Advancing Characterization of Municipal Wastewater Treatment Implications to Aquatic Phosphorus and Eutrophication in Receiving Streams

by

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

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

Statement of Contributions

This thesis consists of an introductory chapter (Chapter 1), followed by four manuscript chapters written for publication in peer-reviewed scientific journals (Chapters 2–5), and a concluding chapter (Chapter 6). Kelvin Nunes Vianini is the sole author of Chapters 1 and 6, which were written under the supervision of Dr. Monica Emelko and Dr. William Anderson and were not prepared for publication. Chapter 2 has been published as an open-access, peer-reviewed paper in *Water Research*. Chapter 3 is in preparation for submission to the *Journal of Water Process Engineering*, while Chapter 4 is in preparation for submission to *Water Research*. Chapter 5 is in preparation for submission to a peer-reviewed journal. Exceptions to sole authorship of material and CRediT (Contributor Roles Taxonomy) details are as follows:

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Abstract

Municipal wastewater treatment remains a critical intervention for reducing phosphorus inputs to receiving waters and mitigating nutrient loadings to prevent eutrophication. However, treatment performance is still commonly evaluated using total phosphorus, which provides limited insight into the environmental relevance of discharged phosphorus because it does not distinguish between dissolved, particulate, reactive, and potentially bioavailable forms. This limitation is particularly important for advanced treatment systems that reduce total phosphorus but may also alter the balance and relative distribution of specific phosphorus fractions discharged to receiving waters. Under these conditions, concentration-based assessment alone may obscure whether residual phosphorus is likely to remain inert or become available after discharge.

The goal of this research was to advance the characterization and interpretation of phosphorus in municipal wastewater effluents by evaluating how treatment affects phosphorus form, release behaviour, and contributions to receiving waters. Full-scale wastewater effluents were characterized across secondary and tertiary treatment configurations using solids collection, phosphorus fractionation, and controlled desorption experiments. These measurements were used to assess the composition and bioavailability of effluent particulate phosphorus, quantify changes associated with tertiary cloth filtration, evaluate phosphorus release behaviour from effluent solids in relation to established sediment-based concepts, and apply a multi-form phosphorus evaluation approach with hydrologic regime analysis to evaluate conditions under which WWTP discharges may materially influence bioavailable phosphorus concentrations post discharge.

Collectively, the findings demonstrated that wastewater phosphorus relevance depends not only on how total phosphorus is removed, but on how remaining phosphorus is partitioned and transformed after discharge. Effluent particulate phosphorus was dominated by reactive inorganic forms, indicating that residual solids can represent a bioavailable phosphorus pool rather than an inert particulate fraction. Tertiary treatment reduced total and particulate phosphorus and lowered the release potential of effluent solids, but did not eliminate dissolved phosphorus inputs or the capacity of remaining solids to act as phosphorus sources. Desorption behaviour was highly influenced by temperature, while pH effects were most evident outside circumneutral conditions. When these experimentally derived behaviours were evaluated under receiving water conditions, the contribution of bioavailable phosphorus was controlled strongly by dilution, background phosphorus concentration, and effluent flow.

This thesis demonstrates that total phosphorus removal alone is insufficient to characterize eutrophication-relevant wastewater performance. A more complete assessment

requires explicit consideration of phosphorus speciation, particulate phosphorus bioavailability and post-discharge release, and receiving water context. By linking treatment performance to phosphorus form and flow patterns, this work provides a stronger basis for interpreting wastewater phosphorus controls in relation to downstream bioavailable phosphorus exposure, without assuming that concentration changes alone directly predict ecological response.

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Dedication

To Ana, Max, and Lincoln, for your unconditional love and unwavering support.

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List of Abbreviations

AIP	Apatite inorganic phosphorus
ANOVA	Analysis of variance
BAP	Bioavailable phosphorus
CFC	Continuous-flow centrifugation
DOCP	Dissolved organic and condensed phosphates
EF	Effluent Fraction
EPC_0	Equilibrium phosphate concentration
AF	Augmentation factor
ICP-MS	Inductively coupled plasma mass spectrometry
MDL	Method detection limit
NAIP	Non-apatite inorganic phosphorus
OP	Organic phosphorus
PEP	Phosphate exchange potential
POCP	Particulate organic and condensed phosphates
PP	Particulate phosphorus
PRP	Particulate reactive phosphorus
RDT	Rotary drum thickener
SRP	Soluble reactive phosphorus
TDP	Total dissolved phosphorus

TP	Total phosphorus
TRP	Total reactive phosphorus
TSS	Total suspended solids
UV	Ultraviolet
WASP	Water Quality Analysis Simulation Program
WWTP	Wastewater treatment plant

Chapter 1

Introduction

1.1 Background

Phosphorus is an essential nutrient for aquatic productivity, but excessive phosphorus inputs remain one of the primary drivers of eutrophication in freshwater systems. Elevated phosphorus availability can stimulate excessive algal and cyanobacterial growth, alter ecological structure and function, reduce dissolved oxygen, impair aquatic habitat, and create challenges for drinking water treatment and source water protection (Carpenter et al., 1998; Correll, 1998; Paerl et al., 2016; Sadegh et al., 2021). Because many freshwater systems are phosphorus-limited, phosphorus management has long been central to water quality protection, wastewater regulation, and eutrophication control. Historically, this has led to regulatory and monitoring frameworks that prioritize reductions in total phosphorus (TP) loads from both diffuse sources, such as agricultural runoff and urban stormwater, and point sources, including municipal wastewater treatment plant (WWTP) effluents (Litke, 1999; Dillon & Rigler, 1974).

Among phosphorus sources to surface waters, WWTP effluents occupy a distinct position because they are continuous, regulated, and relatively controllable point inputs (Carpenter et al., 1998). Unlike diffuse landscape sources, wastewater discharges can often be targeted through treatment upgrades, operational optimization, and effluent monitoring. This makes WWTPs both an important focus of phosphorus reduction and a useful setting for evaluating how treatment processes influence the forms of phosphorus entering receiving waters. However, conventional wastewater performance assessment has relied heavily on TP as the primary indicator of phosphorus removal and compliance (Kardos et al., 2025; Preisner et al., 2020). TP is useful as a regulatory and mass-loading metric, but it is

an aggregate measurement that combines chemically and biologically distinct phosphorus forms (Comber et al., 2015; Li & Brett, 2013). As a result, two effluents with similar TP concentrations may differ substantially in ecological significance if their phosphorus is distributed differently among dissolved, particulate, immediately bioavailable, and potentially bioavailable fractions. Here, bioavailability refers to the capacity of phosphorus to become available for biological uptake following environmental transformation and should not be interpreted as direct evidence of biological utilization or ecological response.

This distinction is important because eutrophication responses are not governed by TP alone. Rather, ecological response depends on the form, bioavailability, persistence, and transformation of phosphorus after discharge, as well as the hydrologic and biogeochemical conditions of the receiving water (Boström et al., 1988; Read et al., 2014; Reynolds & Davies, 2001). Soluble reactive phosphorus (SRP) is generally considered the most immediately bioavailable phosphorus fraction because it is largely composed of orthophosphate that can be directly assimilated by microorganisms and algae (Reynolds & Davies, 2001). Other dissolved fractions, including dissolved organic and acid-hydrolysable phosphorus, may also become bioavailable through hydrolysis or microbial transformation depending on environmental conditions (Qin et al., 2015). Particulate phosphorus (PP), although often considered less immediately available than SRP, can function as a mobile phosphorus reservoir. When transported downstream, retained in depositional zones, or resuspended from sediments, PP may release bioavailable phosphorus through desorption, dissolution, mineralization, or redox-mediated processes (Boström, 1984; Boström et al., 1988; Nürnberg et al., 2012; Read et al., 2014; Reynolds & Davies, 2001; Stone & English, 1993). Therefore, TP-based phosphorus control strategies may not fully represent the bioavailable phospho-

rus load delivered to receiving waters.

The role of PP is particularly relevant in riverine systems because fine suspended particles are important vectors for phosphorus transport. Fine particles have high surface area and may contain iron, aluminum, manganese, calcium, and organic phases that bind phosphate and regulate exchange with the water column (Stone & English, 1993). In natural systems, the mobility and bioavailability of PP have been studied extensively in agricultural, forested, urban, stream sediment, reservoir sediment, and internal loading contexts (Simpson et al., 2021). These studies have shown that phosphorus exchange between solids and water is influenced by sediment mineralogy, redox conditions, pH, temperature, ambient phosphorus concentration, organic matter, and particle size (Holdren & Armstrong, 1980; House, 2003; Huang et al., 2021; Kim et al., 2003; Rydin et al., 2011; Simpson et al., 2021; Watt et al., 2021; Zhang et al., 2022). This literature has led to widely used interpretive concepts such as adsorption–desorption isotherms, equilibrium phosphate concentration (EPC_0), and phosphate exchange potential, which are used to evaluate whether particulate material behaves as a sink or source of dissolved phosphorus under specific environmental conditions (House, 2003; House & Denison, 2000; Simpson et al., 2021).

