The streambed is gravel, and the streambanks are very steep and heavily armored to prevent erosion.

Table 3.1 – Study site classifications and descriptions. Photographs of the study site are provided in Appendix A.

Site ID	Creek	Land use classification	Description/Rationale for study site selection	Drainage area above study site (km^2)
S1	Monastery Creek	Rural - Agricultural	Small, agriculturally dominated headwater tributaries with wetlands and natural vegetation	7.2
S2	Upper Laurel Creek	Rural – Agricultural / Wetland	Most natural site. Used as pristine/reference site for previous LCW water quality studies. Agricultural land draining into a wetland area.	7.7
S3	Beaver Creek	Rural - Agricultural	Highest percentage of agricultural land use, ~1km upstream Laurel Creek Reservoir. Surrounded by row-crop agriculture.	6.7
S4	Laurel above Clair Creek	Mixed - Urban	Urban site in the main channel, close to the University of Waterloo. About 2 km downstream of Columbia Lake.	37.0
S5	Clair Creek	Urban – Residential	Largest Laurel Creek tributary (based on watershed size), draining predominately urban residential land.	13.4
S6	Lower Laurel Creek	Urban – Residential	Main channel below Environment Canada gauging station, highly urbanized land use.	57.8
S7	Upper Forwell	Urban – Industrial	Highly industrialized urban land use, next to highway 85.	4.0
S8	Cedar Creek	Urban – Residential	Highest percentage of urban land use, dominated by residential land.	3.1
S9	Forwell Creek	Urban – Industrial / Residential	Urban tributary with industrial and residential influences.	8.8
S10	Laurel Creek	Urban	Entire watershed, representative of cumulative effects from all upstream sites.	76.1

3.3.3 Sample collection

Streambed sediment was collected during low flow conditions on May 9th, 2024, using the method of Lambert & Walling (1988). Sampling was conducted during low flow conditions, as these periods represent a critical window for stream eutrophication risk (Dodds, 2006) during which streambed sediments exert a particularly strong influence on water column dissolved phosphorus concentrations through sediment-water phosphorus buffering (McDowell, 2015). A plastic cylinder was randomly inserted into the streambed and then fine sediment was resuspended using a plastic rod. The sediment-water slurry was then pumped into a clean 20L bucket using a bilge pump (Figure 3.2). This process was repeated in multiple locations at the sample site to ensure a representative sediment sample was collected for each stream reach. The goal of this sampling method was to sample fine (<63 µm) sediment as this fraction disproportionately impacts sediment-P sorption and transport compared to coarse fractions (Stone & English, 1993; Stone & Mudroch, 1989). The buckets were sealed, and solids settled undisturbed for two days before the overlying water was decanted. The remaining sediment was transferred into plastic containers, refrigerated, and transported to Act Labs in Burlington, ON for geochemical analysis and particulate phosphorus speciation.



Figure 3.2 - Bilge pump used to transfer suspended fine sediment into 20L bucket.

3.3.4 Laboratory analysis

Particulate phosphorus fractionation, geochemical composition and particle size distribution of stream bed sediment was conducted at an accredited commercial laboratory (Act Labs, Burlington, ON). Particulate P forms were determined as five chemically defined fractions in order of decreasing bioavailability using a sequential extraction scheme outlined in Pettersson et al. (1988). A schematic of the sequential extraction procedure is shown in appendix A. The following P forms where extracted: Loosely sorbed P (NH_4ClRP), reductant soluble reactive P (BD-RP), reactive P bound to metal oxides (NaOH-RP), apatite and calcium bound P (HCL-RP) and unreactive organic P (refractory P) (Pettersson et al., 1988; Stone & English, 1993). These fractions are further grouped into three main fractions of particulate P: i) Non-apatite inorganic P (NAIP) is the sum of NH_4CL-RP, BD-RP and NaOH-RP and is the most bioavailable form of P; ii) Apatite P (AP) is HCL-RP; iii) Organic P (OP) is refractory P and is the least bioavailable. Total particulate phosphorus (TPP) is determined as the sum of the previous three fractions.

Major element geochemistry (Al, Fe, Mn, Mg, Ca, Na and K) was determined by acid digestion and measured using AR-MS and results are reported as percent dry weight. Sediment particle size distributions, median diameter (D_{50}) and specific surface area (SSA) were determined using a Malvern Mastersizer 2000. Organic matter (OM) content in sampled sediment was estimated by loss on ignition. Approximately 5 g (dry weight) of sediment was weighed out into a crucible and placed in a furnace at 550°C for 24 hours. Samples were weighed again after ignition and subtracted from pre-ignition weight to determine OM loss. Comparison to the pre-ignition value allows for the calculation of OM% in each sample. Loss on ignition was performed twice for each sample to ensure accurate estimation of OM.

3.3.5 Statistical analysis

Non-parametric statistical analyses were conducted as the P and geochemical data did not meet assumptions of normality. Differences in P form and sediment geochemistry between sites were determined using the non-parametric Mann-Whitney Rank Sums test. Correlation coefficients from the non-parametric Spearman Rank Correlation test were used to examine relationships between sediment PP forms and sediment geochemical properties. A Principal Component Analysis (PCA) was used to examine differences in PP forms and sediment geochemistry between sites. The PCA was used to explore relationships between variables and categorize study sites by land use. Both the Spearman Rank Correlation test and PCA were conducted using R 4.4.2.

3.4 Results

3.4.1 Spatial variation of particulate phosphorus forms in riverbed sediment

The spatial variability of PP forms in bed sediment of Laurel Creek is presented in Figure 3.3. The concentration of total particulate phosphorus (TPP) ranged from 424 to 1220 µg g^{-1}. The lowest and highest TPP concentrations occurred at S5 and S1, respectively. The most bioavailable particulate P form, NAIP ranged from 104 to 738 µg g^{-1}. NAIP was the dominate PP fraction for sites S1, S2, S3, and S10, comprising between 50 – 64 % of the TPP at those sites. The AP fraction ranged from 253 to 382 µg g^{-1}, the lowest and highest values occurring at S2 and S4 respectively. The AP fraction dominated sites S4 – S9, accounting for 45 – 64% of the TPP for those sites. The smallest fraction was OP, ranging between 49 - 186 µg g^{-1} across the watershed. The lowest and highest OP concentrations were observed at S5 and S1, respectively. The proportion of OP was relatively consistent at the study sites, varying between 10 – 15% of the TPP.

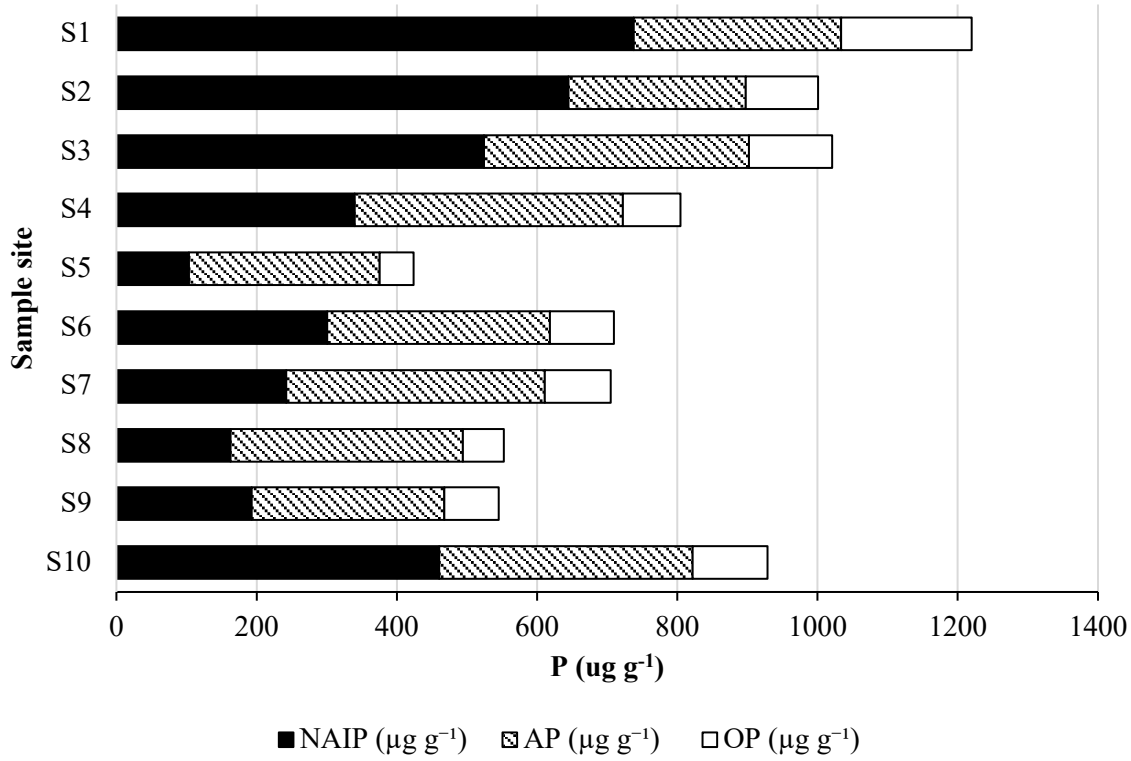

Figure 3.3 - Concentration of particulate phosphorus forms (µg g^{-1}) in riverbed sediment at study sites in the Laurel Creek watershed (n =1).

To evaluate longitudinal trends in particulate P form across the watershed continuum, the PP fractionation data were standardized. Scaled data to a mean equal to 0 and standard deviation equal to 1 are presented in Figure 3.4. The fractional composition of particulate P in riverbed sediment varied as a function

of land use; the upstream agricultural sites (S1 – S3) had considerably higher NAIP, OP and TPP concentrations than urban downstream urban sites (S4 – S9) (Figure 3.4). The data show a general downstream decrease of NAIP and TPP, but no longitudinal trend was observed for AP (Figure 3.4). The TPP values were significantly higher ($U = 0$, $p < 0.01$) at the upstream agricultural sites than at urban sites. Both NAIP and OP particulate phosphorus fractions were significantly higher at agricultural sites ($U = 0$, $p < 0.01$, $U = 1$, $p < 0.05$, respectively) when compared to the downstream urban sites. There was no significant difference in AP between agricultural and urban sites.

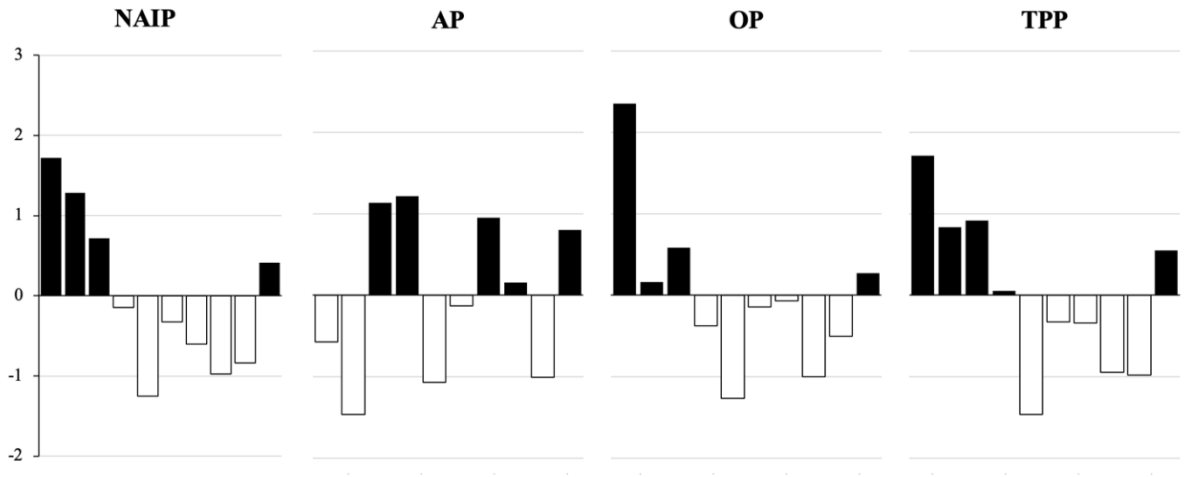

Figure 3.4 - Standardized (mean = 0, standard deviation = 1) comparison of particulate phosphorus forms in riverbed sediments at study sites S1-S10 (left to right) in the Laurel Creek watershed.

3.4.2 Spatial variation of geochemical and physical properties of riverbed sediment

The geochemical composition of riverbed sediment in Laurel Creek is presented in Table 3.2. To examine trends in major elements along the river continuum, the data were standardized (scaled data to a mean equal to 0 and standard deviation equal to 1) and presented in Figure 3.5. The data show a decreasing trend for Al, Mn, Fe, P_2O_5 and OM while concentrations of Mg, Ca, and Na tended to increase downstream. Changes in Al, Mn, Fe, P_2O_5 and OM were consistent with observed trends of NAIP among sites. Site S1 has the highest concentration of Al, Mn, Fe, P_2O_5, and K, whereas S5 has the lowest concentration of Al, Mn, Fe, OM, P_2O_5 and K. Site S1 also had the highest concentrations of NAIP, OP and TPP, whereas S5 had the lowest concentrations.

Table 3.2 - Major element composition (%) of riverbed sediment in the Laurel Creek watershed (n = 1).

	Mg	Al	Ca	Mn	Fe	P_2O_5	Na	K	LOI
S1	1.32	1.77	5.63	0.31	3.59	0.33	0.04	0.32	14.22
S2	0.59	0.93	2.45	0.19	2.32	0.28	0.03	0.12	24.11
S3	1.45	0.95	5.41	0.13	1.84	0.27	0.04	0.15	17.67
S4	2.08	0.64	7.49	0.08	1.65	0.22	0.06	0.13	9.79
S5	1.94	0.29	7.97	0.03	0.96	0.09	0.04	0.07	3.76
S6	2.61	0.71	9.62	0.07	2.17	0.21	0.08	0.15	11.55
S7	3.20	0.65	9.13	0.04	1.64	0.20	0.09	0.12	8.08
S8	3.34	0.61	10.8	0.04	1.40	0.14	0.05	0.13	5.33
S9	3.05	0.57	9.24	0.03	1.40	0.14	0.09	0.10	6.23
S10	2.76	0.88	9.90	0.05	1.91	0.24	0.08	0.16	10.98
Mean	2.23	0.80	7.76	0.10	1.89	0.21	0.06	0.15	11.17
SD	0.91	0.39	2.58	0.09	0.72	0.07	0.02	0.07	6.18

Differences in geochemical composition of bed sediment as a function of land use were observed. Agricultural sites had significantly higher concentrations of Al, Mn, Fe, P_2O_5, and OM ($U = 0$, $p < 0.01$, $U = 0$, $p < 0.01$, $U = 2$, $p < 0.05$, $U = 0$, $p < 0.01$, and $U = 0$, $p < 0.01$, respectively), whereas urban sites were significantly enriched in Mg, Ca, and Na ($U = 0$, $p < 0.01$, $U = 0$, $p < 0.01$, and $U = 1$, $p < 0.05$, respectively).

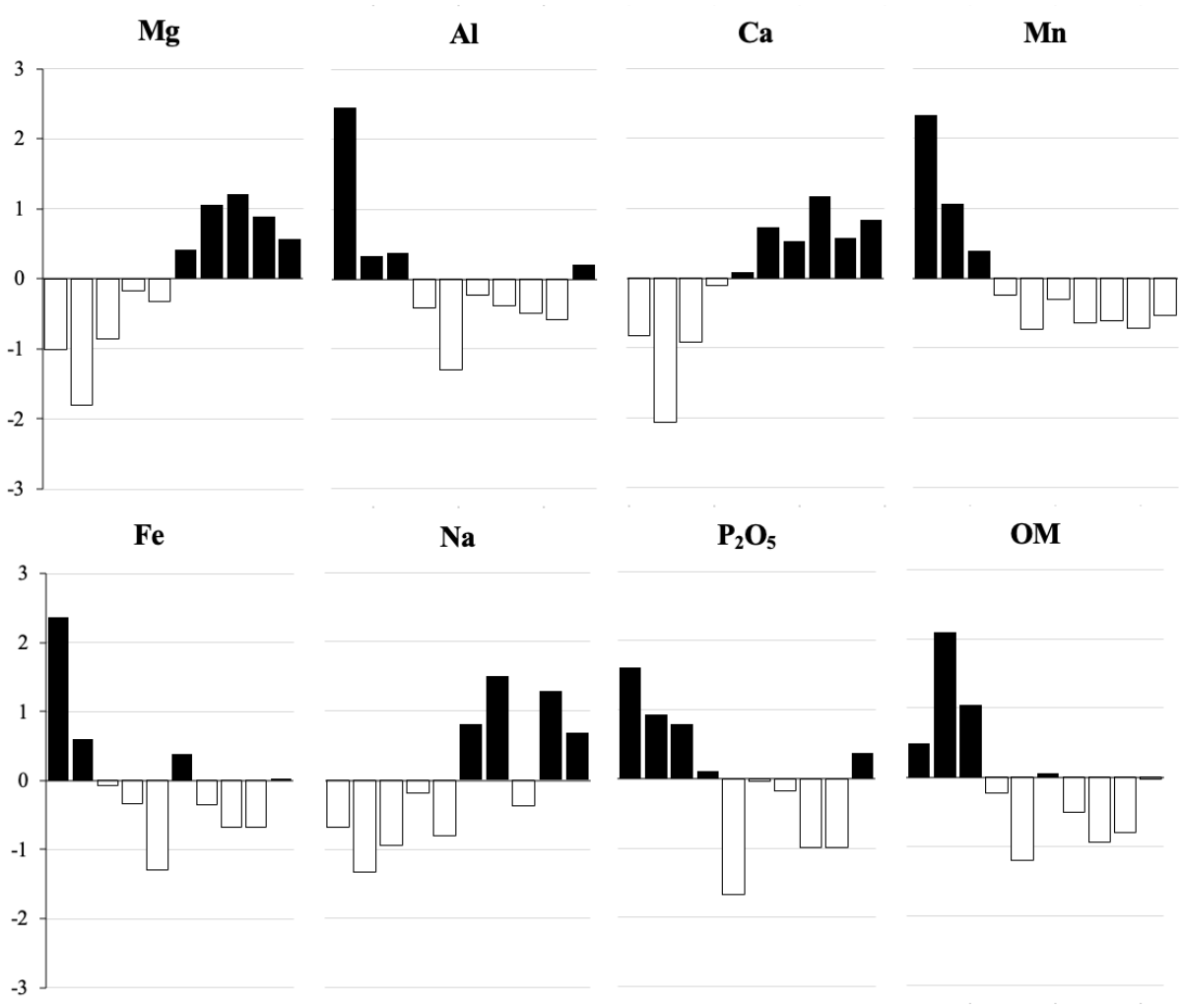

Figure 3.5 - Standardized (mean = 0, standard deviation = 1) comparison of major element composition in riverbed sediments (n = 1) at study sites S1-S10 (left to right) in the Laurel Creek watershed.

The particle size distribution of fine riverbed sediment in Laurel Creek is presented in Figure 3.6 and Table 3.3, respectively. These data show that particle size distributions of fine riverbed sediment were similar at nearly all sites, apart from site S5 which was slightly coarser (Figure 3.6). This is not surprising given the targeted sampling method used for the collection of fine streambed sediment. Additionally, the composite samples were sieved, and larger size fractions were removed. The average D_{10} of the sieved sediment was 1.74 µm, with particle size ranging from 1.35 µm to 2.30 µm. The average D_{50} was 15.68 µm with a range of 10.95 µm to 27.18 µm. The average D_{90} was 65.69 µm, ranging from 50.49 µm to 106.82 µm. The average specific surface area (SSA) of the sieved sediment was 1.29 µm, ranging from 1.04 µm to 1.55 µm. There were no significant differences in particle size fractions and SSA between agricultural and urban sites.