Although these sediment-based concepts are useful, their application to wastewater-derived solids is not straightforward. Wastewater effluent solids are generated through engineered treatment processes, including biological treatment, chemical coagulation, flocculation, clarification, filtration, and disinfection (Panda et al., 2025). Their composition reflects wastewater influent chemistry, microbial biomass, coagulant addition, treatment configuration, solids retention, and hydraulic operation. Consequently, wastewater-derived particles may differ from geogenic, agricultural, or urban runoff-derived particles in par-

ticle size, surface coatings, mineral associations, organic matter content, and phosphorus-binding phases (Fan et al., 2008; Stone & Mudroch, 1989; Zhu et al., 2012). These differences matter because the environmental behaviour of PP depends not only on the amount of particulate material discharged, but also on the chemical forms of phosphorus associated with those particles and the conditions under which those forms are released (Boström, 1984; Nurnberg, 2009; Stone & English, 1993).

This creates a broader concern for wastewater phosphorus assessment: the question is not only whether WWTPs reduce phosphorus, but whether current monitoring and performance metrics adequately characterize the phosphorus forms that matter most for bioavailability and receiving water response. In routine monitoring programs, TP is typically measured and SRP may also be included in some applications. In contrast, the composition of PP in final effluents is rarely characterized in a manner that directly informs bioavailability, partly because the required samples are difficult to obtain. The importance of characterization of effluent solids and associated phosphorus forms is highlighted because PP is not a uniform pool. Non-apatite inorganic phosphorus (NAIP), which is often associated with metal oxides and hydroxides, is generally a more reactive and potentially bioavailable form (DePinto et al., 1981; Kleeberg & Dudel, 1997; Rydin, 2000; Zhou et al., 2001; Kaiserli et al., 2002). Without a proper method for fractionation-based characterization, it is difficult to determine whether effluent PP should be interpreted primarily as a residual solids issue or as a potentially important pool of bioavailable phosphorus (**Research Gap 1**).

This uncertainty also affects how treatment performance is interpreted. Advanced tertiary treatment technologies are increasingly implemented to improve effluent quality and

lower TP concentrations before discharge. However, treatment processes may affect phosphorus forms differently. A treatment process that removes particulate material may reduce TP while shifting the distribution of dissolved and particulate phosphorus fractions in the final effluent. Moreover, by reducing the abundance of fine solids, such treatment may also decrease the amount of particulate phosphorus available for subsequent release in receiving waters. Therefore, understanding treatment performance requires more than the determination of reductions in TP concentration; it also requires evaluation of treatment-induced shifts in phosphorus speciation and the resulting implications for phosphorus bioavailability. Limited information is available on the nuanced effluent phosphorus fractionation and how it should be interpreted in relation to downstream eutrophication potential (**Research Gap 2**).

Phosphorus fractionation provides important insights to determine the environmental relevance of each phosphorus form, but more is known about dissolved phosphorus repercussions (Jarvie et al., 2006). The importance of effluent PP depends on whether phosphorus associated with effluent-derived solids is released under receiving water conditions. Natural sediment studies provide a strong basis for evaluating phosphorus exchange, but wastewater effluent solids have different origins and conditioning histories than natural sediments. They are typically freshly formed, chemically conditioned, biologically derived, and enriched in reactive phosphorus-binding phases, which potentially makes their desorption behaviour difficult to infer from sediment studies alone. It remains unclear whether wastewater-derived solids follow the same adsorption–desorption responses observed for natural sediments, whether established concepts such as EPC_0 provide appropriate descriptors of their behaviour, and how environmental variables such as ambient SRP, pH,

and temperature influence their release potential. This uncertainty limits the representation of wastewater-derived PP in bioavailable nutrient loading assessments (**Research Gap 3**).

Resolving phosphorus forms and release behaviour, although crucial, is not sufficient to determine receiving water relevance. The effect of WWTP-derived phosphorus also depends on the receiving stream conditions and flow regimes into which it is discharged. A given effluent load may be strongly diluted during high-flow conditions but become more influential during low-flow periods when effluent represents a larger fraction of total river flow (Jarvie et al., 2006). Another caveat is that the significance of a given SRP input is dynamic (Li & Brett, 2013) and should be interpreted with caution, as variations in SRP concentration may not always correspond to negative ecological responses. Existing water quality models can represent phosphorus transport in detail, but they often require extensive data, calibration, and site-specific parameterization. Additionally, assessments that rely on static metrics or fixed effluent loads may not adequately capture the relative contributions of bioavailable phosphorus forms or identify the conditions under which WWTP discharges become consequential. Therefore, there is a need to evaluate whether incorporating multiple wastewater phosphorus forms, including dissolved phosphorus and particulate phosphorus release potential, together with receiving water conditions, provides a more meaningful assessment of the true role of municipal WWTP effluents as contributions to downstream nutrient dynamics (**Research Gap 4**).

1.2 Objectives

The overall goal of this research was to improve the characterization and interpretation of bioavailable phosphorus in municipal wastewater effluents by resolving the forms, treatment effects, release behaviour, and receiving water conditions that determine when WWTP-derived phosphorus becomes environmentally relevant. This goal was addressed through four linked research objectives that move from effluent characterization to treatment assessment, environmental behaviour, and potential for receiving water responses. This thesis is written in a manuscript-based format, where Chapters 2–5 consist of individual manuscripts, each addressing one objective of the study. The specific research objectives were to:

1. Develop and apply a method for collecting fine suspended solids from treated wastewater effluents to support characterization of particulate phosphorus forms and bioavailability;

2. Determine how wastewater treatment level influences effluent phosphorus speciation, bioavailability, and particulate phosphorus release potential post discharge;

3. Evaluate phosphorus release behaviour from wastewater effluent solids under receiving-water-relevant conditions and assess whether sediment-based exchange paradigms provide an appropriate interpretive basis; and

4. Evaluate multi-form phosphorus accounting and integration to receiving water's conditions and flow regimes for interpretation of the significance of WWTP phosphorus contributions post discharge.

These objectives were evaluated across municipal activated sludge wastewater treatment plants utilizing iron-based coagulants for chemically assisted phosphorus removal. Given that phosphorus removal mechanisms, speciation, and release dynamics depend heavily on system configuration, the results presented herein should be contextualized accordingly.

1.3 Thesis Organization and Research Approach

This thesis is organized into six chapters. Following the Introduction in Chapter 1, Chapters 2–5 address Research Objectives 1–4, respectively. Chapter 6 presents a synthesis of the main findings, contributions of the research, and practical implications, as well as how the advancements presented herein can be integrated to guide future investigations and research opportunities in the field. Figure 1.1 provides an overview of the thesis structure by showing how the chapters are connected through their respective objectives, knowledge gaps, and transferable findings.