Table 3.3 - Particle size characteristics of fine riverbed sediments at study sites in the Laurel Creek watershed.

	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	SSA (m^2/g)
S1	1.54	10.95	50.49	1.44
S2	2.30	16.44	62.50	1.04
S3	2.05	16.57	65.80	1.12
S4	1.66	14.20	60.44	1.32
S5	1.98	27.18	106.82	1.09
S6	1.35	11.51	50.74	1.55
S7	1.69	16.26	68.49	1.28
S8	1.65	15.70	70.29	1.30
S9	1.48	12.61	56.55	1.44
S10	1.74	15.42	64.80	1.27

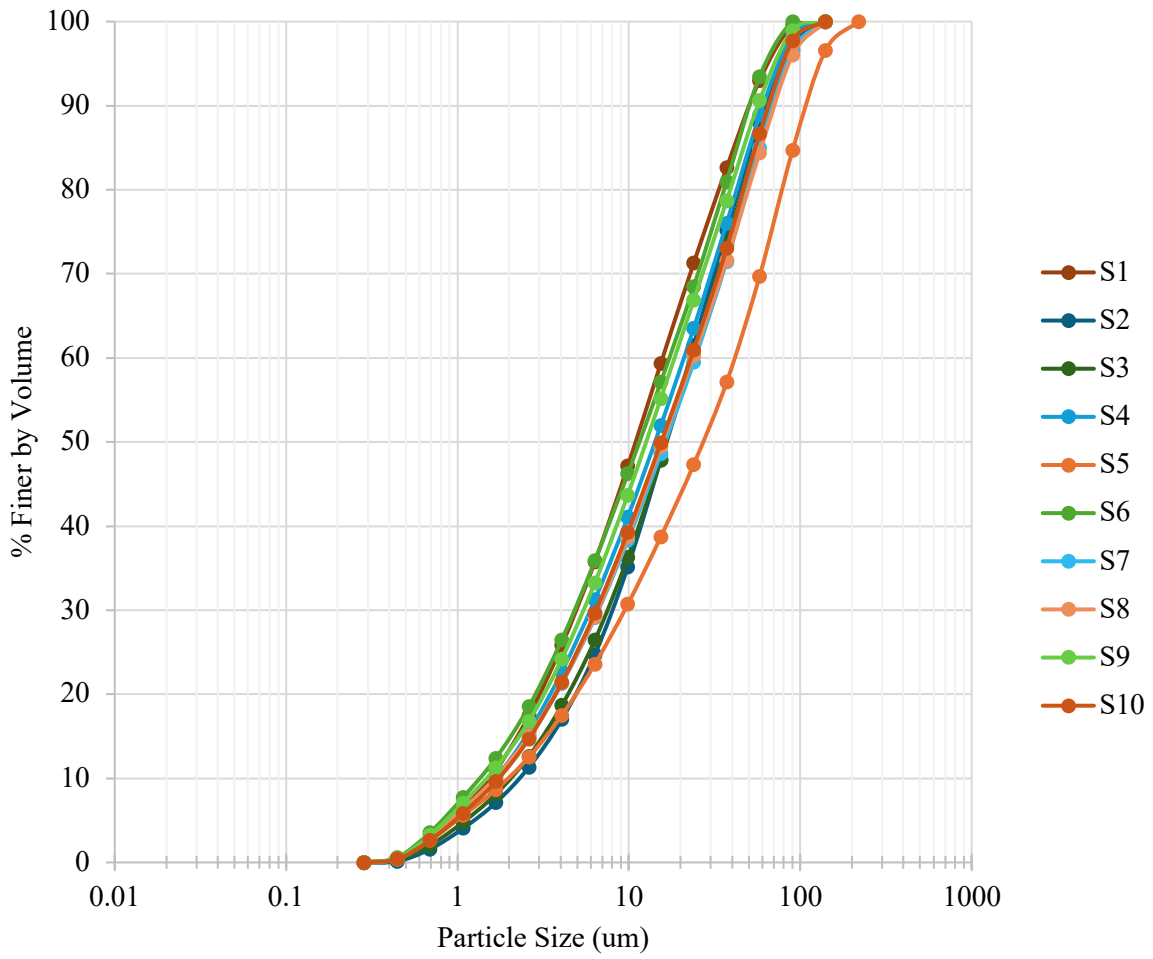

Figure 3.6 - Cumulative particle size distribution of riverbed sediments at study sites in Laurel Creek.

3.5 Discussion

3.5.1 Spatial distribution of particulate phosphorus

The distribution of particulate P forms (NAIP, AP, and OP) and their concentrations in streambed sediment have been well studied in multiple aquatic environments and geographic locations across the globe (Table 3.4). Many of studies have examined the effects of natural (Lannergård et al., 2020; Stone, 2004) and anthropogenic (Falk et al., 2021; Jarvie et al., 2005; McDowell et al., 2019; Owens & Walling, 2002) landscape disturbance on the form, transport, fate and effect of these particulate P forms. The concentrations of particulate P forms in streambed sediment of Laurel Creek are compared to results reported in the literature (Table 3.4). Many studies have examined P forms in agricultural systems (Audette et al., 2018; Falk et al., 2021; Noll et al., 2009; Stone & English, 1993) and recently, wildfire impacted watersheds

(Allin et al., 2012; Emelko et al., 2016; Watt et al., 2021), however, less is known about P forms and distribution in urban stream bed sediment. The concentration of TPP in this study ranged from 424 to 1220 μg g^{-1} and is comparable to data reported in other urban and urban–agricultural watersheds (Barral et al., 2012; Lin et al., 2009). In Laurel Creek the highest values of TPP were found primarily in the agricultural headwaters (1001 – 1220 μg g^{-1}), whereas the lowest TPP concentrations (424 – 709 μg g^{-1}) were measured within highly urban downstream tributaries (sites S5 – S9). A similar pattern in streambed TPP concentrations was reported by Owens & Rutherford (2023) for a small watershed in British Columbia, where streambed TPP concentrations were higher at upstream agricultural sites than at downstream urban sites. The Ontario Provincial Sediment Quality Guidelines (PSQGs) (Government of Ontario, 2016; Persaud et al., 1993) report a Lowest Effect Level (LEL) for TPP of 600 μg g^{-1} and a Severe Effect Level of 2000 μg g^{-1}. Within the LCW, most sampled fine streambed sediment was above the LEL, which suggests it is marginally to significantly polluted. The TPP levels in streambed sediment were below the lowest PSQG effect level and are considered clean to marginally polluted at sites S5, S8, and S9. These data suggest that sensitive benthic organisms may be affected by excess TPP within Laurel Creek, especially within the agricultural headwater sites S1 – S3 and the most downstream sample location site S10.

Table 3.4 - Comparison of streambed particulate phosphorus (µg g^{-1}) in Laurel Creek watershed to other watersheds.

Author	Site, river or watershed	Type	NAIP	AP	OP	TPP	Enrichment factor (NAIP/TPP)
This study	S1- S3	Agricultural	636	309	136	1081	0.58
	S4 – S10	Urban	258	330	80	667	0.37
Stone, (2004)	Slave river delta	Forested	228	38	66	329	0.68
Barral et al., (2012)	Anllóns River	Urban	642	359	564	1565	0.41
		Reference	120	6	134	260	0.46
Kerr et al., (2011)	Brisbane River	Agricultural - Cattle grazing	246	202	209	658	0.37
Stone & English, (1993)	Big Creek	Agricultural - Spring (2µm fraction)	1000	330	250	1580	0.63
	Big Otter	Agricultural – Spring	900	330	220	1450	0.62
Noll et al., (2009)	Graywood Gully	Agricultural	1451	216	356	2023	0.72
Falk et al., (2021)	Big Creek	Agricultural	65	85	45	195	0.33
	Nissouri Creek	Agricultural	160	65	55	280	0.57
	Saaugeen River	Forested – agricultural	85	30	25	140	0.61
Lin et al., (2009)	Daliao River	Urban	271 - 538	228 - 237	176 - 201	675 - 976	0.40 - 0.55
Lannergard et al., (2020)	Sävjaån catchment	Agricultural	838	335	395	1568	0.53
		Forested	173	372	376	922	0.19
Audette et al., (2018)	West Holland Watershed	Marsh – agricultural	891	352	436	1679	0.53
Wang et al. (2013)	Huai River	Agricultural - urban	71 - 231	182 - 618	<100	415 - 758	0.17 - 0.82
Xuan et al. (2014)	Tancheon stream	Urban	57 - 64	26 - 31	10 - 12	100	0.57 - 64

3.5.2 Spatial variation of particulate phosphorus and land use

Spatial variation of the form and concentration of streambed PP within river systems are related to several factors including geology, watershed characteristics, hydroclimatic variability, soil types and land use and management (Lannergård et al., 2020; Owens & Walling, 2002). In Laurel Creek, elevated levels of TPP and NAIP in streambed sediment were measured at headwater agricultural sites. Site S1 had the highest concentration of TPP (1220 μg g^{-1}) and NAIP (738 μg g^{-1}), with 73% agricultural land use above the study site. Agricultural sites S2 and S3 had the following concentrations, TPP (1001 μg g^{-1}, 1021 μg g^{-1}), NAIP (645 μg g^{-1}, 524 μg g^{-1}) and agricultural land use (60%, 74%), respectively. These results are within the range of previously reported TPP data from other studies in agriculturally impacted rivers. Table 4.1 shows that many agriculturally influenced systems have TPP values between 1000 – 2000 μg g^{-1} (Audette et al., 2018; Lannergård et al., 2020; Stone & English, 1993). High concentrations of TPP at sites S1 – S3 are likely a result of diffuse P loading from surrounding agricultural land use such as tile drain and surface runoff, and streambank erosion of P enriched soils (Macrae et al., 2007; Quinton et al., 2010; Withers & Jarvie, 2008).

Lower concentrations of streambed TPP and NAIP were observed at predominantly urban sites. Site S5 which is predominantly urban residential land use (72% of upstream area) had the lowest TPP (424 μg g^{-1}) and NAIP (104 μg g^{-1}) concentrations. Similarly low TPP and NAIP levels were observed at sites S8 and S9 which are characterized by industrial/residential land use (86% and 89% of upstream area, respectively). In contrast, other studies evaluating agricultural and urban streambed TPP in large watersheds have typically reported higher TPP concentrations at urban sites (Barral et al., 2012; Lin et al., 2009), where urban TPP concentrations can exceed 6000 μg g^{-1} in some cases (Owens & Walling, 2002). This may have resulted from the discharge of sewage effluent from WWTPs which can represent a significant point-source of P to rivers (e.g. Jarvie et al., 2005; Owens & Walling, 2002). The Laurel Creek watershed, however, is a comparatively small watershed and has no major point-source inputs from WWTPs. However, site S10, despite being a highly urban site, had TPP concentrations of (929 μg g^{-1}) and NAIP (460 μg g^{-1}) which considerably exceed that of the upstream urban tributaries. This may be a result of sediment and associated inputs from roads during runoff (Czemiel Berndtsson, 2014; Dallmann et al., 2014; Kuoppamäki et al., 2014) and stormwater ponds (Frost et al., 2019; Taguchi et al., 2020). Indris et al. (2020) examined P loading from vehicular emissions and reported that urban runoff from roads was a significant source of P in the City of Waterloo. Comparisons between TP and SRP in the study showed that much of the P existed as PP. This may explain why site S10 had high concentrations of TPP but comparatively low water column SRP concentrations. It is notable that sediment at site S10 was sampled directly downstream from a busy roadway (Bridge St. W., Waterloo ON.) and a storm drain (Appendix A, Figure A11), which is likely an

important source of P during periods of runoff and snowmelt. Overall, TPP concentrations were the highest at headwater agricultural sites but decreased downstream at sites with urban and industrial land use.

3.5.3 Effect of impoundments on fate of PP in LCW

River impoundments can exert significant control on nutrient storage within river systems (Maavara et al., 2015; Miranda et al., 2008; Van Cappellen & Maavara, 2016), and downstream reaches (Dixit et al., 2000). The potential for reservoirs to capture and store nutrients such as P, has been well documented (Kõiv et al., 2011; Paul et al., 1998; Powers et al., 2014; Tiessen et al., 2011). In the present study, reservoirs and impoundments in the Laurel Creek watershed are used for flood control and recreation. The three main reservoirs/impoundments in the watershed include (in order from largest to smallest) Laurel Creek Reservoir (1.01 km^2), Columbia Lake (0.12 km^2), and Silver Lake. Laurel Creek Reservoir and Columbia Lake are located between study site S3 and S4, and Silver Lake is situated between S4 and S6 within the main channel. Considerable differences in PP are observed between upstream sites S1, S2, and S3, and main channel sites S4, S6, and S10 downstream the reservoir and impoundments (Figure 3.7). Main channel sites downstream of the reservoirs had lower concentrations of both TPP and bioavailable NAIP (average 814 ± 110 μg g^{-1} and 367 ± 83 μg g^{-1}, respectively) than sites upstream of the reservoirs (average 1081 ± 121 μg g^{-1} and 636 ± 107 μg g^{-1}, respectively), suggesting that PP may be sequestered within the upstream reservoirs. Previous work on P capture in Laurel Creek impoundments support these observations. Yu & Stone, (2010) found that a redesign of Columbia Lake by the City of Waterloo in 2005 led to a significant decrease in TP export from the impoundment, with the impoundment acting as a sink for TP. Further study on a smaller Laurel Creek impoundment downstream Columbia Lake by Mclellan et al. (2012) determined that the impoundment acted as a sink for both sediment and P during baseflow periods. Therefore, impoundment capture of P may be partially responsible for decreases in downstream fine sediment TPP concentration, and reservoirs within Laurel Creek may be storing considerable amounts of P. However, Shantz et al. (2004) reported that Columbia Lake exported large amounts of TP during periods of drawdown in the fall, which suggests that captured P may only be stored temporarily in some stream reaches within the watershed.

It is worth noting that the decrease in TPP between sites upstream and downstream of the reservoirs is nearly entirely due to the reduction of NAIP between these sites. If the NAIP fraction is removed from TPP, the average TPP upstream and downstream the reservoirs become 445 ± 77 μg g^{-1} and 447 ± 34 μg g^{-1}, respectively (Figure 3.7). This suggests the reservoir and impoundments along Laurel Creek may be particularly effective at retaining bioavailable PP. Similarly, a study by Xuan et al. (2014) on P-dynamics in an urban stream impacted by a series of weirs found higher amounts of bioavailable PP at upstream sites, compared to sites downstream the impoundments. While this may suggest reductions of bioavailable PP

transport to downstream environments, potential exchange of P with overlying water or remobilization may occur when environmental conditions change, potentially causing impoundments to act as a P source (Xuan et al., 2014). Additionally, deposition of bioavailable PP in the Laurel Creek reservoir may increase the risk of internal P loading and algal blooms (Søndergaard et al., 2003; Welch & Cooke, 2005), raising water quality management concerns given the reservoir's recreational use (e.g., camping, swimming, fishing, etc.) from spring through fall. Although the reservoirs may reduce downstream PP transport for much of the year, remobilization of deposited fine sediments during fall drawdown (Mclellan et al., 2012; Shantz et al., 2004) could generate pulses of bioavailable PP to downstream systems, including the Grand River and ultimately Lake Erie. A more systematic investigation is required to better characterize bioavailable PP (NAIP) retention within the Laurel Creek reservoir and impoundments and to evaluate consequences for in-stream and downstream water quality.

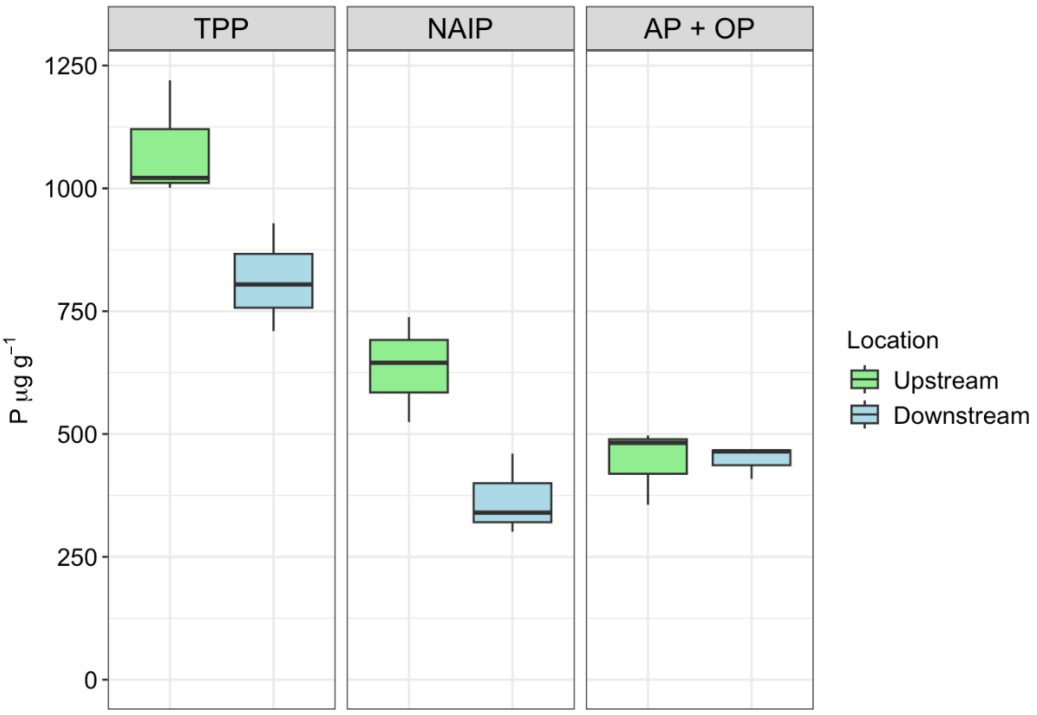

Figure 3.7 - Average TPP, NAIP and AP + OP concentrations (µg g^{-1}) in fine streambed sediment at sites upstream of the Laurel Creek Reservoir and Columbia Lake (S1, S2, S3) compared to average concentrations at downstream sites (S4, S6, S10).

Reservoirs may also be influencing the total quantity of PP storage in the Laurel Creek watershed. Reservoirs and impoundments disrupt the movement of sediment through the fluvial system, more specifically, reservoirs and impoundments can capture and store sediment, leading to sediment exhaustion downstream (Growns et al., 2009; Renwick et al., 2005; Vörösmarty et al., 2003; Williams & Wolman,

1984). According to the Lane balance (Lane, 1955), the reduction of sediment load and excess runoff from urban land use causes an increase in stream power, leading to a more erosive flow regime in the downstream urban sections. Fine sediment is correlated with higher concentrations of TPP and bioavailable NAIP (Owens & Walling, 2002; Stone & Mudroch, 1989), indicating that streambed PP storage may be correlated with the amount of fine material present (Ballantine et al., 2009; Droppo & Stone, 1994). During the field assessment of the present study, excess fine streambed sediment was observed in the agricultural headwater sites (S1, S2, S3) upstream of the reservoirs, and channels appeared to be transport limited. Alternatively, the urban main channel sites (S4, S6, S10) downstream the reservoirs had gravel beds, limited fine sediment storage, and appeared supply limited. Together, these observations suggest that the reservoirs exert a major control on downstream PP storage by altering sediment supply and P transport throughout the watershed, however more research is required to separate and quantify cumulative influences of reservoirs on PP in fine streambed sediment in Laurel Creek.