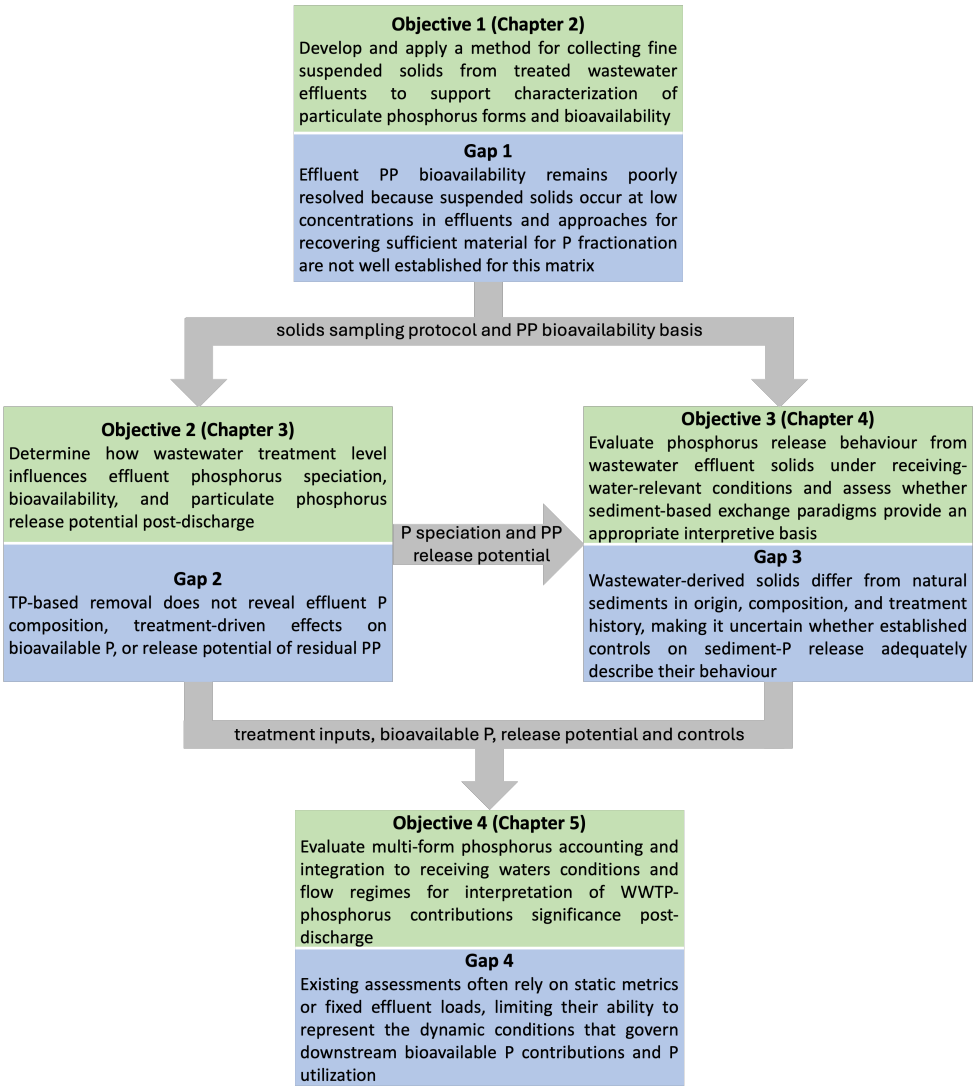


Figure 1.1: Overview of objectives interconnectivity.

To address the overall goal of improving how WWTP-derived bioavailable phosphorus is characterized and interpreted, the thesis follows a progression from effluent solids characterization to treatment effects, to effluent PP release potential, and finally to potential

repercussions assessment. This structure reflects the need to first understand what forms of phosphorus are present in treated wastewater, their characteristics, and how they behave after discharge to then anticipate conditions under which WWTP discharges can become consequential to relevant receiving waters.

For interpreting particulate phosphorus in wastewater effluents, a method was required to collect sufficient quantities of fine suspended solids. These solids are typically present at low concentrations, making them difficult to recover in sufficient quantities for detailed phosphorus fractionation. Chapter 2 focused on adapting a solids collection approach for treated wastewater effluents and applying it to characterize particulate phosphorus forms and bioavailability. This was performed at full-scale WWTPs, and phosphorus fractionation followed a specific sequential extraction. This characterization served as the basis for subsequent reporting and analysis of effluent phosphorus speciation forms and the release potential study.

As treatment performance is often evaluated based on TP removal, Chapter 3 sought to determine whether lower TP also reflects meaningful changes in phosphorus bioavailability. This chapter investigates the influence of treatment level on phosphorus speciation, bioavailability, and particulate phosphorus release potential in treated effluents. Secondary and tertiary effluents from full-scale WWTPs employing advanced tertiary cloth filtration were compared using phosphorus fractionation and release-based characterization of residual solids to assess how treatment modifies the composition and potential availability of phosphorus remaining in the final effluent.

Understanding phosphorus fractions does not fully indicate how effluent-derived solids

will behave after discharge. Chapter 4 focused on phosphorus release behaviour from wastewater effluent solids under receiving-water-relevant conditions and evaluates whether sediment-based source–sink paradigms provide an appropriate interpretive framework. This was accomplished through controlled desorption experiments using effluent solids exposed to varying water chemistry conditions, allowing their release behaviour to be compared with concepts commonly applied to freshwater sediments. These results provide the mechanistic basis for representing the less explored particulate-derived phosphorus fractions as a potential bioavailable pathway in receiving water assessment.

Finally, Chapter 5 connects the experimentally characterized effluent phosphorus forms and release behaviour to the hydrologic conditions that evaluate receiving water exposure to phosphorus increases. Even when effluent phosphorus forms and release potential are known, how they are expressed post discharge depends on dilution, background river SRP, effluent fraction, and the relative contribution of dissolved and particulate-derived phosphorus to the mixed receiving water. This chapter, therefore, provides an evaluation method that integrates wastewater phosphorus speciation, particulate phosphorus release, and flow regimes to interpret the significance of discharge contributions and identify conditions under which they may influence the receiving water bioavailable phosphorus pool. In doing so, the thesis moves from characterization of wastewater phosphorus forms to a practical structure for evaluating when discharges could be potential contributors to adverse nutrient responses downstream.

Chapter 2

Characterization of particulate phosphorus forms and bioavailability in wastewater effluent to benchmark drivers of eutrophication

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Additional methodological information regarding sections "**2.2.3 Sequential extraction of particulate phosphorus forms**" and "**2.3.2 Method Validation**" that was not included in the publication is provided below:

2.2.3 Sequential extraction of particulate phosphorus forms

PP speciation in effluent solids was qualitatively assessed using a standard sequential extraction protocol (Figure 2.1) (Pettersson & Istvanovics, 1988; Stone & English, 1993). This validated methodology mitigates operational limitations, incomplete extraction effi-

ciencies, and mineral readsorption through optimized reagent sequencing and mass-balance controls. The operational fractions are interpreted as phosphorus pools with similar chemical reactivity rather than discrete mineral phases.

2.3.2 Method Validation

Some particles were inevitably not recovered, but complete recovery of the suspended-solid population was not expected. Consequently, recovered solids represent the recovered suspended-solid fraction obtained using the developed methodology.

Summary

Municipal wastewater treatment plants are commonly regulated based on total phosphorus concentrations, yet the environmental relevance of residual effluent phosphorus depends strongly on its chemical form and bioavailability. Here, particulate phosphorus in treated municipal wastewater effluents was characterized to determine whether effluent-derived solids represent inert residual material or a potentially bioavailable phosphorus source. Phosphorus fractionation of collected effluent solids showed that particulate phosphorus was dominated by reactive and potentially bioavailable forms, particularly non-apatite inorganic phosphorus. These results demonstrate that effluent solids can act as carriers of bioavailable phosphorus and should not be interpreted solely as a residual component of total phosphorus. By identifying the composition and potential bioavailability of wastewater-derived particulate phosphorus, this work provides a mechanistic foundation for evaluating how treatment processes alter phosphorus forms and how residual effluent solids may influence downstream phosphorus availability.

2.1 Introduction

Phosphorus (P) inputs from diffuse sources such as agriculture and point sources such as wastewater treatment plant (WWTP) discharges contribute to surface water eutrophication because P is the limiting nutrient for primary productivity in freshwater systems (Carpenter et al., 1998; Paerl et al., 2016). It is primarily transported in association with fine solids that have a high surface area and are composed of positively charged mineral sur-

faces (e.g., iron, aluminum, manganese) that bind or release negatively charged dissolved P species (Stone and English, 1993; Withers and Jarvie, 2008). Landscape disturbances (e.g., agriculture, development, climate shocks such as wildfires) often increase the mobility and delivery of solids from terrestrial to aquatic systems (Paerl & Paul, 2012; Emelko et al., 2016). For example, extreme precipitation can intensify erosion and runoff, increasing solids loads to surface waters (Emelko et al., 2024). Associated increases in particulate (i.e., particle-bound) P (PP) levels in receiving waters can lead to increased downstream transport and deposition of these P-rich fine solids and subsequent release of bioavailable P from the solids to the water column in lakes and reservoirs (Søndergaard et al., 2003; Nürnberg, 2009). This "internal loading" can result from redox-driven release (e.g., anoxic iron dissolution) and physical resuspension, which exposes organic PP to phosphatases and enhances bioavailability (Boström et al., 1988; Søndergaard et al., 2003; Hupfer and Lewandowski, 2008; Qin et al., 2018). PP loading can also impact nutrient spiralling via the uptake, transformation, and release of nutrients by biotic and abiotic processes along the river continuum (Newbold et al., 1982). This can make bioavailable P accessible to aquatic organisms and fuel downstream eutrophication, ecological imbalances, and drinking water treatability challenges by promoting proliferation of cyanobacteria and other algae, which can increase chemical coagulant demand and/or clog filtration and membrane processes. Cyanobacteria can also produce toxins of human health concern and cause service disruptions or outages because most water treatment plants are not designed to treat them (Emelko et al., 2011).