3.5.4 Particulate phosphorus form distribution

To examine the effect of land use on PP form in riverbed sediment along the river continuum, particulate P forms (NAIP, AP, OP) were plotted on a tertiary diagram as a percentage of TPP (Figure 3.8). The results show a decreasing downstream trend in OP (Figure 3.4), however the relative percent of the organic particulate P fraction varied minimally (10-15% of TPP) between sites (Figure 3.8). This observation is consistent with the results of a study by Yi et al. (2017) which found the OP content in urban streambed sediment in China was ~9% of TPP with little variation between sites. The concentration of AP in Laurel Creek constituted a large percentage of TPP (24 – 64%), particularly at urban sites S5 & S8. Particulate P forms in riverbed sediment at study sites in Laurel Creek vary the most on the %AP to %NAIP axis, with much smaller differences in the OP form.

Although there was no downstream trend in the %AP, distinct inter–site differences were observed (Figure 3.8). Three separate clusters were identified based on unique NAIP and AP differences between sites (Figure 3.8). Sites with an agricultural land use percentage of >60% form cluster 1 with high levels of NAIP. Sites with urban land use percentages of >60% are clustered in ellipse 2, with a high enrichment of AP. Sites S4, S6 and S10, which have considerable amount of both agricultural and urban upstream land use are grouped in cluster 3, and show a nearly equal split in %NAIP and %AP. Notably, sites S4, S6 and S10 are also main channel sites, whereas sites in clusters 1 and 2 are all located in the headwaters or tributaries to Laurel Creek. Although enrichment of AP is greatest at urban tributary sites, concentrations of AP are poorly correlated with urban land use. Sites in figure 3.8 are emphasizing the longitudinal trend of NAIP in the Laurel Creek Watershed. AP values remain relatively constant throughout Laurel Creek, and the enrichments at urban sites are primarily a result of low NAIP concentrations, rather than high AP

concentrations. It may be that AP and OP concentrations reflect background levels of PP based on catchment characteristics and geology, whereas NAIP more likely reflects anthropogenic inputs from fertilizer applications and atmospheric deposition which are mobilized and transferred to Laurel Creek during snow melt and high discharge events. Unfortunately, a reference site was not available in Laurel Creek to establish a potential baseline.

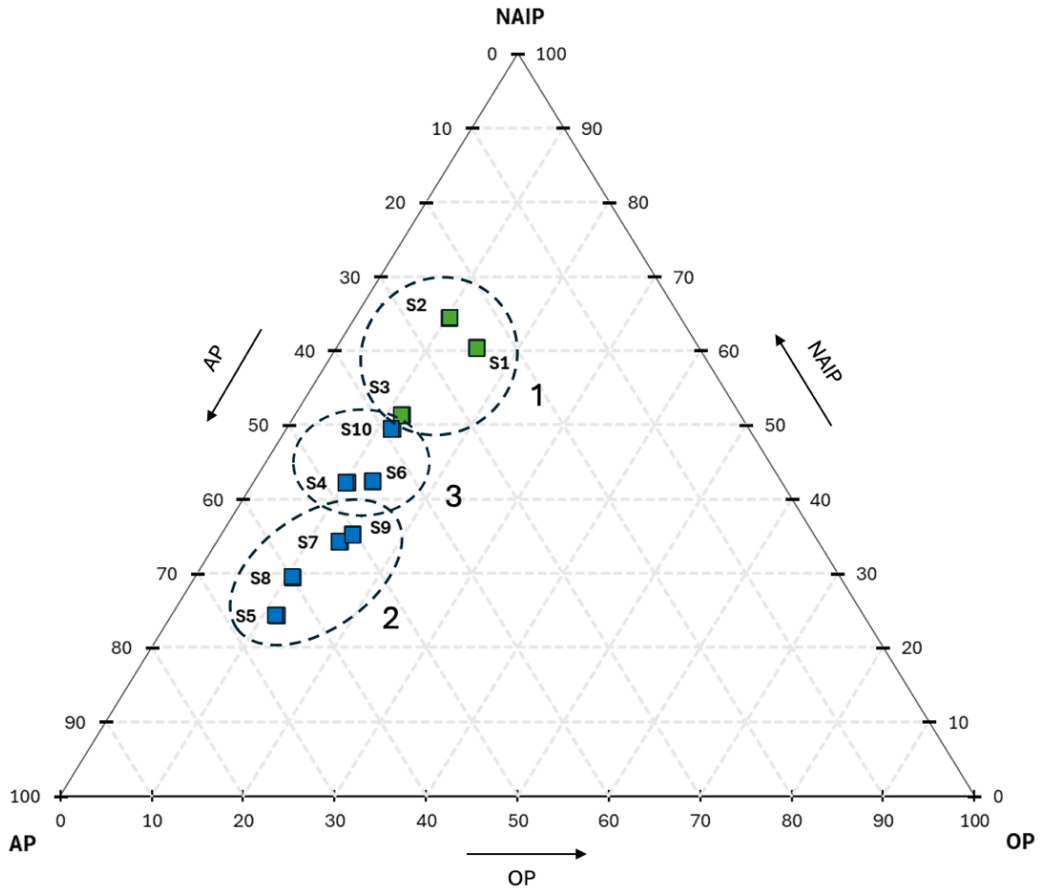

Figure 3.8 - Particulate phosphorus form (%NAIP, AP, OP) in riverbed sediments of agricultural (green) and urban (blue) study sites of Laurel Creek. Ellipse 1 shows the most agricultural sites (agricultural land use >60%), ellipse 2 shows the most urban sites (urban land use >60%), and ellipse 3 shows the main channel sites.

Evaluating the variability of NAIP concentrations and enrichment in streambed sediment is important as its bioavailability has implications for ecosystem health (DePinto et al., 1981). Notably, NAIP concentrations were most variable among sites. The NAIP enrichment was greatest at agricultural sites (Table 3.4), with the highest enrichment found at site S2 at 64%. The average enrichment of NAIP at

agricultural sites was 58%, which is comparable to other agricultural southern Ontario watersheds such as Big Otter (Stone & English, 1993), Nissouri Creek (Falk et al., 2021), and the West Holland watershed (Audette et al., 2018). This suggests that agricultural land use is a key driver related to enrichment of NAIP. This is supported by McDowell et al. (2002), who reported greater bioavailable PP content in downstream agricultural land use attributed to manure and fertilizer inputs. However, NAIP enrichment around and above 60% are not exclusive to agricultural sites but have also been observed in highly forested watersheds (Falk et al., 2021; Stone, 2004) and catchments impacted by wildfires (Tullio, 2022). The highly urban tributary sites (>60% urban land use) in Laurel Creek watershed (S5, S7, S8, & S9) had comparatively low NAIP enrichment of, with an average of 31%. Similar observations have been observed in forested catchments in Sweden (Lannergård et al., 2020), and pastureland systems in Australia (Kerr et al., 2011). Studies on sediment from highly urban rivers in Spain (Barral et al., 2012) and China (Lin et al., 2009) have reported comparatively higher NAIP enrichment at 40% and 55%, respectively. These higher enrichment levels may be explained by greater P loadings, as NAIP and bioavailable PP is often correlated with TPP (Barral et al., 2012; Williams et al., 1980). More point source urban pollution driving high P inputs could therefore explain the higher enrichments in bioavailable PP in these systems. The results of this study suggest that intensive agricultural land use is strongly associated with sediment enriched in bioavailable PP, whereas small highly urbanized watersheds have lower enrichment of bioavailable PP. This may be a result of agricultural practices, capture of NAIP by impoundments, or changes to streambed physio-geochemical properties. Comparisons between other studies show that variation of NAIP may not only be a function of land use, but also factors such as P sources, geology, catchment characteristics and sediment properties (Ballantine et al., 2009; Owens & Rutherford, 2023; Owens & Walling, 2002; Stone & English, 1993).

3.5.5 Physical and geochemical controls on PP forms

Many studies have examined the relationship between sediment-associated P forms and particle (Owens & Walling, 2002; Stone & English, 1993; Vervier et al., 2009). These studies show that particle size is a key factor in understanding transport and storage of sediment-associated contaminants (e.g. PP) (Stone & Droppo, 1994). Phosphorus is strongly associated with sediment grain size, and trends of increasing NAIP and decreasing AP concentrations are commonly reported with decreasing grain size (Stone & English, 1993). A study on sediment in an urban system in China by Yi et al. (2017) found that sediment with particle sizes <10 µm were enriched in NAIP forms, whereas the >10 µm fractions were dominated by AP. Although grain size in the present study had minimal variability between sites due to targeted sampling of fine sediment, sites S1 and S5 had distinct differences. Nearly 50% of the sediment from site S1 was <10 µm while it was about 30% for site S5. This may partly explain the difference in NAIP values between site S1

(738 ug P/g) and S5 (104 ug P/g). No significant differences between grain size and SSA were found between agricultural and urban sites, and no longitudinal trend along the watershed was observed in Laurel Creek sediment. This is likely a result of the sampling methods employed in this study, as the technique preferentially samples fine sediment (<100 μm) that is easily resuspended from the streambed once the armor layer is mobilized. While particle size was not a factor in this study to explain differences in PP form and concentration, other factors such as sediment geochemical composition can influence P form and availability.

Geochemical composition of streambed sediment is an important abiotic control on PP form and availability (Boström et al., 1988; Stone & English, 1993). Coatings of Fe, Al, Mn and organic matter on fine particles are associated with a greater ability to sorb P (Evans et al., 2004; Stone & Mudroch, 1989), and higher concentrations of these metals and organic matter within the streambed sediment typically correlate with increasing PP concentrations while major elements such as Mg and Ca are associated with minerals such as apatite and calcite which have lower P binding capacity than clay minerals (Stone & English, 1993). Therefore, it can be expected that sediments with high concentrations of Ca and Mg will have low levels of NAIP. In Laurel Creek watershed, significant differences and longitudinal trends were observed for major elements between sites. Sediment at agricultural sites was significantly enriched in Mn compared to urban sites ($U = 0$, $p < 0.01$). Notably, site S1 has the highest Mn concentration (0.31%), nearly 6.5 times greater than the average concentration at urban sites (0.0484%). Mn is a vital element for plant growth (Alejandro et al., 2020), which can be supplemented in agricultural systems via fertilizers, manures, or by increasing soil pH (White & Greenwood, 2013). Therefore, greater concentrations of Mn at agricultural sites may reflect inputs of Mn from farming practices (Owens & Rutherford, 2023). Concentrations of Fe, Al and K were also significantly greater at agricultural sites, especially at site S1. Enrichments of K and Fe suggest fertilizer application, as K is a major component in many fertilizers and Fe is an important micronutrient for plants, which can also be supplemented via Fe chelates (White & Greenwood, 2013). High Al and Fe concentrations at site S1 may be a sign of increased transfer of clay to receiving streams during storm events. This might be a result of row crop agriculture, tillage practices and hillslope erosion (Chichester & Richardson, 1992; Collins et al., 2009; Tapia-Vargas et al., 2001), all of which were observed surrounding the agricultural sites during sampling and field assessment. Long-term fertilizer use may also moderately acidify soils (Wallace, 1994), potentially increasing the mobility of Al, which may bind to sediment subsequently deposited in the streambed. Overall, enrichments of Mn, Fe, and Al in streambed sediment are likely driven by upstream agricultural practices. High organic matter content at the agricultural headwater sites may reflect upstream wetland and forested areas contributing significant amounts of leaves, plant and woody debris into the stream (Abelho, 2001; Benfield, 1997).

Fine streambed sediment in urban reaches of Laurel Creek watershed had low concentrations of Mn, Fe, Al, and OM and greater concentrations of Mg, Ca and Na. Low percentages of natural land cover and high amounts of impervious area in urban areas can contribute to low concentrations of OM in the streambed (Walsh et al., 2005; Webster et al., 1990). A study on soil chemistry in Prague, Czech Republic by Poňavič et al. (2018), found trends suggesting enrichments of Ca and Na in urban soils is related to vehicular traffic, and Mg enrichments related to fossil fuel burning. Similar associations between Ca and Na in urban soil were reported by Rate (2018), who attributed trends to dust from building construction, and by Vieira et al. (2019) in lake sediment draining urban land. In the studies by Poňavič et al. (2018), Rate (2018), and Vieira et al. (2019), Ca and Na were correlated with strontium (Sr). This may be because Ca and Sr can occur together in carbonate minerals which are often used in building construction products (i.e. limestone and cement materials) (Rate, 2018). In the present study Ca and Sr were very strongly related ($R^2 = 0.93$, $p < 0.01$), therefore increasing concentrations of Ca in downstream Laurel Creek sediment may represent inputs from construction dust and vehicular traffic. Other influences on the geochemical composition of sediment with respect to PP are sediment grain size (Horowitz & Elrick, 1987; Stone & English, 1993), and underlying geological characteristics of the watershed (Ankers et al., 2003; Ballantine et al., 2009; Stone et al., 2022; Walling et al., 2001). However, there is minimal variability in grain size of the sampled sediment in the present study, and considering Laurel Creek watershed is small, draining relatively uniform glaciofluvial and till deposits, these influences on sediment geochemistry are likely minimal at the watershed scale.

A principal component analysis (PCA) was conducted to examine relationships between sediment geochemistry and PP forms (Figure 3.9). Two principal components were determined, which combined, account for 85.1% of the variance in the data set. The first principal component (PC1) accounted for 66.7% of the variance and had the strongest positive loadings from NAIP, Mn and TPP but also strong positive loadings from OP, Al and Fe and from LOI (OM) and K to a somewhat lesser degree. The loadings for Mg, Ca and Na in PC1 were negative. The second principal component (PC2) accounted for 18.4% of the variance and had strong positive contributions from Na, K and AP. LOI (OM) was the only vector with a negative loading on PC2. Correlations can be observed based on the vectors of the PCA biplot. Strong associations between NAIP and Mn, between Fe, Al and OP and between Ca and Mg were observed. The strongest negative correlation was between LOI and Mg/Ca. Strong positive correlations between the cations associated with metal oxy-hydroxides (Fe, Al and Mn), and NAIP, OP and TPP suggest a considerable influence of metal oxy-hydroxides on PP form. This is consistent with previous work (Agudelo et al., 2011; Evans et al., 2004; Stone, 2004). Strong association between NAIP and Mn is supported by Watt (2018), who determined that NAIP could be modeled by Mn and OM in the Crowsnest River in

Alberta. Based on the loadings of PC1, it seems to reflect variance resulting from the mineralogy and phosphorus content of the streambed sediment.

Streambed geochemistry and PP form were distinct between different land use types in this study. To examine this further, study sites were plotted against the principal components in Figure 3.9. It can be observed that agricultural and urban sites can be separated based on PC1. Agricultural sites S1 - S3, show positive loadings on PC1, whereas urban sites (S4 - S10) show negative loadings. The groups have a clear separation with no intermediate sites, as well as high group homogeneity, indicating similarity among grouped sites. This indicates that the surrounding land use of the sampling site was the primary driver of variance. Comparing the plots in Figure 3.9 one can determine that the agricultural sites are characterized by higher concentrations of Al, Fe, Mn, and various forms of particulate phosphorus (TPP, NAIP, and OP). In contrast, the urban sites are characterized by higher levels of Mg, Ca, and Na. Strong contrasting associations between these sample groups suggest fundamentally different sediment compositions between urban and agricultural sites. Fe and Al suggest presence of clays at agricultural sites, whereas Ca and Mg suggest more resistance minerals such as carbonates and potentially silicates.

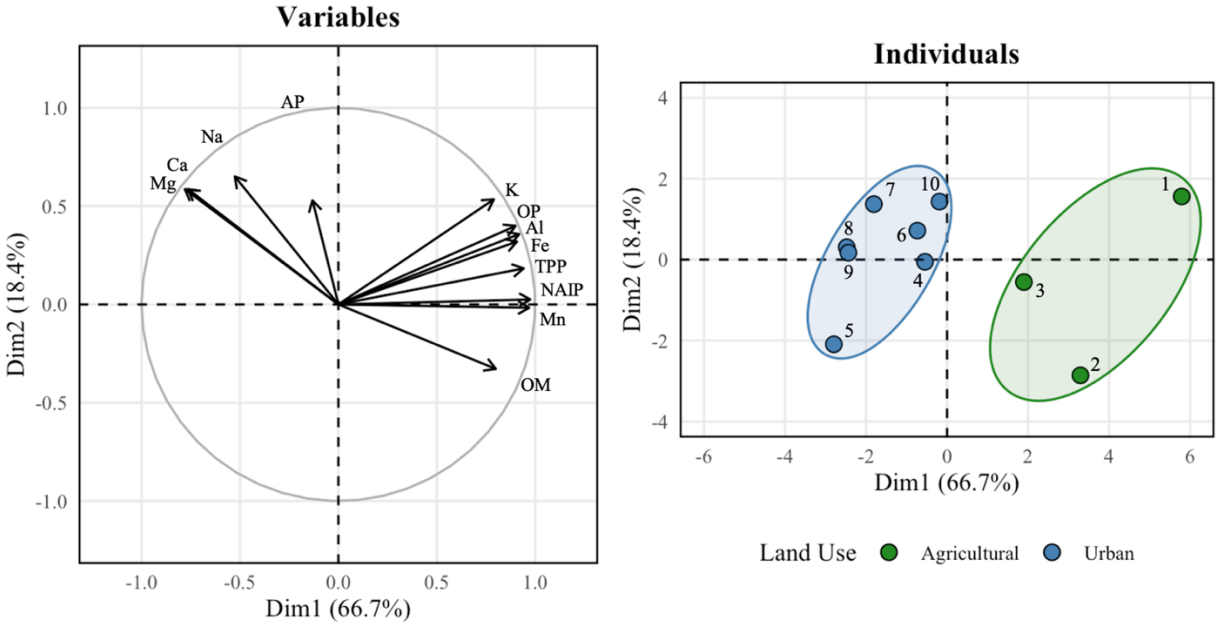

Figure 3.9 - Principal component analysis biplot "Variables" (A), generated using standardized particulate phosphorus and major element data, showing component loadings (labeled arrows), and "Individuals" plot (B), where sample sites are plotted using PC1 and PC2.

To further examine geochemical influences on PP, spearman rank correlation coefficients were determined between major element composition and PP form (Table 3.5). Significant strong positive correlations were observed between TPP and NAIP with Fe, Mn, Al, and OM. A significant (but less strong)

positive relationship was also observed between K and TPP and NAIP. OP was positively correlated with Fe, Mn, Al, K, and OM, however not as strongly as TPP and NAIP for most major elements. TPP and NAIP were negatively correlated with Mg and Ca, yet only the NAIP – Mg correlation was significant to $p < 0.05$. Notably, AP was not significantly correlated with any major element, and there were no significant correlations observed between Na or particle size (D_{50}) for any PP form. The results are consistent with the PCA (Figure 3.9), which showed that NAIP, OP and TPP have strong, similar major element associations, whereas AP has no strong correlations with sediment geochemistry.

Table 3.5 - Spearman Rank Correlation coefficients between particulate P form and major element composition for riverbed sediments (n =10) from Laurel Creek Watershed.

	NAIP	AP	OP	TPP
Mg	-0.68*			-0.64
Al	0.94**		0.96**	0.96**
Ca	-0.61			-0.56
Mn	0.93**		0.77*	0.94**
Fe	0.91**		0.83**	0.88**
Na				
K	0.67*		0.73*	0.76*
OM	0.93**		0.84**	0.90**
D_{50}				

p <0.1, *: p <0.05, **: p <0.01

These results agree with findings of Stone and Mudroch (1989) and Stone and English (1993), which found NAIP positively correlated with Al, Mn, K and OM and clay mineralogy. In contrast, studies by Watt (2018) and Tulio (2022) on wildfire impacted systems in Alberta did not observe significant, strong positive relationships between TPP and NAIP with Fe and Al. However positive relationships between NAIP and Mn were observed in both studies. (Emelko et al., 2016) found NAIP related to OM in stream sediment. TPP may also vary based on coprecipitation with calcite (House & Denison, 1997), however this was not observed in this study. In urban influenced systems in China, Lin et al. (2009) found greater TPP concentrations in sediments with higher Fe content, and associations between NAIP and Fe and Al were found in the Slave River delta by Stone (2004). Overall, TPP and NAIP were strongly influenced by sediment geochemistry in this study, consistent with trends commonly observed in previous research.

Bioavailable PP (NAIP), varied in association with Al, Mn, and Fe metal oxides as well as organic matter, both PP and major elements appearing to reflect impacts from upstream land use.

3.6 Conclusions

The goal of this study was to examine controls on the source and variability of phosphorus forms in bed sediment of an urban stream during environmentally sensitive low flow conditions. Conclusions of this study include:

1. Particulate phosphorus form and concentration reflect watershed-scale land use gradients
    - TPP concentrations in fine streambed sediment ranged from 424 to 1220 μg g^{-1} across LCW and were significantly greater ($U = 0$, $p < 0.01$) at upstream agricultural tributaries than downstream urban sites.
    - Bioavailable PP (NAIP) and OP concentrations in fine streambed sediment were significantly greater ($U = 0$, $p < 0.01$, $U = 1$, $p < 0.05$, respectively) at agricultural tributaries than downstream urban sites.
2. Agricultural headwater sediments represent a significant reservoir of bioavailable legacy phosphorus
    - Bioavailable NAIP enrichment of TPP varied between 24% - 64% across the watershed, with considerably higher enrichments at agricultural headwater sites (average 58%) compared to downstream urban sites (average 37%). Greater NAIP at the agricultural sites reflect increased mobility of fine P-rich sediment from intensive crop agricultural land use to the stream, via overland flow and tile drains.
3. Sediment geochemical composition drives differences in P form between land use types
    - Urban sites had greater concentrations of Ca, Mg, and Na, which may result from concrete weathering and vehicular traffic (Kaushal et al., 2014; Rate, 2018; Vieira et al., 2019).
    - Agricultural sites had greater concentrations of Fe, Mn, Al, and OM, reflecting agricultural fertilizer use, increased transport of clay to stream, and OM contributions from wetland areas.
    - TPP and NAIP concentrations in fine streambed sediment were positively correlated with Al, Mn, Fe, and OM, and negatively correlated with Mg and Ca.
4. Stream impoundments modify longitudinal patterns of PP storage
    - TPP and NAIP concentrations were greater at sites upstream of impoundments compared to those downstream. Notably, this change in PP concentration is reflected primarily in the bioavailable (NAIP) fraction which had an average concentration of 636 ± 107 μg g^{-1} above and 367 ± 83 μg g^{-1} below the impoundments.

Chapter 4

Sediment-phosphorus buffering in an urban stream during baseflow

4.1 Overview

Streambed sediments can buffer dissolved phosphorus (P), particularly during low, summer baseflow conditions. Because buffering strongly influences in-stream P dynamics and downstream export, understanding sediment–P interactions is critical for surface water quality management. As global urbanization accelerates, there is an increasing need to evaluate how urban systems modify sediment-P dynamics. The present study examines P mobility of stream bed sediment during environmentally sensitive low flow conditions in the small (76 km^2), urban, Laurel Creek watershed (LCW), Ontario, Canada. Ten study sites were selected from within the main channel and across all major tributaries, each characterized by different degrees of agricultural and urban land use, to examine how cumulative landscape disturbances affect P mobility. The equilibrium phosphate concentration at net zero sorption (EPC_0) along with water column soluble reactive phosphorus (SRP) concentrations were used to examine P-sorption characteristics. Results show that land use was a key driver of streambed sediment EPC_0. Mean EPC_0 of agricultural sites was 148 µg P L^{-1} and the mean EPC_0 for urban sites was 56 µg P L^{-1}. Agricultural sites had a positive average phosphate exchange potential (PEP) of 0.19, indicating potential to act as a net source of SRP during summer baseflow. Urban PEP was spatially variable, where some sites demonstrated potential P source behavior (S4, S7, S9, and S10) whereas others acted as potential P sinks (S5, S6, and S8). Additionally, sediment in some urban tributaries (S5 & S9) displayed both sink and source potential due to changing SRP concentrations during the summer. Lower EPC_0 was observed at sites downstream impoundments in LCW, compared to upstream sites, suggesting impoundments attenuate mobile P-rich sediment downstream. This study highlights the complexity of urban P-dynamics and the influence of land use and impoundments on sediment P dynamics within a small watershed.

4.2 Introduction

Phosphorus is a key limiting nutrient for primary productivity, and excessive P inputs to surface waters are a primary driver of eutrophication (Vollenweider, 1968). In river networks, elevated P concentrations can rapidly degrade water quality by stimulating excessive algal and plant growth, leading to declines in biodiversity, increased water treatment costs, and potential risks to human health (Burkholder, 2009; Hilton et al., 2006; Yan et al., 2022). These impacts frequently propagate downstream, contributing to harmful algal blooms (HABs) in receiving waters (Anderson, 2009; Heisler et al., 2008) such as Lake Erie, where

continued P enrichment and shifting climatic conditions sustain eutrophication risk despite ongoing management efforts. (Watson et al., 2016; Zhou et al., 2015). While reducing external P inputs remains a central management objective, internal processes within river systems increasingly regulate the timing, form, and bioavailability of P exported to downstream environments (McDowell, 2015; Sharpley et al., 2013; Withers & Jarvie, 2008).

At the watershed scale, P transport is largely sediment-associated (Kronvang et al., 1997; Stone & English, 1993); however, its environmental impact depends on its potential to be mobilized into dissolved, bioavailable forms (Boström et al., 1988; Correll, 1998). Soluble reactive phosphorus (SRP) is of particular concern for eutrophication management in receiving waters because it is immediately available for biological uptake (Dodds, 2003). Although point-source inputs of SRP, such as wastewater effluent, have been reduced in many regions, diffuse sources from agricultural and urban landscapes remain difficult to control (Kronvang et al., 2007; Macintosh et al., 2018). In addition, legacy P stored in watershed soils and streambed sediments can act as a sustained internal source of SRP, buffering or amplifying water column concentrations depending on environmental conditions (Sharpley et al., 2013; Withers & Jarvie, 2008). Consequently, sediment-water interactions play a critical role in regulating in-stream P availability and downstream export (House & Denison, 2002a).

Abiotic sediment-water P exchange is commonly referred to as the phosphate buffer mechanism, where streambed sediments adsorb or release SRP to the overlying water column depending upon ambient SRP concentrations and physicochemical conditions (Froelich, 1988). This behavior is quantified using the equilibrium phosphate concentration at net zero sorption (EPC_0), which represents the concentration of SRP at which no net exchange of P occurs between sediment and the overlying water (Froelich, 1988; Simpson et al., 2021). When ambient SRP concentrations exceed EPC_0, sediments act as a sink; conversely, when concentrations fall below EPC_0, sediments release P to the water column (Froelich, 1988; Taylor & Kunishi, 1971). The magnitude and direction of this exchange are controlled by interacting physical and geochemical factors including sediment source (Stutter & Lumsdon, 2008), grain size (Stone & English, 1993), mineral composition (Stone & Mudroch, 1989), and the abundance of reactive Fe, Al, and Mn phases (Evans et al., 2004), as well as environmental variables such as redox conditions, pH, and temperature (House, 2003). These controls are particularly important under low-flow conditions, when reduced dilution and increased residence time enhance sediment-water interactions and can promote internal P loading (Jarvie et al., 2005; McDowell, 2015).

Many studies of EPC_0 of streambed sediments have focused on agricultural catchments (Agudelo et al., 2011; Haggard et al., 2007; Hoffman et al., 2009; McDowell et al., 2020; McDowell & Sharpley, 2003; Reddy et al., 1996; Simpson et al., 2021). In contrast, investigations on P mobility in urban streambed

sediments have largely examined large watersheds affected by point-source inputs from wastewater treatment plants (Arfania et al., 2025; Ekka et al., 2006; Roberts & Cooper, 2018; Zhang et al., 2019). Consequently, few studies have examined P mobility in streambed sediments of small urban catchments dominated by diffuse P loading. These urban diffuse P sources include stormwater runoff, residential inputs, and legacy sediment stores (Withers & Jarvie, 2008; Zhou et al., 2026), which interact within highly modified ecohydrological systems characterized by hydrologic flashiness, engineered channels, and heterogeneous sediment sources, producing complex and spatially variable controls on sediment P dynamics (Kaushal et al., 2014; Walsh et al., 2005; Xuan et al., 2014).

Small streams are particularly important in this context, as they comprise most of the channel length within a watershed (Wohl, 2017) and are strongly influenced by surrounding land use (Fernández et al., 2014). These systems are highly responsive to urban disturbances and play a disproportionate role in regulating downstream sediment and nutrient transport (Mishra et al., 2025; Verdonschot & Verdonschot, 2023). Urban streams commonly include features such as stormwater ponds and impoundments that disrupt sediment continuity (Renwick et al., 2005), enhance fine sediment deposition (Owens et al., 2005), and create variable redox environments, thereby altering sediment-P retention and release dynamics (Taguchi et al., 2020; Xuan et al., 2014; Yu & Stone, 2010).

Understanding how P mobility varies along the river continuum is therefore critical for predicting downstream impacts. Longitudinal gradients in land use and in-stream features influence sediment composition and geochemical conditions, leading to spatial variability in sediment P buffering capacity and EPC_0. However, P mobility in fine-grained sediments of small urban catchments remains poorly quantified. As urban communities continue to expand across southern Ontario (Statistics Canada, 2022), understanding P dynamics in urban-influenced watersheds becomes increasingly important for managing surface water quality. To address this gap, this study investigates P mobility in fine-grained streambed sediments within a small, predominantly urban watershed in southern Ontario. Phosphorus mobility is quantified using EPC_0 under summer baseflow conditions to assess whether sediments function as sources or sinks of soluble reactive phosphorus (SRP). A longitudinal sampling design is used to evaluate how land use and in-stream features, including impoundments, influence spatial variability in sediment P mobility along the river continuum. The following hypothesis were tested in this study:

H_1: Fine urban streambed sediment acts as a potential source for P to the water column during environmentally sensitive low flow conditions and

H_2: changes in P-mobility of bed sediment are related to changing land use and river impoundments across the watershed.

The specific objectives of this research are to

1. determine water column SRP concentrations in Laurel Creek during summer baseflow,
2. examine P-sorption characteristics (EPC_0) of fine streambed sediment along an agricultural-urban land use continuum; and,
3. examine phosphate exchange potential (PEP) of fine streambed sediment to determine influence of land use and impoundments on P-mobility.

4.3 Methods

4.3.1 Site description

The Laurel Creek watershed (LCW) is a 76.1 km² sub-basin of the Grand River system in southern Ontario, Canada, discharging ultimately into Lake Erie. Situated within the Regional Municipality of Waterloo, the watershed extends across the city of Waterloo and exhibits a strong gradient from predominantly agricultural and rural land use in the headwaters to highly urbanized conditions downstream. The upper watershed is characterized by agricultural land use, woodlands, and wetlands, including designated Environmentally Sensitive Landscapes (ESLs) that provide critical habitat, water source protection, and flood regulation functions (Dougan & Associates, 2016). In contrast, the lower reaches are heavily altered by urban development, featuring channelized sections, culverts, stormwater infrastructure, and erosion control measures. The Laurel Creek Reservoir, Columbia Lake, and Silver Lake reservoirs are located within city limits, serving flood management and recreational purposes.

The surficial geology of the basin reflects Quaternary glaciofluvial processes, with the Waterloo Moraine dominating the southwestern portion; this landform exhibits hummocky terrain and complex stratified deposits interbedded with various tills (Karrow, 1993; Frind et al., 2014). The local climate between May and September is temperate, with average monthly temperatures ranging from 12.6 °C in May to 20.2 °C in July and precipitation between roughly 67 mm and 96 mm (Environment Canada, 2024a). Stream channel elevations range from 395 to 298 msl, corresponding to a mean longitudinal slope of approximately 3.7 m km^{-1}. Streamflow at the Environment Canada station (02GA024) during this period varied widely, from low baseflows of 0.060 m³/s to peak discharges of 34.1 $m^3\ s^{-1}$, reflecting the dynamic hydrological response of this highly modified watershed (Environment Canada, 2024b).

4.3.2 Sampling design

Streambed fine sediment was collected during low flow conditions on May 9th, 2024, using the method of Lambert & Walling (1988). A plastic cylinder was randomly inserted into the streambed and then disturbed using a plastic rod to mechanically resuspend fine sediment. The sediment-water slurry was then pumped

into a clean 20 L bucket using a bilge pump. This process was repeated in multiple locations (five to seven) at each sample site to ensure a representative sample of each stream reach. The buckets were sealed, and the sediment was left to settle undisturbed for two days before the water was decanted. The remaining sediment was transferred into plastic containers, refrigerated, and transported to Act Labs in Burlington, ON for geochemical analysis and phosphorus speciation.

4.3.3 Laboratory analysis

4.3.3.1 Water column soluble reactive phosphorus concentrations

Water samples were collected in the centroid of flow at the time of sediment sampling to determine the ambient concentration of soluble reactive phosphorus (SRP) in the water column and for bench top batch experiments to measure the sorption capacity of sediment. Further samples were collected between May and September 2024 (May 28th, June 14th, August 5th, and September 9th) during periods of low flow. Water was collected using clean, 250 ml plastic bottles and were tripled rinsed with river water before collection. Water samples were then refrigerated immediately upon returning to the lab and filtered through 0.45 µm polypropylene syringe filters within 24 hours into 20ml glass scintillation vials for analysis. Filtered river water was analyzed in triplicate by spectrophotometry using the molybdenum blue method on a SEAL AA500 Autoanalyzer (Worsfold et al., 2005).

4.3.3.2 Equilibrium phosphate concentration experiments

The Equilibrium Phosphorus Concentration (EPC_0) of the sediment samples was determined using bench-scale, batch equilibrium experiments and calculated based on methods outlined in Froelich (1988). Freeze-dried ground sediment was used for equilibrium experiments. In 50 ml polypropylene tubes, 0.25 g of dry sediment was combined with 25 ml of filtered river water sampled on the day of analysis. The sediment and 25ml of river water were then spiked with P concentrations of 10, 25, 50 and 100 µg P L^{-1} in triplicate. This process was then duplicated with a second set of experiments with river water to ensure accuracy. Both sets of river water were sampled from site S4 (on different days) with base SRP concentrations 14 and 25 µg P L^{-1}. Site S4 was selected due to its low water column SRP concentrations and mixed upstream land use. The tubes were then shaken for 18 hours at 100 rpm using a shaker table in a dark room at room temperature. Samples were then filtered through 0.45 µm polypropylene syringe filters into 20 ml glass scintillation vials and refrigerated. The final SRP concentrations were measured with colorimetric analysis using the molybdenum blue method on a SEAL AA500 Autoanalyzer.

The amount of phosphorus adsorbed during the equilibrium experiments was calculated using the following equation:

$$P_{ads} = \frac{[(P_{initial} - P_{final}) * 0.025L]}{wt_{sed}} \quad (1)$$

Where P_{ads} = µg P adsorbed per gram of sediment (dry weight), $P_{initial}$ = initial phosphate concentration (µg P L^{-1}), P_{final} = final phosphate concentration (µg P L^{-1}), and wt_{sed} = weight of sediment (g). EPC_0 buffer diagrams were created by plotting P_{ads} (y-axis) against $P_{initial}$ (x-axis), where the sediment ECP_0 is the concentration at net zero sorption or desorption, determined by the x-intercept. Calculated EPC_0 values were compared to water column soluble reactive phosphorus (SRP) concentrations from the sample site to determine P mobility.

4.3.4 Phosphate exchange potential

The phosphate exchange potential (PEP) was proposed by Simpson et al. (2021) as a metric to estimate the potential of sediment to buffer phosphorus. The PEP is the difference in magnitudes between EPC_0 and SRP in the river water and is determined using the following equation:

$$PEP = log_{10}\left(\frac{EPC_0}{SRP}\right) = log_{10}(EPC_0) - log_{10}(SRP) \quad (2)$$

Where EPC_0 is the sediment equilibrium phosphate concentration at net zero sorption and SRP is the soluble reactive phosphorus concentration in the water column at a sampling site. A negative PEP represents potential P adsorption by sediments, whereas a positive value indicates potential P release. In the meta-analysis by Simpson et al. (2021), the PEP was used to compare potential sediment-water P exchange between studies, as the metric is scale independent and a similar comparison is done herein to place this study in the context of the literature.

4.3.5 Statistical analysis

Due to the limited sample size of this study, the data did not meet assumptions of normality. Differences in water SRP and sediment EPC_0 between sites were determined using the non-parametric Mann-Whitney Rank Sums test in Excel.

4.4 Results

4.4.1 Soluble reactive phosphorus concentrations

Spatial and temporal variability of SRP concentrations in the water column at the study sites from May 9 to September 9, 2024, are presented in Figure 4.1. The average SRP concentration for all sample periods and study sites in Laurel Creek was 66 µg L^{-1}. SRP concentrations ranged from <20 to >170 µg L^{-1} during the study period. The highest average SRP concentrations were observed at sites S3 and S8 (135 µg L^{-1} and 126 µg L^{-1}), respectively, whereas the lowest average concentrations were observed at sites S4, S9, and S10 (35 µg L^{-1}, 28 µg L^{-1}, and 34 µg L^{-1}, respectively).

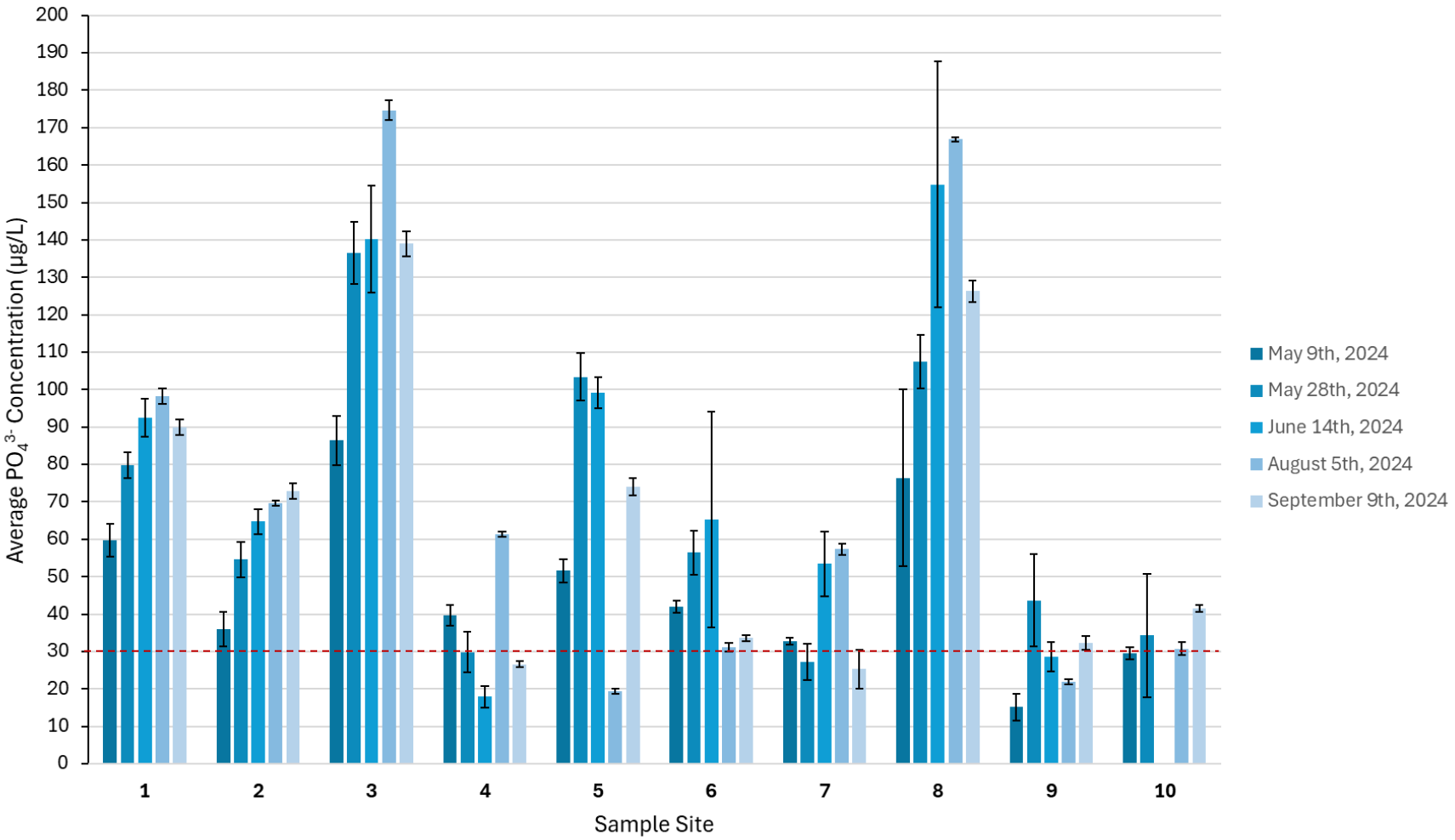

Figure 4.1 - SRP concentrations (µg L^{-1}) during low-flow conditions at study sites in Laurel Creek between (May 9 to September 9, 2024). The red line represents the provincial water quality guideline for total P in surface waters (Ontario Ministry of Environment and Energy, 1994).