Although domestic wastewater is rich in P due to the breakdown of human and food waste (Xiong et al., 2020), WWTPs can reduce total P (TP) concentrations to relatively

low levels (Dueñas et al., 2003). Likewise, nutrient inputs from urban runoff are managed through stormwater controls, green infrastructure, and low-impact development (Yang & Lusk, 2018). It is generally believed that nutrient—and particularly P—loading to surface water supplies and associated eutrophication threats are sufficiently controlled at point sources such as WWTPs and targeted stormwater retention systems (Ramasahayam et al., 2014). However, treatment performance and compliance assessments typically only involve TP and/or soluble reactive P (SRP) (Sedlak, 1991; Smith, 2016). Thus, they do not reflect P dynamics because they do not account for internal loading of bioavailable PP forms when SRP has been utilized.

Environmental factors such as water temperature, stream chemistry, and redox conditions can change in receiving waters (e.g., due to periods of low flow) to favour the release of bioavailable P from bed sediments and the proliferation of cyanobacteria and algae more broadly that they can fuel (Withers and Jarvie, 2008). Although it has been shown that WWTPs can become primary contributors to P loading in receiving streams during low-flow periods (Jarvie et al., 2006), the removal of specific PP forms—including NAIP, the most readily bioavailable PP form—by various wastewater treatment processes has not been evaluated. While PP forms have been characterized in wastewater sludge (González Medeiros et al., 2005; García-Albacete et al., 2012; Zhang et al., 2019), the composition of biowastes formed from the settling of larger solids likely does not reflect the composition of fine suspended solids discharged in WWTP effluents. Notably, previous studies have demonstrated that particle size is often inversely proportional to P binding to freshwater suspended sediments (Stone & English, 1993). While contemporary WWTPs have increasingly adopted advanced treatment technologies that target P removal (e.g.,

tertiary treatment) to further reduce TP in effluent streams (Bunce et al., 2018), their effectiveness at removing bioavailable PP forms typically associated with colloidal solids remains uncertain. Addressing this gap is essential for understanding and mitigating risks to downstream drinking water providers with raw water storage reservoirs, which are especially vulnerable to algal/cyanobacterial proliferation fueled by internal P loading (Rast & Holland, 1988).

PP concentrations in treated wastewater effluents are typically too low to collect sufficient mass to assess PP forms. While solid–liquid separation methods such as membrane filtration and lab-scale centrifugation have been used to concentrate solids from wastewater streams (Hasing et al., 2021; Fonseca et al., 2022), they are not practical for processing the large volumes (e.g., thousands of litres) of wastewater effluents needed to concentrate PP for characterization. As continuous-flow centrifugation approaches have been used to concentrate river sediments (Conn et al., 2016) and wastewater viruses (Hejkal et al., 1981), they may be effective for this purpose.

Given the lack of wastewater effluent PP characterization information and methods for sample collection to evaluate it, the goal of this research was to characterize PP forms in treated wastewater and compare the effectiveness of secondary (2°) and tertiary (3°) treatment in removing bioavailable PP. To our knowledge, this is the first study of its kind to (1) characterize PP forms in wastewater effluents and (2) adapt a continuous-flow centrifuge (CFC)-based river solids sampling method for the collection of suspended solids from large volumes of WWTP effluents. Bioavailable PP in 2° and 3° treatment process effluent streams from two large WWTPs in Ontario, Canada was evaluated. Such information is essential to modelling the effects of wastewater effluent discharges on receiving

water P dynamics, especially during low-flow periods when dilution is reduced.

2.2 Materials and methods

2.2.1 Sampling sites

This research was conducted at two activated sludge WWTPs (referred to as Plant W and Plant K) that discharge into the same river in southwestern Ontario, Canada. Both plants include primary (1°) treatment (i.e., chemical coagulation and subsequent clarification), 2° treatment with aeration tanks and clarifiers, and subsequent ultraviolet (UV) disinfection prior to discharge. In Plant W, ferric sulphate coagulant (7–10 mg/L) is added prior to 1° clarification and aeration (4–6 mg/L). In Plant K, ferric chloride coagulant (4–7 mg/L) is added immediately upstream of 1° clarification, and ferrous chloride coagulant (10–13 mg/L) is added prior to aeration. Waste activated sludge solids from the 2° clarifier are thickened using a rotary drum thickener (RDT). Solids from the 1° and 2° clarifiers undergo anaerobic digestion and dewatering; the supernatant is returned to the aeration tank. Water from the RDT is returned to the 1° clarifier. The key difference between the plants is that Plant K incorporates a 3° cloth filtration system prior to UV disinfection to further remove suspended solids and concurrently reduce TP concentrations in the final effluent. In Plant W, suspended solids were collected from the effluent tank where UV disinfection occurs prior to final effluent discharge. In Plant K, solids were collected at two locations: at the outflow of the 2° clarifiers and the outflow of the 3° filters. Historically, Plant W effluent TP concentrations average 250 µg/L, while in Plant K they average

200 µg/L.

2.2.2 Suspended solids collection using continuous-flow centrifugation

A continuous-flow centrifugation method developed for use in rivers was adapted for collecting suspended solids from WWTP effluents. A portable centrifuge (CFC Express, Scientific Methods Inc., Granger, Indiana) was connected to a peristaltic pump (Cole Parmer Masterflex L/S, Vernon Hills, Illinois) that continuously pumped water into a disposable rotating 300 mL plastic bowl (fixed at 10,000 rpm), enabling centrifugation of large volumes of water. Solids capture is proportional to the intake flow velocity, which was set to 600 mL/min.

When adapting the CFC method for WWTP application, the effluent was collected directly from the tank after UV disinfection (30–45 mJ/cm^2) in Plant W, prior to discharge. It should be noted that UV application at these levels is generally understood to be inconsequential for chemical water quality. As the focus was on evaluating fine solids that do not easily settle, the pump tubing inlet was placed at a depth of approximately 1 m below the water surface to avoid collecting either settled sludge or floating material at the surface. The required time to collect these fine solids ($\sim$60 and $\sim$160 h for 2° and 3° effluents, respectively) was substantially longer than what was reported for river sediments ($\sim$8 h) by Conn et al. (2016). Original estimates were based on a minimum total suspended solids (TSS) concentration of 20 mg/L in river water, assuming a recovery efficiency of 90% and a requirement of 5 g of dry mass (Conn et al., 2016), but the 2° effluent

averaged 5–6 mg TSS/L, and the 3° effluent averaged 1–2 mg TSS/L; thus, substantially high volumes of effluent were needed to achieve the mass required for PP extractions (i.e., 2 g dry weight [dw]; at least 0.25 g per analysis of NH_4Cl-RP, BD-RP, NaOH-RP, HCl-RP, and refractory P extractions [Pettersson & Istvanovics, 1988; Stone & English, 1993] as detailed in Section 2.2.3, and the remainder for characterization of P release potential by equilibrium phosphate concentration analysis, which is described elsewhere).

To avoid potential P release, transformation, bacterial cell lysis, microbial activity, and sample contamination, the contents of the centrifuge bowl (approximately 300 mL) were immediately transported to the laboratory for processing after centrifugation. The disposable bowls have an enclosed design that prevents the removal or opening of any parts. To retrieve the solids, the bowls were shaken vigorously to dislodge any clumps or material adhering to the walls, and the contents were swirled and poured onto an aluminum tray via outlet channel. Rinsing was unnecessary. The wet solids were dried at 105 °C on the day of collection and refrigerated until analysis (U.S. EPA, 2001).

Three sampling campaigns were conducted to provide a synoptic characterization (i.e., a "snapshot") of PP in treated wastewater effluent streams: Campaign 1 (September 2022), Campaign 2 (December 2022), and Campaign 3 (April 2023). During each campaign, suspended solids were collected daily from the secondary effluents (Plants W and K) and the tertiary effluent (Plant K) streams over several (i.e., 5 to 10) consecutive days and composited. In total, nine composited samples were collected over approximately three months and analyzed.

Continuous-flow centrifugation method validation

The recovery efficiency of the CFC wastewater effluent suspended solids sampling method was evaluated on-site by measuring TSS concentrations before and after centrifugation to determine the change in TSS concentration. For this test, three samples were collected from the secondary effluent tank in Plant W prior to running the centrifuge. After the centrifuge started, three additional samples were taken from the outlet tubing. TSS was determined according to Standard Method 2540 D (APHA, 2017) using a 1.2 µm glass microfiber filter (Whatman^{TM}) and a Sartorius MSE224S-000-DU analytical balance (reproducibility of $\pm$0.07 mg). This approach is used to quantify solids retention in the CFC; however, it may not necessarily represent the dry mass available to be recovered from the CFC for analysis due to losses that may occur during sample retrieval from the one-piece disposable centrifuge bowl. To address this, CFC performance was further evaluated in triplicate by adding 10 g of kaolin powder (Sigma-Aldrich) to 10 L of ultra-pure water in a single high-density polyethylene pail. Kaolin was chosen over previously collected solids to avoid potential partial dissolution and associated losses of fine solids during the experiment. The kaolin suspension was pumped into the centrifuge bowl at a fixed rate of 600 mL/min, which is the same rate used in the field (Conn et al., 2016). During centrifugation, the kaolin suspension was mixed on a stir plate with a magnetic stir bar over the entire duration of the experiment to avoid settling. Additionally, a pump rate of 300 mL/min was tested in duplicate to determine if a lower pump rate would improve recovery. The recovered mass was determined by subtracting the initial weight of the aluminum tray from its final weight. This method ensured that the final mass represents the dry mass available for

analyses after accounting for any losses during centrifugation, as well as sample transfer from the centrifuge bowl and drying tray. Reproducibility was assessed by calculating the coefficient of variation, defined as the standard deviation divided by the mean and expressed as a percentage. Method validation results are presented in Section 2.3.2.

2.2.3 Sequential extraction of particulate phosphorus forms

A sequential extraction method (Pettersson & Istvanovics, 1988; Stone & English, 1993) was used to qualitatively assess the relative fractional composition of PP forms in effluent solids (Figure 2.1). The three PP forms evaluated during this sequential extraction include NAIP, apatite inorganic P (AIP), and organic P (OP) (Pettersson et al., 1988; Stone & English, 1993). NAIP is the sum of three fractions that can desorb from solids surfaces to the water column and, thus, are considered readily bioavailable (DePinto et al., 1981; Kleeberg & Dudel, 1997; Rydin, 2000; Zhou et al., 2001; Kaiserli et al., 2002). These are: (1) loosely sorbed P, typically the first extraction as it readily desorbs and includes P compounds dissolved in solids interstitial water (extracted by 1 M NH_4Cl); (2) reductant-soluble P, which is considered a potentially mobile P pool and available for microorganisms (extracted by 0.11 M $NaHCO_3$· $Na_2S_2O_4$); and (3) metal-oxide-bound P, which is mainly associated with Fe and Al and can be released under both anoxic and aerobic conditions (extracted by 1 M NaOH). The AIP form (extracted by 0.5 M HCl) is sensitive to low pH and comprises natural and detrital P, carbonate-bound P, and traces of hydrolyzable organic P, making it a very stable fraction and unlikely to become bioavailable (Kaiserli et al., 2002). Lastly, OP (extracted by 1 M NaOH at 85 °C) includes P forms bound to organic compounds

like nucleic acids, phospholipids, phosphomonoesters and diesters, phosphonates, and nucleotides; this fraction is not considered readily bioavailable but can become bioavailable after hydrolysis and mineralization in fresh waters (Worsfold et al., 2008). After extraction and subsequent centrifugation, the P concentrations in supernatants were determined via inductively coupled plasma mass spectrometry (Agilent 7900 ICP-MS, Agilent, California, USA) and an unpaired, two-tailed t-test was conducted to assess whether the mean difference between measured P fractions was statistically significant; if variances were not equal, Welch's t-test was used.

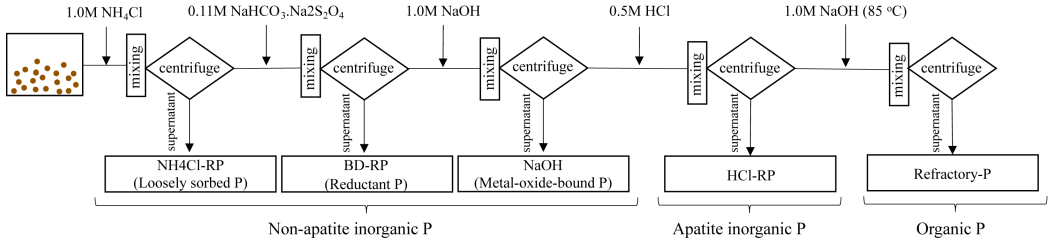


Figure 2.1: Sequential extraction method for evaluating PP forms, adapted from Stone & English (1993).

2.3 Results and Discussion

2.3.1 Continuous-flow centrifugation for rapid wastewater solids concentration

Higher TSS concentrations collected in 2° effluents led to faster solids accumulation using CFC compared to 3° effluents (Figure 2.2). When collecting suspended solids from 2°

effluents, the CFC could be operated for a maximum of ∼17 hours, at which point the centrifuge bowl was full and replaced with an empty bowl so that the collected solids would neither impact CFC operation nor become compacted, making their retrieval more difficult. In contrast, the lower TSS concentration in the 3° effluents required sample collection over a period of 24 h.

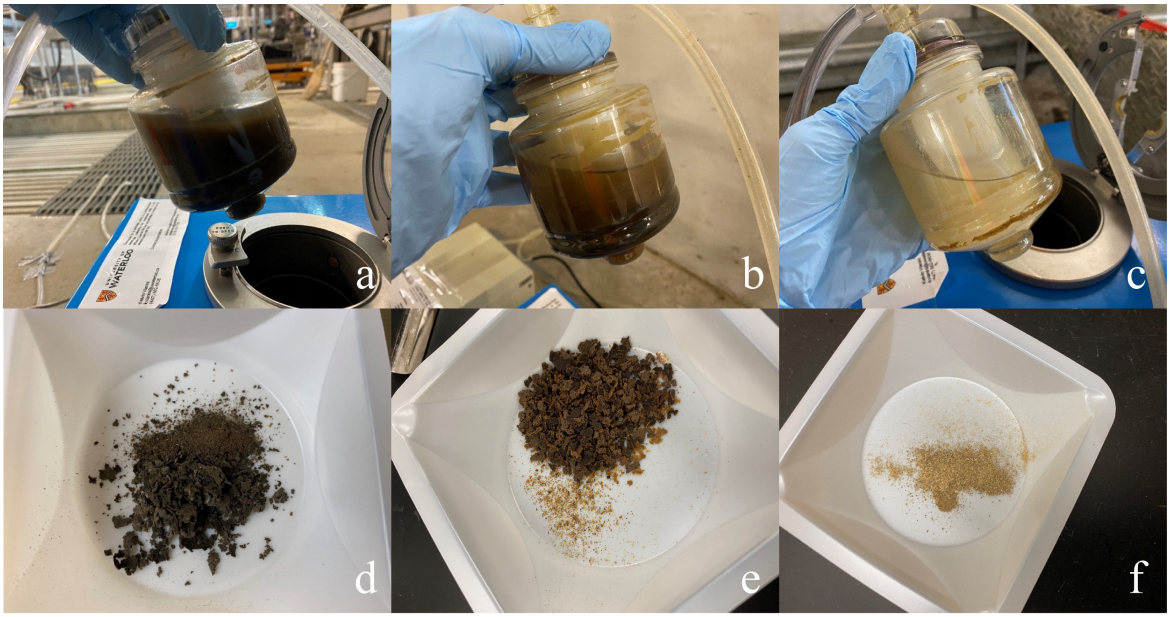


Figure 2.2: CFC: (a) bowl after collecting solids from 2° effluent at Plant W for 17 h; (b) bowl after collecting solids from 2° effluent at Plant K for 17 h; (c) bowl after collecting solids from 3° effluent at Plant K for 17 h; (d) collected dried solids from 2° effluent at Plant W; (e) collected dried solids from 2° effluent at Plant K; and (f) collected dried solids from 3° effluent at Plant K.

Access to the sampling sites was restricted to business hours (i.e., 8 hours per day). Thus, samples were collected and composited over several days to collect sufficient mass of

suspended solids (i.e., 2 g [dw]) needed for PP characterization. It typically took one week (i.e., five 8-hour days) to collect one composite suspended solids sample from 2° effluent. In contrast, it took 2 to 3 weeks to collect one composite suspended solids sample from 3° effluent, which highlights that the method is feasible but substantially constrained by the collection time. Based on an average TSS concentration of ∼5 mg/L in 2° effluents, approximately 2,000 L were centrifuged per composite sample. In the 3° effluent, TSS averaged ∼1 mg/L, and approximately 6,000 L were centrifuged per composite sample.