The concentrations of SRP varied within and between study sites but no downstream trend in SRP concentrations was observed (Figure 4.2). SRP concentrations were generally higher at agricultural sites than urban sites ($U = 3$, $p < 0.05$). Significant differences between agricultural and urban sites occurred during the August 5th and September 9th sampling periods ($U = 2$, $p < 0.05$, $U = 3$, $p < 0.05$, respectively).

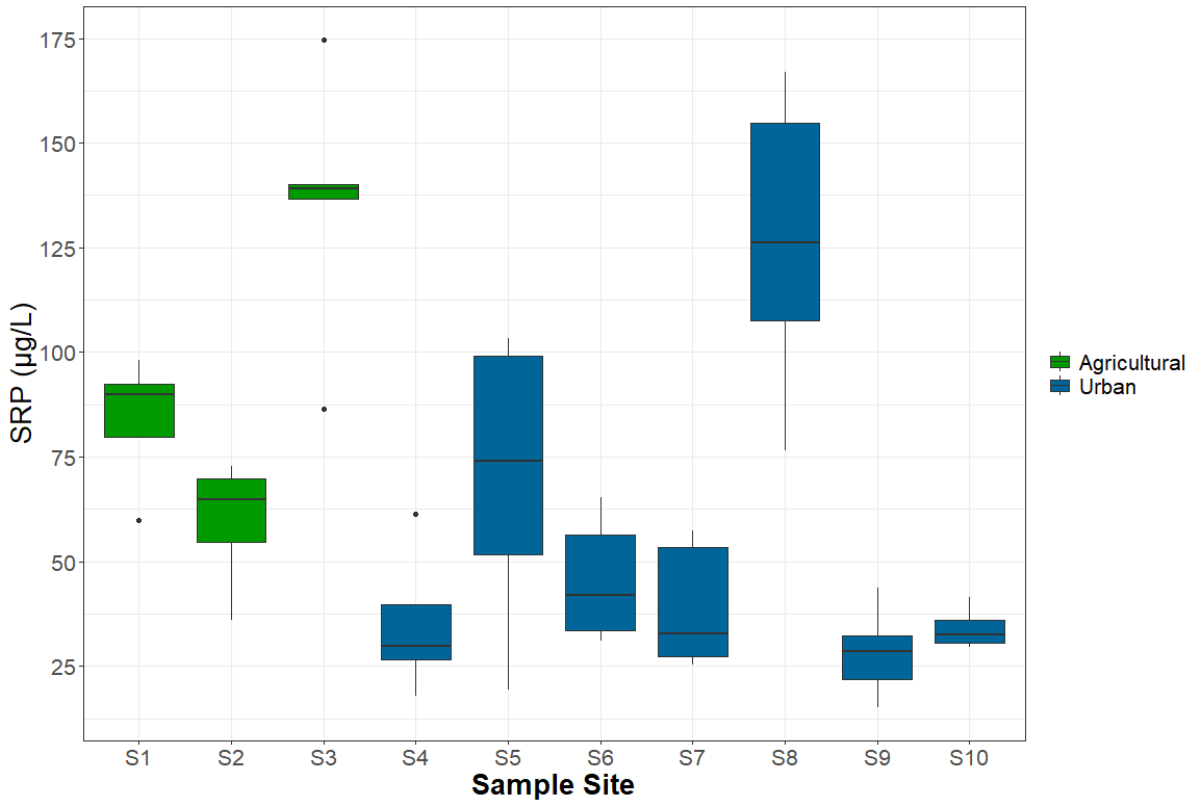

Figure 4.2 - Water column SRP concentrations (µg L^{-1}) during low-flow conditions between (May – September 2024) at agricultural (green) and urban (blue) study sites in Laurel Creek.

Temporal trends in SRP concentrations are presented in Figure 4.1. For most sites, SRP increased with time in response to warmer weather and increased stream temperature. Notably, the agricultural sites S1, S2, and S3, as well as urban site S8 showed general increases in SRP concentrations between May 9th and September 9. Average SRP concentrations increased from 47 µg L^{-1} on May 5th to a maximum of 80 µg L^{-1} on June 14th and decreased to 66 µg L^{-1} by September 9th at study sites in the Laurel Creek watershed. Highest overall average SRP was observed on June 14th, however, sites S1, S3, S4, S6, S7, and S8 had their highest average SRP values on August 5th. Sites with the highest temporal variability include S3, S5 and S8, with an 80 – 90 µg L^{-1} difference in minimum and maximum SRP. Sites S9 and S10 had the lowest temporal variability in SRP, only varying 29 µg L^{-1} and 12 µg L^{-1}, respectively throughout the study period (Figure 4.1).

4.4.2 Sediment equilibrium phosphate concentrations

The results of the phosphorus sorption experiments are presented in Figure 4.3. Although inter- and intra-site variability was observed, EPC_0 values were similar across many of the study sites within Laurel Creek. There was no apparent longitudinal trend in EPC_0 concentrations in Laurel Creek, but land use was a key driver of EPC_0. The data show agricultural sites had significantly higher EPC_0 values compared to urban sites ($U = 2$, $p < 0.05$). The highest median EPC_0 concentration was measured at agricultural site S3 (252 $\mu g\ L^{-1}$), and the lowest was at urban site S9 (30 $\mu g\ L^{-1}$). The overall median EPC_0 concentration for sampled Laurel Creek sites was 86 $\mu g\ L^{-1}$. The mean EPC of agricultural sites was 148 $\mu g\ L^{-1}$ and the mean EPC_0 for urban sites was 56 $\mu g\ L^{-1}$. Agricultural sites S1 and S3 had the greatest variability in EPC_0 (± 23 and ± 21 around the mean respectively), whereas urban sites S7 and S9 had the lowest variability (± 7 and ± 8 around the mean respectively) (Table 4.1). Overall, agricultural sites had a greater standard deviation than urban sites.

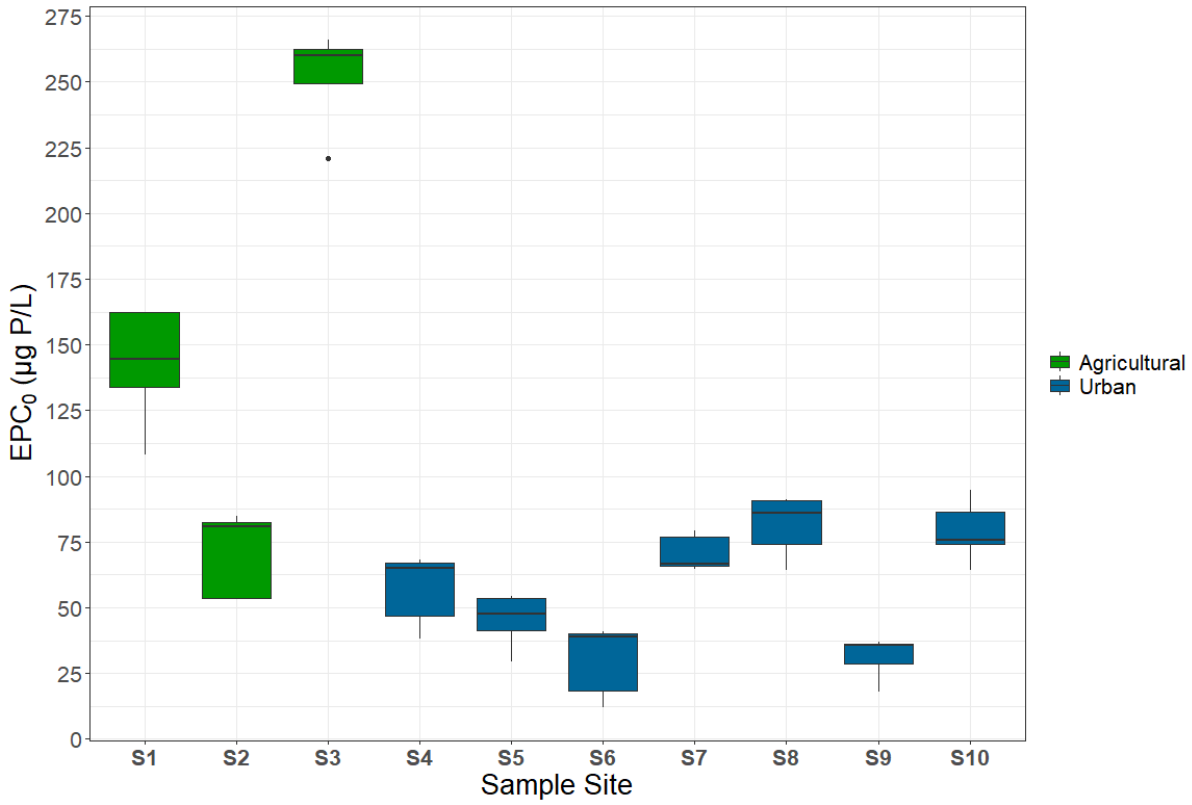

Figure 4.3 - EPC_0 ($\mu g\ L^{-1}$) of riverbed sediment for agricultural (green) and urban (blue) study sites in Laurel Creek (n = 5).

Table 4.1 - Mean (± standard deviation) EPC_0 (µg L^{-1}) of riverbed sediments.

S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
142 ± 23	71 ± 16	252 ± 21	57 ± 14	45 ± 10	30 ± 14	71 ± 7	81 ± 12	31 ± 8	79 ± 12

The potential for riverbed sediment to release P was determined by the EPC_0 for a range of SRP concentrations measured in Laurel Creek (Table 4.2). Minimum and maximum water column SRP concentrations at baseflow were compared to the average EPC_0 isotherm for each site to determine potential P release from riverbed sediment. The data show P release occurred at all sites except for site S6 when SRP concentrations in the water column were at their minimum during the study period. The abiotic control of the SRP concentration in the water column is apparent from the experimental data. During the period of maximum stream SRP, P release likely occurred at S1, S3, S7 and S10. The highest potential P release occurs at site S3 and S1 (range of 6.20 - 13.30 µg g^{-1}, and 4.32 - 8.07 µg g^{-1}, respectively). Site S6 was the only site that had no potential for P release for the entire range of measured water column SRP concentrations during this study (potential P release, -3.28 to -0.10 µg g^{-1}). Site S8 and S5 showed the highest potential P adsorption, at 7.42 µg g^{-1} and 5.55 µg g^{-1} respectively at maximum water column SRP. Sites with the greatest range in potential P release were sites S3, S5 and S8 (7.10, 8.02, and 7.83 µg g^{-1}, respectively), whereas sites S7, S9, and S10 showed the smallest range of potential P release (2.76, 2.59, and 1.28 µg g^{-1}, respectively).

Potential P release from riverbed sediment did not vary longitudinally in Laurel Creek (Table 4.2). However, agricultural sites had a significantly greater potential for P release at both maximum and minimum measured water column SRP concentrations ($U = 2$, $p < 0.05$, $U = 3$, $p < 0.05$, respectively).

Table 4.2 - SRP concentrations (µg L^{-1}) during low-flow between May – September 2024. Average EPC_0 of riverbed sediment (µg L^{-1}) and estimated potential SRP release from sediment (µg g^{-1}) at maximum (A) and minimum (B) observed water column SRP concentrations. Negative P mobility values indicate adsorption.

	Water Column [SRP] (µg L^{-1})		EPC_0	P Mobility (µg g^{-1} sed)	
Site	**Max**	**Min**	**River**	**A**	**B**
1	98.21	59.82	142.32	4.32	8.07
2	72.89	36.05	71.00	-0.18	3.40
3	174.66	86.42	251.68	6.20	13.30
4	61.41	17.88	56.98	-0.42	3.72
5	103.42	19.39	45.26	-5.55	2.47
6	65.21	31.12	30.07	-3.28	-0.10
7	57.37	25.31	70.65	1.15	3.91
8	166.85	76.42	81.14	-7.42	0.41
9	43.65	15.18	31.18	-1.14	1.46
10	41.54	29.48	79.01	3.98	5.27

4.5 Discussion

4.5.1 Water column soluble reactive phosphorus concentrations

Baseflow water column SRP concentrations can vary considerably within and between watersheds due to the impact of upstream land use (Withers & Jarvie, 2008). In Laurel Creek, SRP concentrations in the water column during baseflow varied by an order of magnitude, ranging from 36 – 175 µg L^{-1} at agricultural sites and 15 – 167 µg L^{-1} at urban sites. Soluble reactive P concentrations exceeded the Ontario Provincial Water Quality Objectives (PWQO) for total P of 30 µg L^{-1} at most study sites, indicating a high risk of eutrophication and nuisance aquatic plant and algal growth in these streams (Ontario Ministry of Environment and Energy, 1994). Concentrations of SRP at agricultural sites are comparable to those observed in agricultural systems in other studies (Agudelo et al., 2011; Falk et al., 2021; Hoffman et al., 2009; McDaniel et al., 2009). Significantly higher water column SRP concentrations were observed at agricultural sites, compared to urban sites in this study ($U = 3$, $p < 0.05$) (Table 3.3). Notably, this is contrary to other observations between agricultural and urban SRP (Arfania et al., 2025; Zhang et al., 2019). However, this may be due to inputs from point-sources skewing urban P loads in these studies. For example, McDaniel et al. (2009) found mean SRP concentrations in predominately agricultural Illinois rivers to be

81μg L^{-1} whereas the mean SRP downstream an urban area with a WWTP was 691 μg L^{-1}. As the present study only compares diffuse sources of P, the difference between mean SRP at urban (54 μg L^{-1}) and agricultural (93 μg L^{-1}) sites is lower. Indeed, the mean SRP concentrations at urban sites in Laurel Creek (54 μg L^{-1}) are considerably lower than observations from studies on urban systems influenced by point-source P inputs (Arfania et al., 2025; Ekka et al., 2006; Roberts & Cooper, 2018; Zhang et al., 2019). However, mean urban SRP concentration in Laurel Creek is comparable to the ~35 – 40 μg L^{-1} reported by Haggard et al. (2007) for urban and agricultural pastureland streams in Arkansas, both of which were affected only by diffuse P loading. The Laurel Creek SRP levels are also comparable to observations by Brett et al. (2005) who found mean SRP concentrations of ~30 μg L^{-1} in urban systems with no WWTPs in Washington, USA, and to Sonoda & Yeakley (2007) who found an urban stream SRP of 40 μg L^{-1} in Oregon, USA. Previous research in the Laurel Creek watershed by Rusmir (2001) also found greater SRP concentrations at agricultural headwater sites (S1 & S3 in present study), compared to SRP concentrations at an urban residential site (S5 in present study).

It is widely reported that intensive agriculture lands can be a source of SRP to nearby streams (Foy et al., 1995; Smith et al., 1995), often because of P-rich fertilizer applications. In the present research, site S3 had the highest average SRP concentration (135 μg L^{-1}) and the greatest percentage of upstream agricultural land use (74%). The lowest average SRP concentrations occurred at urban sites S4, S9 and S10 (average 28 - 35 μg L^{-1}). The difference in SRP between site S3 and downstream urban sites (S4 & S6) may partially result from the Laurel Creek and Columbia Lake reservoirs which can retain and store excess P from the agricultural headwaters (Powers et al., 2015; Straškraba et al., 1995; Yu & Stone, 2010). Urban sites S5 and S8 had higher SRP concentrations (97.9 μg L^{-1} combined average) than other urban sites (36.5 μg L^{-1} combined average). Both sites are characterized by a high percentage of urban residential land use (S5: >45%, S8: >50%) and high percent impervious area (S5: >40%, S8: >55%) which suggests sources of P may include residential fertilizer and inputs from road runoff (City of Waterloo, 2023; Indris et al., 2020; Withers & Jarvie, 2008). Changing levels of SRP within Laurel Creek watershed may also be related to stream reaches where P rich groundwater contributes to stream flow. While intensive agriculture has been correlated with elevated levels of TP in groundwater (Holman et al., 2008), SRP concentrations >100 μg L^{-1} in urban streams have also been attributed to the influx of urban groundwater (Qian et al., 2011; Roy & Bickerton, 2014; Roy & Malenica, 2013; Wolf et al., 2012). Groundwater contributes to streamflow in several sections of Laurel Creek; however, only the Monastery and Beaver Creek agricultural tributaries are classified as coldwater streams due to substantial groundwater inputs (Aquifer Beech Ltd., 2019). Melitzer Creek, located in an urban area just southeast of Laurel Creek, is also designated as a coldwater stream, suggesting that groundwater discharge may occur within urban reaches of the LCW study area. If

present, groundwater enriched in P could exert a disproportionate influence on stream SRP concentrations and may help explain the variability observed at urban sites in this study. Future investigations of P dynamics in the LCW would benefit from evaluating potential groundwater sources of P in urban tributaries, particularly Clair and Cedar Creek.

No longitudinal trend was observed for SRP along the Laurel Creek continuum; however, a temporal trend was observed at some sites during the sampling period. Notably, continual increases in SRP concentrations were observed between May – August and the overall average SRP concentration (for all sites) peaked in June for sites S1, S2, S3, and S8. The observed increase in SRP at these sites may partially be related to decreases in baseflow within Laurel Creek during the summer months, although, average daily discharge measurements taken by Environment Canada (gauge #: 02GA024) at site S6 during the sampling period do not fully support this hypothesis. However, base flow at small tributary sites (i.e. S1, S2, S3, & S8) may not fully reflect main channel P dynamics at some sites (i.e. S4, S6, & S10) which are influenced by reservoirs and impoundments in Laurel Creek watershed. During periods of baseflow, water column SRP concentrations are also dependent on interactions with benthic sediments, coprecipitation reactions, and biological cycling (House, 2003; Jarvie et al., 2002; Withers & Jarvie, 2008) which may exert varying influences on SRP as stream conditions change. For example, changing stream pH may influence water SRP concentrations due to increased P sorption of sediment metal oxides at low pH (Strauss et al., 1997; Zhou et al., 2005), or increased co-precipitation of P with Ca minerals at high pH (Corman et al., 2016; House, 2003). Therefore, changes in stream chemistry may be responsible for changing SRP concentrations during the sampling period, however additional data is needed for Laurel Creek to test this.