2.3.2 Method validation

To evaluate the wastewater effluent solids collection efficiency of the CFC, TSS concentrations were measured before and after centrifugation. They were 5.0 ± 0.3 mg/L (mean ± standard deviation) prior to centrifugation and 1.3 ± 0.5 mg/L after. Thus, ∼74% recovery of wastewater suspended solids was achieved using the CFC ($n = 3$). To further investigate recovery efficiency, a controlled experiment was conducted. Kaolin powder was added to deionized water, and 7.1 g of the initial 10 g were recovered when a CFC flow rate of 600 mL/min was used. Overall recovery was 71 ± 2% (mean ± standard deviation). TSS measurements obtained prior to centrifugation yielded a coefficient of variation of 3.85%; it was 25% post-centrifugation. The higher uncertainty observed in post-centrifugation TSS is likely attributable to suspended solids adhering to the internal surfaces of the disposable centrifuge bowls, which can only be emptied and rinsed but not opened, and tubing, as well as potential losses during sample handling and transfer. While the CFC-based method for concentrating suspended wastewater effluent solids could be further refined, the primary

objective here was to obtain a sufficient sample mass (i.e., ∼2 g [dw]) within a practical timeframe.

2.3.3 Effluent particulate phosphorus characterization

Particulate phosphorus forms

The solids concentrations of PP forms (NAIP, OP, and AIP) in wastewater effluents from the two study WWTPs are presented in Figure 2.3. The mean solids NAIP concentration after 2° treatment in Plant W was ∼33% higher than in Plant K (18,900 µg P/g solid vs. 12,600 µg P/g solid, respectively). NAIP concentrations in the 2° wastewater treatment process effluents were marginally significant ($p = 0.06$), potentially reflecting variability introduced by differences in treatment process trains, which are typically not tightly controlled. Examination of the individual fractions composing NAIP is provided in Section 2.3.3.2 and can provide further mechanistic insight into these differences.

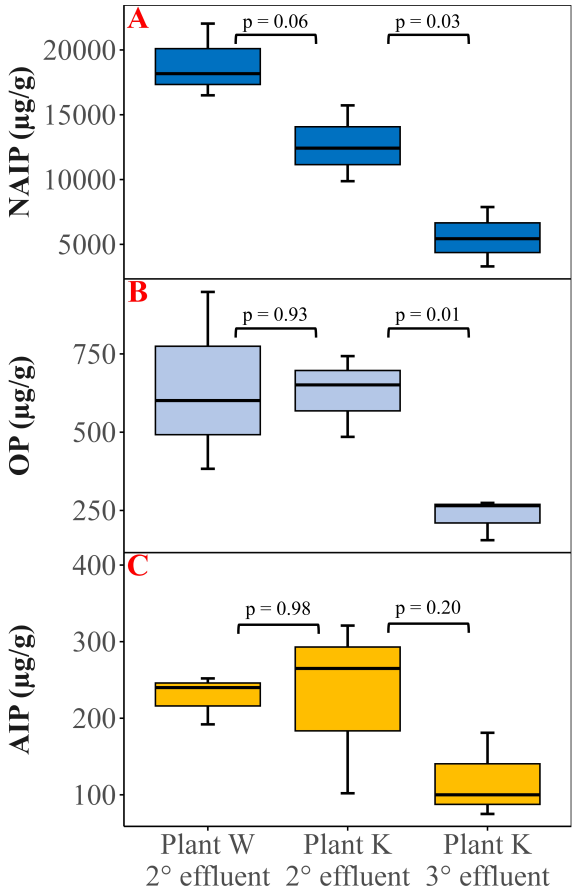


Figure 2.3: The solids concentrations (µg P/g solid) of (A) NAIP, (B) OP, and (C) AIP in 2° and 3° wastewater effluents ($n = 3$). In each chart, the boxes represent the interquartile range, with the lower boundary at the first quartile (Q1) where 25% of the data falls below, and the upper boundary at the third quartile (Q3) where 75% of the data falls below. The height of the box (Q3–Q1) covers the middle 50% of the data. The horizontal line inside the box indicates the median, which reflects the central tendency of the data. The whiskers extend from the minimum value to Q1 and from Q3 to the maximum value, representing the overall data spread.

NAIP removal by 3° treatment was investigated at Plant K. Approximately 56% of the NAIP was removed by 3° treatment using cloth filtration. Here, NAIP solids concentrations decreased from 12,600 µg P/g solid in 2° effluent to 5,500 µg P/g solid in 3° effluent. This reduction was statistically significant ($p = 0.03$).

Unlike NAIP, solids concentrations of OP and AIP following 2° treatment in Plants W and K were similar (Figures 2.3B and 2.3C), but substantially lower than the NAIP concentrations. The mean solids OP concentrations were 644 and 626 µg P/g solid after 2° treatment in Plants W and K, respectively, and were not significantly different ($p = 0.93$). AIP concentrations in the suspended wastewater solids were slightly lower. Mean solids AIP concentrations were 228 and 229 µg P/g solid after 2° treatment in Plants W and K, respectively, and were not significantly different ($p = 0.98$). Approximately 63% of the OP was removed by cloth filtration 3° treatment at Plant K, where mean solids OP concentrations significantly decreased from 626 µg P/g solid in 2° effluent to 231 µg P/g solid in 3° effluent ($p = 0.01$). Mean solids AIP concentrations decreased from 229 µg P/g solid in 2° effluent to 119 µg P/g solid in 3° effluent, indicating that 48% of the AIP was removed at Plant K. This removal was variable, however, and not statistically significant ($p = 0.20$).

NAIP composition

NAIP consists of three reactive P fractions: loosely sorbed, reductant-soluble, and metal-oxide-bound P, which make NAIP readily bioavailable (Sonzogni et al., 1982). These fractions are operationally defined according to the sequential extraction described in Fig-

ure 2.1. In Table 2.1, the NAIP composition of the wastewater effluent solids is contrasted with previous reports of NAIP fractions in river sediments. The prevalence of metal-oxide-bound P in the effluent solids is noteworthy as it serves as an indicator for both short- and long-term P availability, mainly representing P bound to iron and aluminum that can be released at aerobic or, more readily, anoxic conditions (Ting & Appan, 1996; Kaiserli et al., 2002). The metal-oxide-bound fraction is considered highly bioavailable, as it is easily mobilized into SRP because Fe/Al–P associations are destabilized in response to common aquatic system fluctuations such as pH shifts, fluctuations in competing ions and ligands (i.e., dissolved organic matter, silicates, carbonate, and sulfate can displace phosphate from oxide surfaces), and redox fluctuations, where anoxic conditions reduce Fe(III) oxides to soluble Fe(II), releasing sorbed phosphate (House et al., 1998). This can fuel primary production and eutrophication; as P is less tightly bound in this fraction, it is more easily desorbed, making it a key indicator of algal-available P (Froelich, 1988; Manning, 1996; Zhou et al., 2001). Variations in the concentrations of loosely sorbed P and reductant-soluble P are not surprising and can be attributed to P release from decaying cells and bacterial biomass activity (Pettersson, 2001; Wang et al., 2006).

Table 2.1: NAIP fractions in WWTP effluent solids and river sediments.

Reference	Site	Loosely sorbed P + Reductant-soluble P ($\mu g\ P\ g^{-1}solid$)	Metal-oxide-bound P ($\mu g\ P\ g^{-1}solid$)	Ratio
Sampling campaign 1	Plant W 2° Effluent	8,937	13,095	2:1
	Plant K 2° Effluent	866	9,010	10:1
	Plant K 3° Effluent	188	3,110	16:1
Sampling campaign 2	Plant W 2° Effluent	1,569	16,600	11:1
	Plant K 2° Effluent	1,523	10,900	7:1
	Plant K 3° Effluent	1,076	4,360	4:1
Sampling campaign 3	Plant W 2° Effluent	2,100	14,400	7:1
	Plant K 2° Effluent	2,521	13,200	5:1
	Plant K 3° Effluent	2,290	5,590	2:1
Emelko et al., 2016 (reference sites only)	Crowsnest River	88	75	1:1
	Castle River	56	71	1:1
Fogal, 1995 Nith River Watershed - Spring (partitioned by stream order 1-4)	1	106	306	3:1
	2	119	275	2:1
	3	135	203	2:1
	4	76	109	1:1
Fogal, 1995 Nith River Watershed - Fall (partitioned by stream order 1-4)	1	156	255	2:1
	2	140	206	1:1
	3	147	227	2:1
	4	130	166	1:1

The concentration of the metal-oxide-bound P fraction in the effluents investigated was the most pronounced (Table 2.1). Moreover, when comparing the composition of PP in wastewater effluent to that in fine (i.e., <63 µm in size) riverine sediments in natural waters such as the Crowsnest and Castle Rivers in Alberta (Emelko et al., 2016) and the Nith River in Ontario (Fogal, 1995), a striking difference in NAIP composition is evident. The metal-oxide-bound P per gram of wastewater effluent solids is one to two orders of magnitude higher than in riverine sediments impacted by land disturbance (Table 2.1). This dominant prevalence of the metal-oxide-bound P fraction of NAIP in the wastewater treatment process effluents was expected because iron- or aluminum-based coagulants are used in 1° and 2° treatment processes to improve the removal of suspended solids, organic matter, and nutrients, particularly P, by destabilizing particles to enable efficient aggregation and settling and, if relevant, removal by 3° treatment processes. Accordingly, most of the remaining solids suspended in wastewater treatment process effluent streams and discharges can be expected to contain either metal hydrolysis species or metal hydroxide solids, which can bind P by forming metal–P complexes or precipitates. The basic reactions for P precipitation with aluminum (Eq. 2.1) and iron (Eq. 2.2) are presented below (Tchobanoglous et al., 2003):

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \tag{2.1}$$

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \tag{2.2}$$

Thus, while substantial suspended solids reductions, often >90%, are generally achieved through these processes collectively, colloidal solids remain in suspension after 2° clarification and are often visible as pin flocs or turbidity (i.e., "cloudiness"). Although well-operated 3° treatment with cloth filtration can achieve 90 to 99% reductions in suspended solids remaining after 2° treatment (Ramasahayam et al., 2014) and thus meet discharge targets (Holeton et al., 2011), suspended solids are not eliminated, and PP forms within them will likely be predominantly composed of metal-oxide-bound P.

Distribution of PP forms in WWTP effluent PP

The fractional composition of PP forms expressed as a percentage of PP in the 2° and 3° wastewater treatment process effluents is presented in Figure 2.4. Notably, NAIP accounted for >90% of the total PP in the wastewater effluents regardless of treatment type. Thus, while the PP concentration in suspended wastewater solids decreased after 2° and 3° wastewater treatment (Figure 2.3), the composition of PP remained essentially unchanged, indicating that the reduction in PP forms concentrations is primarily driven by solid-phase removal rather than a change in the composition of PP forms. This suggests that almost all PP discharged from the WWTPs to receiving waters may become bioavailable when environmental conditions favour P release from the solids. This helps to explain observations of epiphyte proliferation observed downstream of WWTPs even when treatment achieves substantial reductions in SRP concentrations (Jarvie et al., 2004).

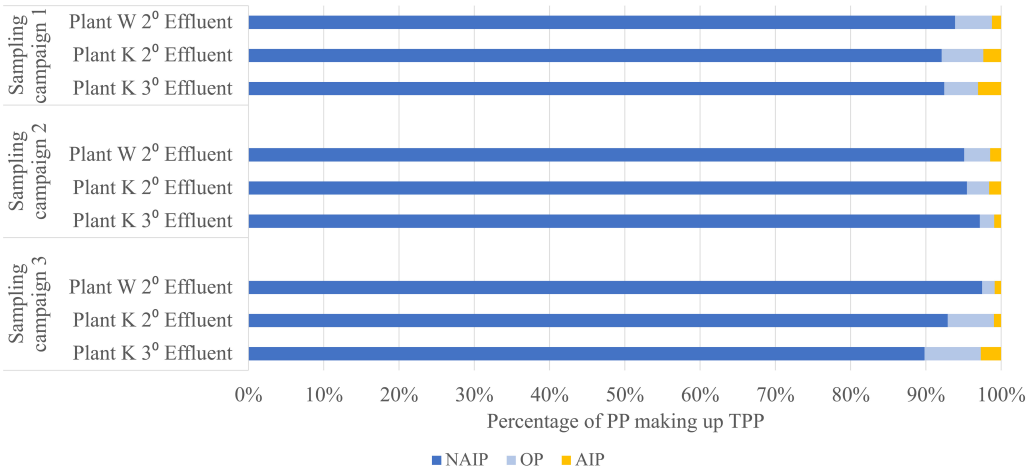


Figure 2.4: Percentage distribution of NAIP, OP, and AIP in 2° and 3° wastewater treatment process effluents collected during three synoptic sampling campaigns.

Although wastewater treatment performance and compliance assessments typically only involve TP and/or SRP (Sedlak, 1991; Smith, 2016), the observations presented herein underscore that these metrics alone are insufficient for characterization of eutrophication threats (Li & Brett, 2015; Wang et al., 2021) because they obscure critical differences among PP fractions: some are stable and largely inert, while others (e.g., NAIP) are readily bioavailable and can fuel eutrophication once discharged. TP includes non-bioavailable fractions (e.g., stable calcium phosphate minerals such as hydroxyapatite that have low solubility in natural waters), while SRP underestimates bioavailable P by excluding dynamic processes such as internal loading from PP. While PP has been evaluated as the difference between TP and SRP (Dueñas et al., 2003; Gu et al., 2011), it does not differentiate between various PP forms and is thus less useful for informing eutrophication threats. Critically, none of these metrics alone fully capture P dynamics, as they overlook both the

immediate availability of aqueous P (i.e., SRP) and the potential for internal loading from bioavailable PP, particularly NAIP, once SRP is depleted. Accordingly, more comprehensive assessment of wastewater treatment performance and downstream eutrophication risk should explicitly include monitoring of NAIP alongside SRP.

2.3.4 Benchmarking WWTP effluent PP relative to other watershed sources

The presence of various PP forms in rivers, lakes, and reservoirs, particularly those situated in areas with agricultural and urban development, has been extensively documented and compared to the results of the present investigation in Figure 2.5. This comparison is not quantitatively absolute because PP composition and mobility are not only governed by land use; they are collectively governed by several factors, including flow regimes, suspended solids size distributions, and sediment ages. High flows mobilize coarse, mineral-bound particles, while finer and colloidal fractions dominate long-range transport and are often enriched in more reactive forms. Sediment age further governs lability, with fresh particles retaining bioavailable P and older sediments undergoing transformations that stabilize or release P depending on redox conditions. Thus, while PP composition and mobility can vary substantially even within a watershed, this comparison nonetheless highlights that solids in discharged wastewater effluents are likely disproportionately enriched in NAIP relative to solids originating from other land uses (e.g., agriculture, wildfire).

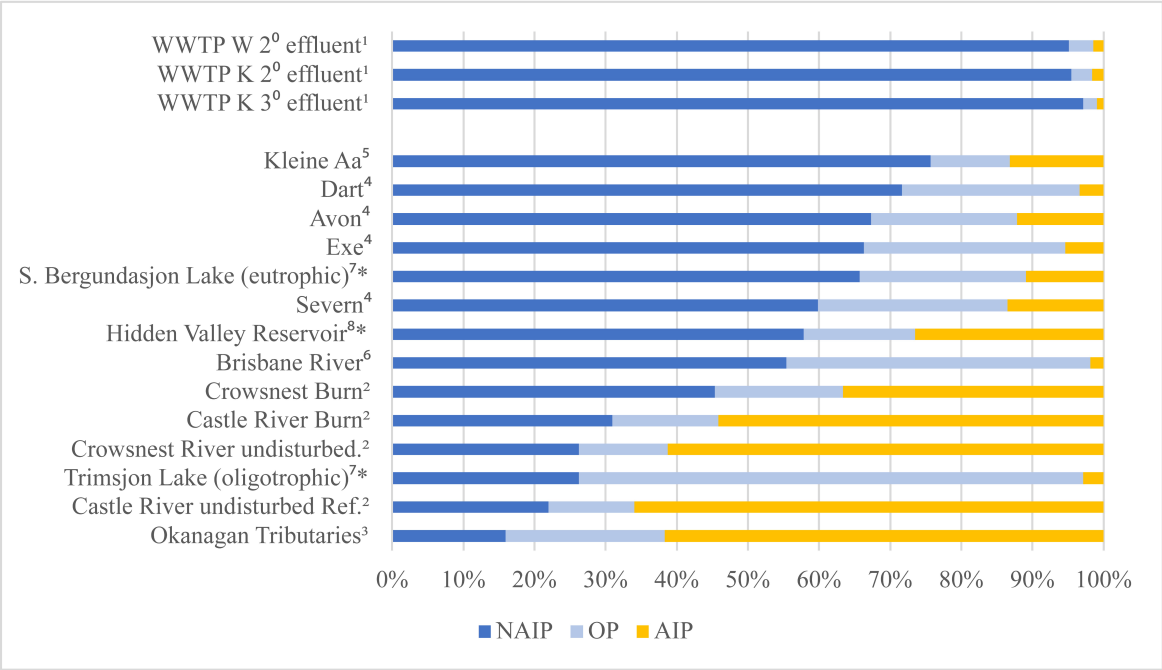


Figure 2.5: Suspended sediment-associated phosphorus forms and their percentage occurrence, ranked from the highest NAIP concentrations to the lowest, in agricultural and urbanized watersheds versus those found in effluent wastewater suspended solids in the current study. WWTP W and K[1], Emelko et al. (2016)[2], Gray & Kirkland (1986)[3], DePinto et al. (1981)[4], Pacini & Gächter (1999)[5], Kerr et al. (2011)[6], Pettersson (1986)[7], Knezic (2021)[8]. Deposited sediments are included for perspective.