Table 4.3 - EPC_0 and SRP concentrations (µg L^{-1}) and associated phosphate exchange potential (PEP; at maximum EPC_0 and SRP) for different riverbed sediments across a variety of landscapes and land use.

Authors	Location	Land use/Impacts	Site/ River	EPC_0	SRP	PEP	Sediment P buffering
This study	Ontario, Canada	Agricultural	Upper Laurel Creek	71 - 252	36 - 175	0.16	Source
This study	Ontario, Canada	Urban	Mid – lower Laurel Creek	30 - 81	15 - 167	-0.31	Sink
Hoffman et al., 2009	Wisconsin, USA	Agricultural	Dorn Creek	6.2 - 710	80	0.95	Source
Arfania et al., 2025	Iran	Urban	Shahar Chai	230	250	-0.04	Sink
Arfania et al., 2025	Iran	Agricultural - Urban	Lake Urmia watershed	360 - 700	130 - 320	0.34	Source
Reddy et al., 1996	Florida, USA	Dairy farms/pasture	Otter Creek	120 - 150	590 - 1900	-1.10	Sink
Jarvie et al., 2005	SW, UK	Agricultural/pasture/ sewage	Avon	2 - 230	3 - 573	-0.40	Sink
Wang and Pant, 2015	New York, USA	Urban, WWTP	Bronx River	20 - 730			
Falk et al., 2021	Ontario, Canada	Agricultural	Big Creek	5	71	-1.15	Sink
Zhang et al., 2019	Eastern China	Urban	Shiwuli River	325	1030	-0.50	Sink
Zhang et al., 2019	Eastern China	Rural	Hangbu River	143	18	0.90	Source
Agudelo et al., 2011	Kansas, USA	Agricultural	Upper West Emma Creek	125	140	-0.05	Sink
Machesky et al., 2010	Illinios, USA	Agricultural	Spoon River	13 - 87	23 - 33	0.42	Source
McDaniel et al., 2010	Illinios, USA	WWTP	Vermilion watershed (SF)	251 - 347	238 - 1670	-0.68	Sink
McDaniel et al., 2010	Illinios, USA	Agricultural	Emarras watershed (BLS)	56	51	0.04	Source
Haggard et al., 2007	Arkansas, USA	Urban	Ozark streams (various)	100	38	0.42	Source
Haggard et al., 2007	Arkansas, USA	Pasture	Ozark streams (various)	125	36	0.54	Source

4.5.2 Equilibrium phosphate concentrations

At baseflow, concentrations of SRP in the water column are regulated by streambed sediment through process referred to as the "phosphate buffer mechanism" (Froelich, 1988). This is commonly measured using the equilibrium phosphate concentration (EPC_0) which represents the SRP concentration at which adsorption and desorption of phosphate from the sediment are equal (Froelich, 1988; Taylor & Kunishi, 1971). Values of EPC_0 vary widely in many locations across the globe as a function of land use (Table 3.3). For example, EPC_0 concentrations >1000 μg L^{-1} have been measured in agricultural (Weigelhofer, 2017), urban point-source (Ekka et al., 2006) and wildfire influenced (Son et al., 2015) landscapes. Alternatively, EPC_0 concentrations <10 μg L^{-1} have been observed in other catchments, across a variety of different geologies, stream morphology and flow characteristics, as well as land use (Falk et al., 2021; Hoffman et al., 2009; Jarvie et al., 2005; McDowell, 2015; Stutter & Lumsdon, 2008). This variability exists because the EPC_0 of streambed sediments reflects underlying geochemical processes that are influenced by the physical and geochemical composition of streambed sediment, sediment - water interactions, water chemistry, biological activity, and methodological considerations (Simpson et al., 2021). Notably, comparisons of EPC_0 across various landscapes and land management practices studies should be done cautiously but data from similar landscapes can be useful to interpret hydrological and geochemical processes that are relevant for modelling P dynamics in streams.

Studies on P sorption behavior in rivers have primarily focused on systems influenced by agricultural and urban point sources (WWPTs) (Simpson et al., 2021), with considerably less research on bed sediment-P dynamics in small urban watersheds. In Laurel Creek the average streambed sediment EPC_0 was 148 μg L^{-1}, and 56 μg L^{-1} for agricultural sites and urban sites, respectively. The EPC_0 for bed sediment at agricultural sites in Laurel Creek was comparable to results from other agricultural watersheds from around the globe (Agudelo et al., 2011; Haggard et al., 2007; Jarvie et al., 2005; Reddy et al., 1996). The highest average EPC_0 was observed at agricultural site S3 (252 μg L^{-1}) which falls within range of observations from point-source influenced urban systems (Arfania et al., 2025; McDaniel et al., 2009; Zhang et al., 2019). When considered alongside the elevated SRP concentrations at site S3, these results suggest that this site receives substantial P inputs, likely from agricultural nonpoint runoff or from the deposition of P-enriched sediments derived from surrounding soils and streambanks. As this site was located directly adject row-crop agriculture, enhanced P input at this site may also stem from tile-drain inputs depending on hydrological events (Macrae et al., 2007),

soil moisture conditions (Lam et al., 2016), fertilizer timing (Macrae et al., 2010), and irrigation (Stone & Krishnappan, 2002). Although site 2 had >60% upstream agricultural land cover, its EPC_0 did not reflect the elevated values observed at other agricultural sites. The comparatively low EPC_0 at this site is likely attributable to its location within a wetland area, where enhanced P sorption capacity associated with greater organic matter accumulation (Evans et al., 2004), and reduced SRP loading driven by increased biotic uptake (Reddy et al., 1999), may collectively suppress EPC_0 relative to other agriculturally influenced sites.

The EPC_0 of urban streambed in Laurel Creek is considerably lower than values from other urban studies (Table 4.3), likely due to a lack of point source P inputs which has been shown to increase streambed EPC_0 in other studies (Ekka et al., 2006; Simpson et al., 2021). Additionally, differences in sediment physio-geochemical properties, exchangeable P, and water chemistry may also influence P sorption (Froelich, 1988; Simpson et al., 2021; Stone & Droppo, 1994). The EPC_0 values at urban sites in the present study are comparable to EPC_0 concentrations reported by Haggard et al. (2007) in diffuse P influenced urban systems in Arkansas, USA (Table 4.3).

No obvious longitudinal downstream trend in EPC_0 was observed along Laurel Creek, however, agricultural sites had a significantly higher EPC_0 than urban sites ($U = 2$, $p < 0.05$), which may be related to P loading and streambed sediment physio-geochemistry. Streambed EPC_0 can reflect upstream P inputs (Ekka et al., 2006; Jarvie et al., 2005; Stutter et al., 2010) suggesting a decrease in EPC_0 with downstream distance from P sources. In LCW, there was a considerable decrease in EPC_0 between the agricultural headwaters and downstream site S4, followed by a smaller decrease in EPC_0 between site main channel sites S4 and S6 and an increase at S10. Assuming diffuse P loading in Laurel Creek is greatest in the agricultural headwaters, a decrease in downstream EPC_0 within the main channel is expected. The dramatic change in EPC_0 between the headwaters (S1 – S3) and S4 may be explained by the reservoirs attenuating downstream transport of P-rich sediment and SRP (Powers et al., 2015; Shantz et al., 2004; Straškraba et al., 1995). Indeed, a study by Yu & Stone (2010) found that the Columbia Lake impoundment in LCW acted as a sink for fine sediment and P. The smaller decrease in EPC_0 between S4 and S6 may be related to the downstream distance from the P source. The higher EPC_0 at S10 likely reflects additional non-point P sources in the lower reaches of Laurel Creek, such as runoff from storm sewers.

To determine the P mobility, sediment EPC_0 measurements are compared to overlying water column SRP concentrations. It was observed that streambed sediment can act as a potential P source for nearly all sites during periods of low SRP. Alternatively, the streambed may act as a potential sink for sediment at most urban sites (S4, S5, S6, S8, & S9) and at agricultural site S2 during periods of high stream SRP. It is important to note that streambed sediment was only sampled once (May 9th, 2024), therefore P mobility for subsequent sampling periods assumes that EPC_0 in Laurel Creek did not change dramatically after sampling. Sediment-water P exchange at most sites does not appear to be at equilibrium, based on the ±20% EPC_{sat} range [$EPC_{sat} = 100 \times [(EPC_0 - SRP)/EPC_0]$; from Jarvie et al., (2005)], which corresponds to results from published literature (Simpson et al., 2021). The lack of equilibrium may suggest insufficient water residence time within the stream to achieve a steady state, or it may represent the variability of water column SRP relative to the EPC_0, which reflects stream conditions over longer timescales (Jarvie et al., 2005). Other studies have reported sediment P buffering behavior for rivers with different land use (Table 3.3). Like some urban sites in this study, sediment appears to act primarily as a potential P sink in urban systems (Arfania et al., 2025; Ekka et al., 2006; Roberts & Cooper, 2018; Zhang et al., 2019), although many of these watersheds are characterized by high SRP loading from WWTPs. In the literature, results from agricultural streambed sediment appear to be more variable, some acting as a potential P sink (Agudelo et al., 2011; Falk et al., 2021; Jarvie et al., 2005; Reddy et al., 1996; Stutter & Lumsdon, 2008), while others act as a potential P source (Arfania et al., 2025; Haggard et al., 2007; Hoffman et al., 2009; Machesky et al., 2010; McDaniel et al., 2009; Zhang et al., 2019). In Laurel Creek, agricultural streambed sediment primarily acted as a potential source for P. The variability in P mobility within these systems demonstrates the complex influences on sediment-water interactions and may also represent differences in methodology used for determining the EPC_0.

4.5.3 Phosphate exchange potential

To better compare differences in P mobility within Laurel Creek and with previous research, the phosphate exchange potential (PEP) was calculated for each site based on work by (Simpson et al., 2021). The PEP reflects differences in SRP concentration of the water column and EPC_0 which permits comparison between systems with high and low P loading while accounting for scale (Simpson et al., 2021). Phosphate exchange potential has only been used in a handful of studies to evaluate P mobility (Kreiling et al., 2023, 2025; Li et al., 2023); therefore, PEP has been calculated retroactively for some

studies citied in this thesis to compare (Table 4.3). In this study average PEP at agricultural sites was 0.19, demonstrating P release potential, although not to the same degree as other agricultural watersheds, which had PEPs >0.40 (Haggard et al., 2007; Machesky et al., 2010; Zhang et al., 2019). Urban sites S4, S7, S9, & S10 had a positive average PEP of 0.22, whereas sites S5, S6, & S8 had a negative average PEP of -0.19, indicating changing sediment P sink/source behavior within Laurel Creek. Although urban systems generally act as a sink for P, the PEP varies considerably among studies, from values >0.40 (Haggard et al., 2007; McDaniel et al., 2009; Roberts & Cooper, 2018; Zhang et al., 2019) to values <0.05 (Arfania et al., 2025; Ekka et al., 2006). Notably, agricultural sites had a positive PEP over nearly the entire range of observed SRP concentrations, indicating agricultural streambed sediments are functioning as consistent net sources of SRP to the water column during summer baseflow. Similarly, Kreiling et al. (2023) found that streambed sediment in the agricultural headwaters of the Maumee River watershed (USA) acted as a P source during periods of low SRP. Alternatively, urban sites displayed divergent sink and source behavior likely reflecting the complexity of urban P inputs, altered sediment geochemistry (Chapter 3), and hydrological interactions (House et al., 1995) within the urban stream network. Variation in urban streambed sink/source behavior was also observed by Kreiling et al. (2025) in the urban watersheds of Milwaukee USA, where PEP reflected changes to streambed physio-geochemical properties and P inputs. The absence of a consistent pattern in P sink/source behavior at urban sites in this study demonstrates the complexity of P dynamics in urban stream systems and the inability to assume uniform behavior across urban reaches.

The PEP for Laurel Creek study sites during low SRP is shown in Figure 4.4. Nearly all sites show a relatively similar potential to release P (except for S6 and S8), a detail which cannot be observed with calculated potential P release values (Table 4.2), as they haven't been corrected for scale. Notably, although SRP and EPC_0 vary considerably within the watershed, the potential P mobility is relatively uniform throughout Laurel Creek during low SRP. This does not appear to be the case for high SRP conditions (Figure 3.4). At high SRP a diminished positive PEP remains at sites S1, S2, S7, & S10, with large negative PEP at sites S5, S6, & S8 and a smaller negative PEP at S9. Sites S6 and S8 fall within the range of equilibrium (±20% EPC_{sat}; Jarvie et al., 2005) during low SRP and S2 and S4 are at equilibrium during high SRP. Interestingly, site S5 shows a high positive PEP (≈ 0.35) during low SRP and a high negative PEP (≈ -0.35) during high SRP. This is due to the large variation of SRP around the EPC_0 at S5. This means that P adsorbed by the streambed during periods of high SRP could be released back into the water column as SRP changes within the tributary, suggesting the streambed

at site S5 can only buffer stream SRP over short time periods. Overall, sediment appears to act primarily as a source for P in Laurel Creek, with high sediment buffering potential (i.e. negative PEP) only occurring at 40% of the sites while the SRP concentrations are elevated during summer low flows. Potential equilibrium was only observed at 20% of the sites during both minimum and maximum SRP periods, suggesting EPC_0 and SRP were substantially different during baseflow in Laurel Creek.

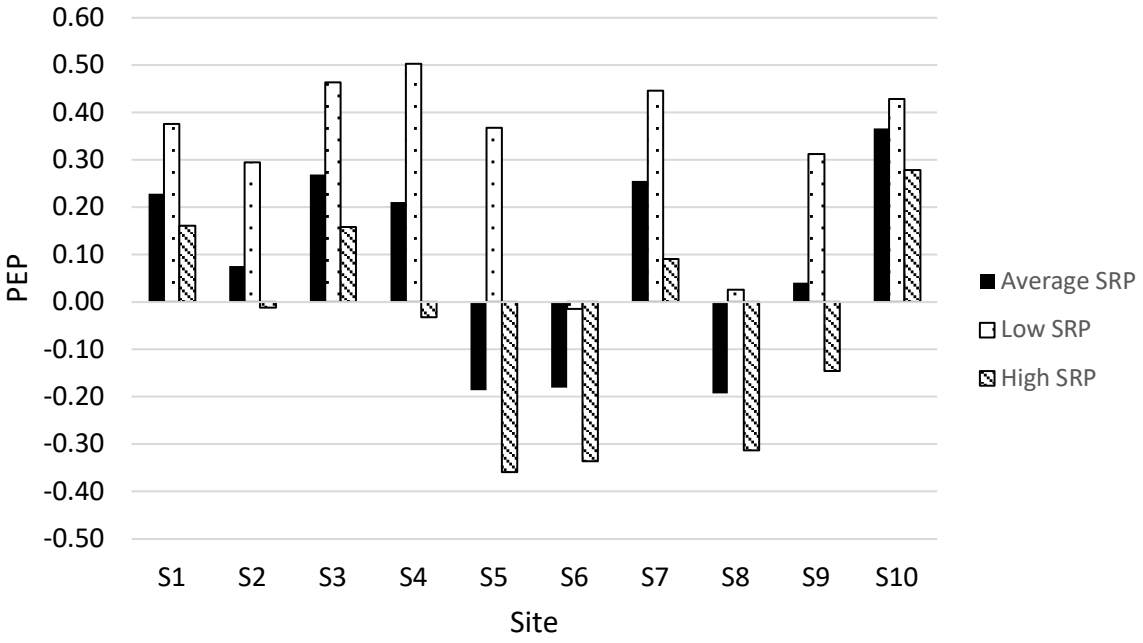

Figure 4.4 - Phosphate exchange potential (PEP; from Simpson et al., 2021) at Laurel Creek Sampling sites for average, minimum, and maximum observed water column SRP concentrations.

4.5.4 Relationship between EPC_0 and SRP

Previous studies have shown that streambed EPC_0 and SRP are well-correlated during baseflow (Agudelo et al., 2011; Haggard et al., 2007; Jarvie et al., 2005; Lottig & Stanley, 2007), which makes EPC_0 a good potential indicator for long-term baseflow SRP concentrations in streams (McDowell, 2015). In the present study, average site SRP and EPC_0 were well correlated ($\rho = 0.62$, $p = 0.0502$) (Figure 4.5), which matches closely to the correlation between SRP and EPC_0 observed over a range of riverine environments in a systematic review of literature ($\rho = 0.717$, $p = 1.8 \times 10^{-149}$) by Simpson et al. (2021). This suggests that sediment-P exchange is a meaningful driver of water column SRP

concentrations in LCW. However, examining the relationship between SRP and EPC_0 separately for agricultural and urban sites shows that SRP and EPC_0 have a much stronger positive correlation at agricultural sites than at urban sites (Figure 4.6). This suggests potentially varying biogeochemical influences on P mobility between different reaches of the Laurel Creek watershed. The disparity between SRP and EPC_0 at urban sites may be a result of reduced sediment-water interactions (Withers & Jarvie, 2008), limited P sorption affinity (McDowell, 2015), variable SRP concentrations, or the altering of streambed sediment EPC_0 by high-flow events (McDowell et al., 2019; Stutter et al., 2009; Stutter & Lumsdon, 2008).

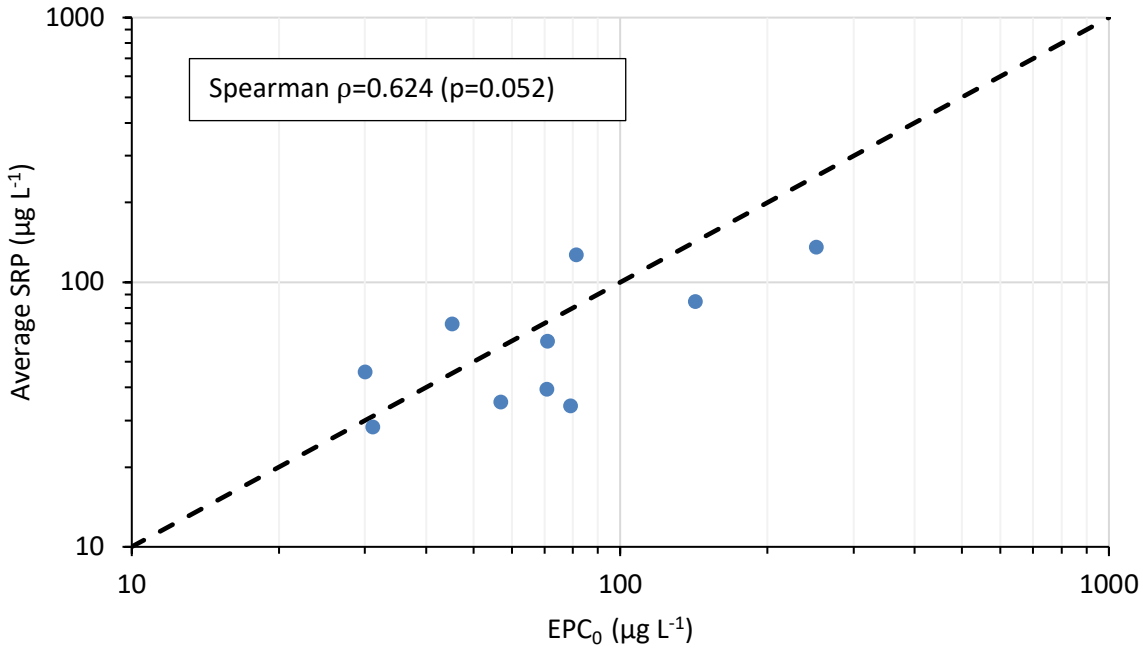

Figure 4.5 - Correlation between average water column SRP (µg L^{-1}) during study period (May – September 2024) and EPC0 (µg L^{-1}) for Laurel Creek sampling sites. The dashed line is the 1:1 line.

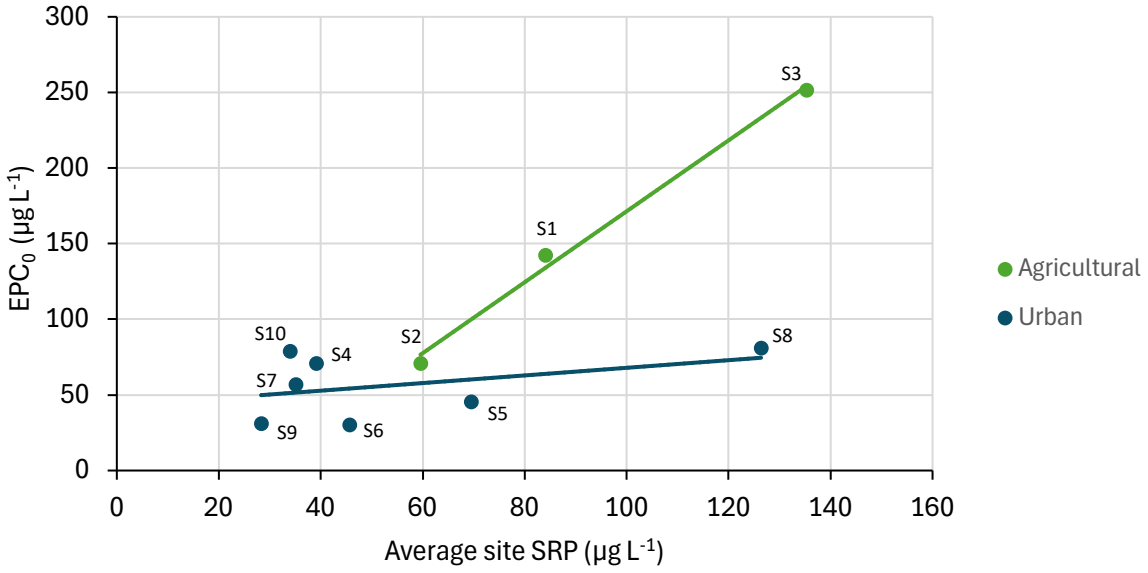

Figure 4.6 - The relationship between average water column SRP (µg L^{-1}) concentration during study period (May – September 2024) and EPC_0 (µg L^{-1}) at Laurel Creek study sites, separated by land use (agricultural = green, urban = blue). Agricultural R-square = 0.97 ($p < 0.05$), Urban = no significant relationship.

4.5.5 Controls on phosphorus mobility

Stream characteristics such as geomorphology and flow velocity may influence P mobility by affecting sediment properties and sediment – water interactions (Agudelo et al., 2011; House et al., 1995). For example, fine sediment is preferentially transported downstream and deposited in stream pools compared to coarser sediment (Hoffman et al., 2009). Since fine sediments have a greater P-sorption capacity (Stone & Mudroch, 1989), stream features storing more fine sediment may have altered P-mobility (Hoffman et al., 2009). Furthermore, geomorphic characteristics of the channel can influence flow and residence of water within a stream, changing sediment-water contact times possibly impacting sediment-P equilibrium (Withers & Jarvie, 2008). Urban sites in the present study are generally channelized, with steep banks, and some in channel deposits (i.e. midchannel bars). They are often characterized by high flow velocities and limited fine sediment storage (Walsh et al., 2005). Conversely, the agricultural headwater streams are more sinuous, generally have shallow banks and have more in-stream structures and vegetation. This stream environment favors lower flow velocity and

increased fine sediment storage, which can increase sediment – water interactions leading to greater nutrient uptake and retention (Bukaveckas, 2007; Withers & Jarvie, 2008). In such transport-limited agricultural headwaters P-rich sediment can accumulate and act as a persistent source of P (Kreiling et al., 2023; Williams et al., 2016). Therefore, in the present research, higher flow velocities and limited fine streambed sediment may limit streambed nutrient storage at urban sites, which may partially explain the poor relationship between EPC_0 and SRP at these sites.

Although EPC_0 cannot be compared based on sediment grain size in this study due to the similarity of sampled sediment, the distribution of fine sediment within Laurel Creek may still provide some insights into the P cycling within the watershed. Fine sediment generally has a greater ability to adsorb P due to higher surface area and geochemical composition (more clay minerals), resulting in higher PP but lower EPC_0 than coarse sediment (Lottig & Stanley, 2007; Stone et al., 1995; Stone & Mudroch, 1989). In the present research, abundant fine sediment was collected within the streambed at the agricultural sites (S1-S3), whereas the stream bed at urban sites (S4-S10) was dominated by sand, coarse gravel and boulders. Generally, streams with a high fine sediment concentration and high SRP loading act as a sink for P (Simpson et al., 2021), whereas the agricultural sites in this study acted as a P source. Notably, this may indicate saturation of P sorption sites (Sposito, 2004) in the agricultural streambed sediment (particularly S1 & S3) due to continuous high P loading, or the deposition of P-rich agricultural field soils in the streambed (Agudelo et al., 2011). In this case the streambed sediment may act as a source of P to the water column (Jarvie et al., 2005).

Prolonged high SRP loading may lead to increased EPC_0 and exchangeable P (Ekka et al., 2006; Jarvie et al., 2006; Stutter et al., 2010). Long-term SRP loading from agricultural activities at sites S1 and S3 may therefore result in high EPC_0. Alternatively, urban sites in Laurel Creek may experience predominately low SRP loading with high variability, leading to low streambed EPC_0 and exchangeable P. Exchangeable P can influence EPC_0 (Simpson et al., 2021), however, given the multitude of operationally defined P extraction schemes (Condron & Newman, 2011), exchangeable P can be difficult to define. In the present study, NAIP is the most labile P fraction and may act as a rough proxy for exchangeable P. Jarvie et al. (2005) determined that streambed sediment with low exchangeable P concentration will have a high affinity for SRP uptake. In the present research, sites with the lowest concentration of NAIP (S5 and S8) also had the greatest negative PEP (Figure 3.4) and potential P adsorption values (Table 3.2). Positive relationships between EPC_0 and exchangeable P have been

reported (Ezzati et al., 2020; Zhang & Huang, 2007), suggesting a weaker potential P buffer for sediments with high concentrations of exchangeable P (Simpson et al., 2021). In Laurel Creek, NAIP was not correlated with either EPC_0 or PEP, however sites with high NAIP (i.e. S1, S2, S3, & S10) generally all had high positive PEP indicating potential for P release.

Stream temperature may also influence EPC_0 by increasing anoxia at the sediment-water interface, resulting in an increased release of SRP into the water column (Cai & Sayles, 1996; House & Denison, 2002a). Although stream temperature was not measured directly in this study, it is well known that urban streams suffer from increased stream temperature (Caissie, 2006; Walsh et al., 2005). Monitoring work in the Laurel Creek watershed by Aquifer Beech Ltd. (2019) and the City of Waterloo (2023) has shown higher stream temperatures in the urban reaches of the watershed compared to the groundwater fed agricultural headwaters. Therefore, an increased release of sediment P as SRP due to high stream temperature could result in reduced sediment P storage and explain a lower EPC_0 at urban sites. Furthermore, higher stream temperatures can also be associated with higher pH, which has also been observed to increase SRP release from sediment (House & Denison, 2002a). However, pH data from the Laurel Creek Water Monitoring study City of Waterloo (2023), show no considerable difference in pH among sample sites in the present study. It is suggested that future research on P mobility within Laurel Creek considers measuring stream temperature, dissolved oxygen, and pH to properly examine the influence of stream water chemistry on P mobility.

Additionally, the EPC_0 in lotic systems may be altered by high-flow events or changing sediment sources by the deposition of new streambed sediment (Emelko et al., 2016; McDowell et al., 2019). Given that streambed sediment was only sampled once (May 9th, 2024) in the present study, P mobility estimations assume a stable EPC_0. However, a large storm event on July 16th, 2024, may have been sufficiently large to significantly alter streambed sediment composition (Peak discharge of 5.49 m^3/s). Therefore, water column SRP results for the August and September sampling periods could be based on a fundamentally different streambed sediment EPC_0 or sediment P buffering capacity (Smith et al., 2006). Concentrations of SRP are considerably different between the June 14th and August 5th sampling periods at sites S3, S4, S5, & S6, which may be representative of new streambed sediment influencing P mobility, however more detailed sediment and water sampling would be required to test this.

Finally, another control on sediment transport and deposition within Laurel Creek are the Laurel Creek reservoir, and Columbia Lake and Silver Lake impoundments located between site S3 and S4.

The stark contrast in SRP and EPC_0 between the agricultural headwaters (S1, S2, & S3) and downstream urban sites (i.e. S4 & S6) suggest that the multiple reservoirs are functioning as a control on downstream P transport in the watershed (Powers et al., 2015). This pattern reflects the findings of Chapter 3, where TPP and NAIP were considerably higher upstream of the impoundments. Downstream of impoundments, the reduced supply of high-EPC_0 agricultural sediment and its replacement by sediment with different geochemical characteristics may reduce the net P release potential of the streambed. However, the retention of P behind impoundments may be temporary as the reservoirs may release this stored P during drawdown in the Fall. It has been observed by Shantz et al. (2004) that abundant P-rich fine sediment is resuspended within the Columbia Lake reservoir during drawdown, which may get transported and deposited in the downstream streambed. Therefore, sediment EPC_0 and associated streambed P dynamics may change significantly during this period. It is recommended that future research examine the change in streambed EPC_0 before and after reservoir drawdown to further understand P dynamics within Laurel Creek.

4.6 Conclusions

This study was conducted to examine abiotic controls on P-mobility of fine streambed sediment across the small urban Laurel Creek watershed during environmentally sensitive low flow conditions. Conclusions of this study include:

1. Sediment P mobility reflects land use, but with important spatial differences
    - Average EPC_0 at agricultural sites was 148 µg L^{-1} and 56 µg L^{-1} at urban sites, indicating greater P release potential at the agricultural sites.
    - Strong correlation (ρ = 0.62, p = 0.0502) between EPC_0 and average SRP concentrations in LCW suggests that sediment-P mobility is a meaningful driver of water column SRP concentrations.
    - However, the insignificant correlation between EPC_0 and SRP at urban sites implies that water column SRP in urban reaches is governed by additional or alternative processes (e.g. complex P sources and limited P sorption affinity) that decouple sediment-water P exchange from ambient dissolved P concentrations.
2. Agricultural sites are a potential net source of P to the water column
    - The positive average phosphate exchange potential (PEP) at agricultural sites (0.19) suggest that agricultural streambed sediments are functioning as net sources of SRP to the water column.
3. Urban sediment source/sink behavior is spatially variable and complex
    - Unlike agricultural sites, urban sites displayed divergent sink and source behavior. Sites S4, S7, S9, and S10 exhibited positive average PEP (0.22), indicating net P release, while sites S5, S6, and S8 showed negative PEP (-0.19), indicating net P retention.
    - This spatial heterogeneity likely reflects the complexity of P inputs, sediment geochemistry, and reduced sediment-water interactions within the urban stream network.
4. Impoundments likely attenuate EPC_0 downstream
    - Lower EPC_0 values at sites downstream of impoundments relative to upstream sites mirrors the pattern observed for TPP and NAIP (Chapter 3), and is consistent with the role of impoundments in trapping fine, P-enriched sediment.

Chapter 5
Synthesis and conclusions

5.1 Study context

Phosphorus loading from agricultural and urban land use remains a primary driver of eutrophication in freshwater ecosystems (Schindler, 2006), with tributary streams playing a central role in regulating P form, storage, and delivery to receiving water bodies such as Lake Erie (Steffen et al., 2014; Withers & Jarvie, 2008; Zhou et al., 2015). While the importance of sediment-bound P as a legacy source is well established (Sharpley et al., 2013), critical gaps exist in the understanding of how urban land use influences PP form and concentration, and how streambed sediment mediates P mobility in small, diffuse-source urban catchments. Small streams are disproportionately impacted by surrounding land use and engineered hydrological modifications (Fernández et al., 2014; Graf et al., 2016), yet P dynamics along these stream continuums remains poorly characterized. As urban areas continue to expand, a full understanding of how urban landscapes alter P transport and transformations along a stream system is needed to predict P loading trajectories and inform targeted management of downstream water quality (Kaushal et al., 2014). The present research sought to address these gaps by examining the form and mobility of P in streambed sediments across the small, urban, Laurel Creek Watershed.

5.2 Chapter 3 – Controls on the source and variability of phosphorus forms in bed sediment of an urban stream

Fine streambed sediment was sampled across different tributaries and main channel sites within the Laurel Creek Watershed (LCW), revealing substantial spatial variability and strong land use controls on streambed sediment P dynamics. TPP concentrations of LCW fine streambed sediment ranged from 424 to 1220 µg g^{-1}, where the highest concentrations of TPP were found in sediment from agricultural headwaters (1001 – 1220 µg g^{-1}), and the lowest TPP concentrations (424 – 709 µg g^{-1}) were measured within highly urban downstream tributaries (sites S5 – S9). The range in TPP observed in this thesis is comparable to other studies on urban-agricultural systems (Barral et al., 2012; Lin et al., 2009), however, urban TPP concentrations were considerably lower than TPP in urban systems impacted by WWTPs. Bioavailable NAIP enrichment of TPP ranged from 24% to 64%, with significantly greater

enrichment at agricultural sites (average 58%) relative to downstream urban sites (average 37%). These patterns were closely linked to differences in sediment geochemical composition. Agricultural sediments were enriched in Fe, Al, Mn, and organic matter, whereas urban sediments were dominated by Ca, Mg, and Na. The strong positive correlations between NAIP and Fe, Al, Mn, and organic matter both from spearman rank correlation and PCA loadings, confirm that sediment geochemistry as a primary control on bioavailable P retention in LCW. Impoundments further modified longitudinal P patterns, with greater TPP and NAIP concentrations observed upstream of impoundments relative to downstream reaches, consistent with their ability to capture and store fine sediment and P.

These results emphasize differences in the severity of diffuse P loading from agricultural and urban reaches of LCW. The elevated TPP and NAIP concentrations at agricultural headwater sites reflect the legacy of long-term fertilizer applications and sustained P enrichment of soils and fine sediment, which persists as an ongoing source of bioavailable P to the stream network. The high proportion of NAIP at agricultural sites should be noted, as this fraction is the most readily exchangeable with the water column and therefore most likely to contribute to in-stream SRP concentrations and downstream eutrophication risk. Remobilization events driven by high flows or shifts in redox conditions could release SRP from these sediments, independent of external P inputs. This reinforces the concept of sediment P legacy as a long-term water quality concern that must be considered alongside efforts to reduce current P loading from the landscape.

The unique geochemical composition of agricultural and urban sediments has important implications for how P is retained and released along the stream continuum. In urban streambed sediments, the elevated concentrations of Ca, Mg, and Na, and their negative correlation with NAIP, reflect a lower capacity for bioavailable P retention relative to Fe and Al-rich agricultural sediments. This suggests that urban streambed sediment in LCW has a lower inherent capacity to retain bioavailable P, reducing the ability of streambed sediment to buffer P inputs, potentially increasing the proportion of SRP transmitted downstream. Impoundments introduce additional complexity by acting as potential P sinks, attenuating downstream fluxes of fine sediment and associated PP. However, P stored in these captured sediments may be remobilized under altered hydrological or geochemical conditions, such as Fall drawdown, representing a future loading risk to receiving waters.

Collectively, these results demonstrate that effective management of P loading in urbanizing watersheds requires continuum-based approaches that account for the interacting influences of land

use, sediment geochemistry, and engineered infrastructure. Agricultural headwaters warrant particular attention as disproportionate sources of bioavailable sediment-bound P, even within predominantly urban watersheds. As urban expansion continues to modify the ecohydrological and geochemical character of stream networks draining to Lake Erie and other sensitive receiving waters, understanding the spatial distribution of legacy P stores and the factors controlling their mobility will be essential for accurately predicting P loading trajectories and designing targeted interventions to protect downstream water quality.

5.3 Chapter 4 – Sediment-phosphorus buffering in an urban stream during baseflow

This study examined sediment-P mobility and water column SRP dynamics across an agricultural-urban watershed continuum, revealing spatial variability in P exchange behavior that was strongly governed by land use and the presence of impoundments. Water column SRP concentrations varied considerably across the watershed, ranging from 28 to 135 µg L^{-1}, with significantly higher concentrations at agricultural headwater sites relative to downstream urban reaches ($U=3$, $p<0.05$). However, SRP concentrations at highly residential urban sites (S5 & S8) were comparable to those measured at intensive agricultural sites, suggesting that residential land use can generate dissolved P loading of equivalent magnitude to agricultural sources. This is likely due to P inputs from stormwater runoff, lawn fertilization, and leakage from sewer or septic infrastructure. The increase in SRP at many sites across LCW between May and August raise water quality concerns, as declining dilution and elevated temperatures during summer baseflow create conditions conducive to eutrophication in downstream receiving waters.

Results from the EPC_0 bench-scale experiments reinforce the land use-driven pattern observed in water column SRP. Sampled sediment in the LCW had a mean EPC_0 of 86 µg L^{-1}, with significantly higher averages ($U = 2$, $p<0.05$) at agricultural sites (148 µg L^{-1}) compared to urban sites (56 µg L^{-1}). The strong positive correlation between EPC_0 and ambient SRP across the watershed, and particularly at agricultural headwater sites, indicates that sediment P release is a primary driver of dissolved P concentrations in headwater reaches. This suggests that EPC_0 is a meaningful predictor of P loading potential in agricultural portions of the watershed, consistent with findings from comparable catchments. In contrast, the weak correlation between EPC_0 and SRP at urban sites implies that water column dissolved P concentrations in urban reaches are governed by processes beyond sediment-water

exchange alone, including episodic stormwater inputs and spatially variable P sources that introduce dissolved P largely decoupled from sediment dynamics.

The phosphate exchange potential (PEP) results highlight the variable source and sink behavior of P across LCW. Most agricultural streambed sediments acted as net sources of SRP to the water column, with an average PEP of 0.19. This suggests that streambed sediment legacy P within headwater reaches of LCW represents a sustained internal loading mechanism. While the magnitude of release appears moderate relative to other agricultural systems, this source behavior has implications for downstream P loading, particularly during ecologically sensitive summer baseflow periods. Alternatively, urban sediments displayed more complex and spatially variable behavior. Several urban sites exhibited net P release potential (average PEP of 0.22), while others functioned as net P sinks (average PEP of -0.19), with no consistent longitudinal pattern evident across the main channel. Additionally, select urban sites (S4, S5) alternated between potential sink and source behavior based on fluctuations of water column SRP throughout the study period. This heterogeneity of P mobility likely reflects the complexity of P inputs, variable sediment composition, and the influence of engineered hydrological features across the urban stream network and highlights the limitations of treating urban watersheds as uniformly behaving systems in watershed P assessments.

Impoundments may act as important structural controls on P mobility in LCW, as EPC_0 was substantially lower directly below impoundments relative to those upstream. This suggests that impoundments attenuate the downstream transmission of mobile, P-enriched sediment, reducing the net P release potential of streambeds in downstream reaches. While this may represent a short-term reduction in P delivery to receiving waters, P accumulated in impoundment-associated sediments may be remobilized when reservoir conditions change, representing a long-term loading risk. These findings further highlight the need for continuum-based approaches to P management in urbanizing watersheds, accounting for heterogeneous behavior of urban streambed sediments, and the modifying influence of engineered infrastructure, to effectively reduce P loading to sensitive downstream receiving waters such as Lake Erie.

5.4 Future work

5.4.1 Suspended sediments and event sampling

This study provides novel insight into PP form and mobility along an agricultural–urban continuum; however, further work is required to fully resolve P dynamics in such systems. While streambed sediment P buffering can dominate under summer baseflow conditions (Simpson et al., 2021), P flux is also strongly governed by suspended sediment transport during high-flow events (Kerr et al., 2011). Future research should therefore incorporate event-based sampling and suspended sediment collection to better constrain P mobilization under variable hydrological regimes.

5.4.2 Temporal variability of sediment-P dynamics

Although streambed sediments integrate past conditions and provide a useful indicator of potential P loading (McDowell, 2015), they are not static. Shifts in hydrological or geochemical conditions may alter sediment composition through deposition or transformation processes (Emelko et al., 2016; Evans et al., 2004). As such, the results presented in this study only represent a snapshot of LCW P dynamics. Expanded temporal sampling would enable identification of seasonal variability and critical periods of P export in LCW.

5.4.3 Examining additional controls on diffuse P loading and transport

In urban reaches, P storage and flux are likely influenced by additional processes, including fine-sediment ingress into the bed armor layer (Karna et al., 2015), sediment redox conditions (Ye et al., 2024), and groundwater contributions (Holman et al., 2008). Quantifying sediment ingress and streambed erosivity would improve understanding of sediment-associated P storage and transport risk, while direct measurement of hyporheic redox conditions would help constrain the mobility of Fe-P phases. Further, to gain a better perspective of urban diffuse sources of P, it would be recommended to measure inputs from storm drains, stormwater ponds, and storm sewers (Zhou et al., 2026). Additionally, measuring potential groundwater contributions to stream P concentrations could be informative, as groundwater has been observed to increase P concentrations in other urban watersheds (Roy & Bickerton, 2014).

5.4.4 Water chemistry and impoundment sampling

This study was limited in its ability to take comprehensive and repeat measurements of various stream water conditions that may influence P-mobility, such as temperature, pH and redox. Therefore, published or publicly available data was used to make general statements about possible water chemistry impacts on P mobility across LCW. To improve confidence and reliability, it is recommended that future studies examine these stream water characteristics, when evaluating P-mobility. Finally, impoundments appear to exert an important control on PP form and mobility within the LCW. However, more detailed sampling of inflows, outflows, and deposited sediments is needed to better resolve P retention and transformation within these impounded systems.

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Appendix A

Supplementary information and data

Photographs of study sites:



Figure A1 – Site 1 (S1): Monastery Creek, agricultural headwater stream with some wetland/forest.



Figure A2 – Site 2 (S2): Upper Laurel Creek, agricultural headwater stream, also drains wetland.



Figure A3 – Site 3 (S3): Beaver Creek, agricultural headwater stream. Highest percentage of agricultural land use, ~1 km upstream Laurel Creek Reservoir.



Figure A4 – Site 4 (S4): Mid-Laurel Creek, urban site in main channel. About 2 km downstream Columbia Lake impoundment, directly upstream Clair Creek (S5).



Figure A5 – Site 5 (S5): Clair Creek, urban residential tributary. Largest Laurel Creek tributary by area.



Figure A6 – Site 6 (S6): Mid-Laurel, highly urban main channel site directly downstream Environment Canada stream gauging station.



Figure A7 – Site 7 (S7): Upper Forwell Creek, highly urban industrial land use, next to highway 85.



Figure A8 – Site 8 (S8): Cedar Creek, highly urban residential tributary. Converges with Forwell Creek ~500 m downstream site 7.



Figure A9 – Site 9 (S9): Lower Forwell Creek, large urban tributary draining industrial and residential land use.



Figure A10 – Site 10 (S10): Laurel Creek, final main channel site, ~ 100 m upstream Grand River confluence.



Figure A11 – Site 10: Storm sewer drain input upstream S10 sample site. Abundant periphyton growth observed on rocks. Storm drain appeared to be discharging water into Laurel Creek even during dry weather.

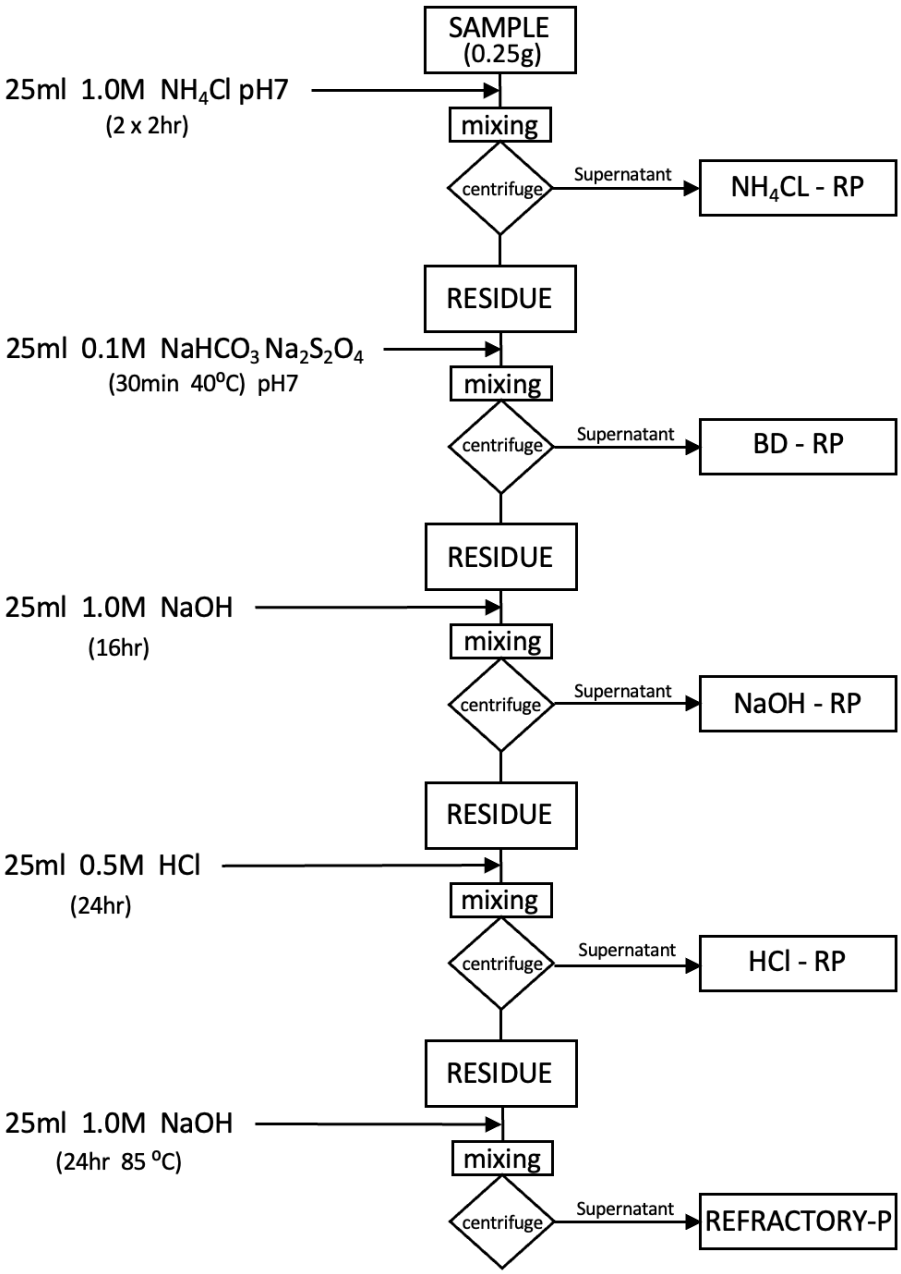

Figure A12 – Sequential extraction scheme for PP forms adapted from Stone & English (1993)

Data

Table A1 – Phosphate sorption isotherm values for set 1 of bench scale sediment–phosphate equilibrium experiments (EPC_0) conducted with sampled river water ([P] = 25 µg L^{-1}).

Set	P initial (µg L^{-1})	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
A	25	-12.616	-2.831		0.457	0.481	0.343	-2.327	-6.408	-0.412	-6.613
	35	-12.589	-1.430		-2.463	-0.939	1.409	-3.257	-2.716	1.309	1.361
	50	-9.496	-1.147		-1.417	3.339	2.889	-2.940	-1.725	1.684	-4.024
	75	-3.545	1.872		3.336	5.206	5.656	0.131	-0.140	5.145	-0.040
	125	1.594	8.175		10.474	9.991	9.116	6.786	4.596	10.788	7.497
B	25	-10.100	-2.971	-17.536	-1.236	-1.040	0.453	-4.346	-4.836	0.543	-4.508
	35	-9.395	1.576	-15.966	-1.566	-2.737	1.556	-3.115	1.124	1.544	-2.860
	50	-9.112	-1.444	-12.258	3.136	2.606	3.087	-2.750	-2.772	2.926	-4.837
	75	-5.871	-0.099	-12.884	4.253	4.690	5.554	2.074	-0.241	5.523	1.272
	125	-3.142	8.098	-9.722	8.075	9.311	6.866	6.044	5.387	9.767	4.349
	EPC_0 - A	**108.195**	**53.513**		**46.990**	**29.313**	**18.335**	**64.785**	**74.152**	**28.767**	**64.120**
	EPC_0 - B	**162.440**	**53.546**	**220.967**	**37.943**	**41.344**	**12.087**	**65.634**	**64.135**	**18.044**	**74.100**

Table A2 – Phosphate sorption isotherm values for set 2 of bench scale sediment–phosphate equilibrium experiments (EPC_0) conducted with sampled river water ([P] = 14 µg L^{-1}).

Set	P initial (µg L^{-1})	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
A	14	-12.477	-7.074	-19.651	-4.566	-3.455	-3.344	-4.977	-6.844	-1.928	-7.752
	24	-11.234	-5.823	-19.415	-4.068	-2.914	-1.745	-3.532	-5.044	-0.565	-6.204
	39	-9.764	-4.435	-18.272	-2.597	-0.636	0.493	-2.316	-2.035	0.189	-4.674
	64	-7.463	-1.802	-15.609	0.115	0.658	2.669	-1.650	-2.586	1.883	-2.869
	114	-4.368	2.741	-11.917	4.063	5.265	7.270	2.803	1.608	6.503	2.998
B	14	-12.754	-6.655	-19.268	-4.827	-3.464	-2.697	-5.547	-6.707	-2.361	-7.839
	24	-11.440	-5.530	-19.680	-4.585	-2.758	-0.660	-4.078	-5.434	-0.860	-6.355
	39	-9.745	-3.799	-17.973	-2.650	-0.767	0.178	0.400	-3.642	0.290	-5.070
	64	-7.296	-1.931	-15.676	-0.588	1.866	1.754	-1.188	-2.424	2.880	-3.190
	114	-3.180	2.972	-12.118	4.481	6.930	7.103	2.935	1.817	7.133	1.852
C	14	-12.626	-6.704	-19.622	-4.742	-3.423	-2.695	-5.027	-6.761	-2.111	-7.927
	24	-11.305	-5.747	-19.102	-3.704	-2.634	-0.979	-4.005	-6.048	-0.877	-5.783
	39	-9.668	-3.861	-17.847	-2.311	-1.349	-0.375	-2.671	-4.995	0.108	-5.253
	64	-7.802	-1.226	-16.719	0.213	1.055	1.595	-1.540	-2.673	2.370	-1.805
	114	-1.959	2.998	-11.630	4.249	4.911	8.384	2.659	2.246	6.506	5.080
	EPC_0 - A	**162.504**	**84.664**	**258.729**	**66.842**	**53.521**	**40.838**	**77.001**	**85.816**	**36.220**	**86.461**
	EPC_0 - B	**144.448**	**82.577**	**265.983**	**68.086**	**47.640**	**38.925**	**66.531**	**90.613**	**35.913**	**94.833**
	EPC_0 - C	**134.004**	**80.691**	**261.025**	**65.024**	**54.474**	**40.189**	**79.315**	**91.005**	**36.950**	**75.536**

Appendix B

Quality Assurance/Quality Control

Sediment Analysis QA/QC

Table B1 – Major element geochemistry quality assurance analysis from Act Labs.

Analyte Symbol	Na	Mg	Al	Ca	Mn	Fe	K
Unit Symbol	%	%	%	%	ppm	%	%
Detection Limit	0.001	0.01	0.01	0.01	1	0.01	0.01
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
OREAS 520 (Aqua Regia) Meas	0.051	1.14	1.33	3.8	2240	15.7	0.41
OREAS 520 (Aqua Regia) Cert	0.052	1.14	1.56	3.84	2280	15.74	0.506
OREAS 907 (Aqua Regia) Meas	0.081	0.19	1.05	0.27	332	8.55	0.31
OREAS 907 (Aqua Regia) Cert	0.086	0.221	0.945	0.28	330	8.18	0.286
OREAS 907 (Aqua Regia) Meas	0.081	0.19	1.02	0.28	327	8.32	0.3
OREAS 907 (Aqua Regia) Cert	0.086	0.221	0.945	0.28	330	8.18	0.286
OREAS 907 (Aqua Regia) Meas	0.09	0.22	1.04	0.27	325	8.27	0.31
OREAS 907 (Aqua Regia) Cert	0.086	0.221	0.945	0.28	330	8.18	0.286
Oreas 620 (Aqua Regia) Meas	0.115	0.22	1.12	1.22	407	2.57	0.28
Oreas 620 (Aqua Regia) Cert	0.117	0.27	1.12	1.29	414	2.58	0.31
Oreas 610 (Aqua Regia) Meas	0.052	0.11	1.05	0.1	64	2.2	0.24
Oreas 610 (Aqua Regia) Cert	0.049	0.11	0.847	0.12	66	2.27	0.21
Oreas 610 (Aqua Regia) Meas	0.057	0.11	1.13	0.12	66	2.29	0.26
Oreas 610 (Aqua Regia) Cert	0.049	0.11	0.847	0.12	66	2.27	0.21
Oreas 610 (Aqua Regia) Meas	0.059	0.12	1.03	0.13	65	2.26	0.26
Oreas 610 (Aqua Regia) Cert	0.049	0.11	0.847	0.12	66	2.27	0.21
OREAS 609b (Aqua Regia) Meas	0.059	0.07	0.75	0.72	205	2.32	0.26
OREAS 609b (Aqua Regia) Cert	0.06	0.067	1	1	210	2	0.279
OREAS 609b (Aqua Regia) Meas	0.051	0.07	0.8	0.78	210	2.27	0.32
OREAS 609b (Aqua Regia) Cert	0.06	0.067	1	1	210	2	0.279
OREAS 45h (Aqua Regia) Meas	0.042	0.19	4.57	0.11	287	18.7	0.09
OREAS 45h (Aqua Regia) Cert	0.036	0.165	3.89	0.106	260	18.18	0.084
Method Blank	0.007	< 0.01	< 0.01	< 0.01	< 1	< 0.01	< 0.01
Method Blank	0.005	< 0.01	< 0.01	< 0.01	< 1	< 0.01	< 0.01

Sorption QA/QC

Table B2 – Concentrations of calibrants used for the calibration curve in runs when determining SRP concentrations of collected water samples.

Calibrants ($\mu g\ L^{-1}$)	Set 1	Set 2	Set 3	Set 4	Set 5	**Average**	**SD**
0	0.46	0.77	-0.18	-0.99	0.74	**0.16**	**0.75**
10	10.15	10.03	9.43	9.37	9.97	**9.79**	**0.36**
25	24.84	24.60	24.64	26.85	25.14	**25.21**	**0.94**
50	47.28	49.27	49.98	50.03	49.87	**49.29**	**1.16**
100	103.16	100.21	102.10	99.90	98.51	**100.77**	**1.84**
200	199.11	200.13	199.03	199.84	200.76	**199.77**	**0.72**

Table B3 – Concentrations of calibrants used for the calibration curve in runs when determining SRP concentrations of samples for bench-scale equilibrium experiments (EPC_0).

Calibrants ($\mu g\ L^{-1}$)	Set 1, Run 1	Set 1, Run 2	Set 2, Run 1	Set 2, Run 2	**Average**	**SD**
0	1.016	0.572	0.287	0.360	**0.56**	**0.33**
10	10.626	10.363	9.918	9.815	**10.18**	**0.38**
25	25.052	25.21	25.411	25.208	**25.22**	**0.15**
50	49.583	50.052	50.284	50.539	**50.11**	**0.41**
100	97.314	97.72	98.439	98.461	**97.98**	**0.56**
200	201.41	201.083	200.662	200.618	**200.94**	**0.38**

Table B4 – Quality control cups of 10, 25, 50, 100, and 200 µg L^{-1} were inserted in triplicate into runs when determining SRP concentrations of collected water samples. All standard deviations fell below 1 µg L^{-1}.

Calibrant 10 µg L^{-1}	Average	SD	Calibrant 25 µg L^{-1}	Average	SD	Calibrant 50 µg L^{-1}	Average	SD	Calibrant 100 µg L^{-1}	Average	SD	Calibrant 200 µg L^{-1}	Average	SD
10.002			23.534			52.964			99.626			198.753		
9.307	9.453	0.493	23.953	23.715	0.215	49.208	50.222	2.401	98.865	99.526	0.618	199.699	199.553	0.738
9.049			23.658			48.494			100.088			200.208		
11.382			24.355			49.094			101.241			201.104		
10.622	10.820	0.493	24.07	24.153	0.176	49.46	49.373	0.248	101.61	101.416	0.185	201.652	201.789	0.762
10.457			24.033			49.566			101.398			202.61		
7.983			23.568			48.452			97.224			199.489		
7.718	7.756	0.210	24.167	23.684	0.436	48.287	48.344	0.093	98.746	98.331	0.968	198.706	199.131	0.396
7.568			23.318			48.294			99.022			199.198		
11.134			25.552			50.642			98.816			202.523		
10.588	10.659	0.443	25.213	25.450	0.206	50.109	50.390	0.268	98.932	98.778	0.176	201.95	202.555	0.622
10.256			25.585			50.419			98.586			203.193		

Table B5 – Quality control cups of 10, 25, 50, 100, and 200 µg L^{-1} were inserted in triplicate into runs when determining SRP concentrations of samples for bench-scale equilibrium experiments (EPC_0). All standard deviations fell below 2.5 µg L^{-1}.

Calibrant 10 µg L^{-1}	Average	SD	Calibrant 25 µg L^{-1}	Average	SD	Calibrant 50 µg L^{-1}	Average	SD	Calibrant 100 µg L^{-1}	Average	SD	Calibrant 200 µg L^{-1}	Average	SD
10.804			25.256			50.055			98.876			201.533		
10.437	10.466	0.324	25.223	25.261	0.040	50.244	50.151	0.095	98.545	98.468	0.452	202.953	203.397	2.122
10.157			25.303			50.153			97.982			205.706		
10.356			25.002			49.629			97.567			202.282		
10.053	10.091	0.248	24.798	24.824	0.167	49.348	49.452	0.154	96.962	97.263	0.303	202.964	202.902	0.591
9.864			24.671			49.378			97.261			203.459		
9.553			23.793			49.702			97.728			201.425		
9.394	9.345	0.236	24.338	24.161	0.319	49.326	49.610	0.251	97.978	97.907	0.156	201.267	201.892	0.949
9.089			24.353			49.801			98.015			202.984		
9.534			24.917			51.965			100.293			203.895		
9.346	9.363	0.163	24.754	24.898	0.136	50.358	51.034	0.833	99.752	99.715	0.598	204.171	204.765	1.275
9.21			25.023			50.778			99.099			206.228		