The implications of wastewater effluent enrichment with NAIP for receiving water quality are case-specific as they depend on the relative magnitude and timing of NAIP loading from these and other watershed sources. For instance, solids loading from wastewater discharges can be relatively minor in watersheds with limited or no de facto reuse while they might be substantial during periods of low flow. Thus, these findings underscore the

importance of rigorously benchmarking the relative contributions of WWTP discharges and other drivers of nutrient—and particularly NAIP—enrichment to receiving waters and further emphasize the need for comprehensive investigation of these relationships in the future.

2.4 Conclusions

Key conclusions from this work and their associated implications are detailed below:

1. PP in 2° and 3° wastewater effluent suspended solids was predominantly (>90%) composed of NAIP, most of which was bound to metal oxides, thereby suggesting that these solids may contribute to eutrophication, especially if present in sufficiently high concentrations in aquatic systems under conditions favourable for SRP release.

2. While the relative composition (i.e., per cent NAIP, OP, and AIP) of PP did not substantially differ between 2° and 3° treatment process effluents, NAIP concentrations in effluents from cloth filtration 3° treatment were approximately 50% lower than those in 2° treatment effluents. Thus, 3° wastewater treatment via cloth disc filtration can substantially reduce not only TP, but also PP and thus NAIP concentrations in wastewater process effluent streams and discharges.

3. Wastewater solids appear to be among the most NAIP-rich compared to other PP sources in a watershed. Their impact on receiving water quality is case-specific, as it will depend on the relative magnitude and timing of NAIP loading from these and other watershed sources.

4. Unlike traditional filtration methods for evaluating TSS, a CFC-based method enabled relatively rapid concentration of solids from large volumes of wastewater effluents, requiring approximately 5 days for 2° treatment process effluents and approximately 10 days for 3° effluents.

Additional evaluation of PP forms is needed at other WWTPs across a wide range of operational conditions to assess the broader generalizability of these findings. Future research also may expand the scope of this investigation to examine potential seasonality effects on these types of water quality characterizations. In addition, quantitative evaluations of particle size, flow regime, and sediment age impacts on PP composition are needed to strengthen benchmarking, while refinement of the CFC sampling protocol can help to improve recovery and reproducibility and facilitate broader method application.

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Chapter 3

Phosphorus Speciation Reveals Dichotomy in Tertiary Cloth Filtration Performance and Effluent Assessment

Summary

Phosphorus removal in municipal wastewater treatment is commonly evaluated using total phosphorus concentrations, although this aggregate metric does not distinguish among phosphorus forms that differ in bioavailability and receiving water relevance. Here, phosphorus speciation and particulate phosphorus release potential in secondary and tertiary effluents from full-scale wastewater treatment plants were examined to assess how tertiary cloth filtration alters both bulk phosphorus removal and the composition of phosphorus remaining in final effluents. Tertiary treatment consistently reduced total phosphorus and particulate phosphorus fractions, but the residual effluent phosphorus pool became increasingly dominated by dissolved and more readily bioavailable forms. In some cases, soluble reactive phosphorus increased after tertiary filtration despite reductions in total phosphorus. Effluent solids collected after secondary treatment exhibited greater phosphorus release potential than solids remaining after tertiary treatment, indicating that tertiary filtration reduced the pool of particulate phosphorus capable of contributing to downstream release. These findings demonstrate that total phosphorus removal and bioavailable phosphorus reduction are not equivalent outcomes. Phosphorus speciation therefore provides a more meaningful basis for interpreting wastewater treatment performance and potential downstream eutrophication relevance.

3.1 Introduction

Phosphorus removal has long been a critical objective in municipal wastewater treatment, driven by the need to limit nutrient enrichment of receiving waters and meet regulatory discharge requirements. The establishment of phosphorus discharge limits in municipal wastewater effluents and the recognition of diffuse, non-point source pollution trace back to large lake system eutrophication mitigation efforts in the 1960s and 1970s, including Lake Erie phosphorus control initiatives (De Pinto et al., 1986). Early empirical models linking phosphorus loading to algal biomass provided the foundation for regulating phosphorus inputs to aquatic systems (Dillon & Rigler, 1974). Since then, phosphorus control has remained central to wastewater management, water quality protection, and eutrophication mitigation.

Total phosphorus (TP) is the dominant regulatory and operational metric used to evaluate phosphorus removal in municipal wastewater treatment. TP is valuable because it provides a simple, aggregate measure of phosphorus discharged to receiving waters and can be directly related to loading calculations. However, TP is an aggregate measure that encompasses a range of particulate and dissolved phosphorus forms with differing chemical characteristics and ecological implications; not all forms of phosphorus are bioavailable. Particulate phosphorus (PP) is operationally defined as the material retained by a 0.45 µm filter (APHA, 2023). Composed of several forms depending on the extraction scheme, PP is generally less immediately bioavailable than dissolved phosphorus but can act as a long-term nutrient source through desorption, dissolution, mineralization, or sediment-associated transformations. Soluble reactive phosphorus (SRP), by contrast, is generally

considered immediately bioavailable because it is dominated by orthophosphate. Dissolved organic phosphorus and condensed phosphates may also become bioavailable through microbial or chemical transformation (Qin et al., 2015). Therefore, changes in TP do not necessarily represent proportional changes in bioavailable phosphorus.

Wastewater treatment has evolved from conventional primary and secondary processes aimed primarily at removing settleable solids and organic matter to further inclusion of tertiary treatment designed to control nutrient discharges to receiving waters (Ashley et al., 2011). Contemporary secondary treatment typically includes enhanced biological phosphorus removal, which relies on microbial uptake under alternating anaerobic and aerobic conditions, and/or chemical precipitation with metal salts that remove phosphorus by forming insoluble precipitates and particle-associated complexes. Tertiary treatment, including cloth disc filtration, is increasingly applied to reduce residual suspended solids and meet more stringent effluent TP limits. However, because tertiary cloth filtration primarily removes particulate material, it may alter effluent phosphorus speciation in ways that are not fully represented by TP alone. A reduction in TP may reflect removal of less immediately bioavailable particulate fractions while dissolved and reactive fractions persist or become proportionally more dominant.

This creates an important interpretive challenge for wastewater phosphorus assessment. If tertiary treatment reduces TP but leaves behind a larger relative fraction of dissolved or reactive phosphorus, then treatment performance based solely on TP may overestimate the reduction in eutrophication-relevant phosphorus. Conversely, if tertiary filtration removes fine solids enriched in reactive particulate phosphorus, it may reduce the pool of phosphorus capable of downstream release even if dissolved phosphorus remains. Therefore,

resolving phosphorus speciation is necessary to determine whether lower TP corresponds to meaningful reductions in bioavailable phosphorus and receiving water relevance.

The objective of this chapter was to evaluate how tertiary cloth filtration influences phosphorus speciation, bioavailability, and particulate phosphorus release potential in municipal wastewater effluents. Specifically, this work compared phosphorus fractions in secondary and tertiary effluents from full-scale wastewater treatment plants and assessed whether tertiary treatment changes the phosphorus release potential of residual effluent solids. This chapter builds directly on Chapter 2 by extending the characterization of particulate phosphorus forms into an assessment of how treatment level affects effluent phosphorus composition and post-discharge release potential.

3.2 Methodology

3.2.1 Study sites

This research was carried out at three full-scale municipal activated sludge WWTPs located in southwestern Ontario, Canada. Most experiments and sampling campaigns were conducted at Plants K and G, while additional samples were collected at Plant W. All three facilities discharge to the same river, which has an average base flow of approximately 10–15 $m^3\ s^{-1}$. Despite improved water quality over the last decade due to upgrades in wastewater treatment, the river can still present key issues such as high nutrient levels and algal growth. Table 3.1 summarizes the treatment configurations and key processes employed at each WWTP.

Table 3.1: Summary of treatment processes at the investigated wastewater treatment plants.

Feature / Process	Plant W	Plant K	Plant G
Treatment level	Primary + Secondary	Primary + Secondary + Tertiary	Primary + Secondary + Tertiary
Screening & grit removal	✓	✓	✓
Primary clarification	✓	✓	✓
Primary coagulant	$Fe_2(SO_4)_3$	$FeCl_3$	$FeCl_3$
Biological treatment	Activated sludge (aeration tanks)	Activated sludge (aeration tanks)	Activated sludge (aeration tanks)
Secondary coagulant	$Fe_2(SO_4)_3$ before secondary clarification	$FeCl_2$ after primary clarification	$FeCl_3$ before secondary clarification
Secondary clarification	✓	✓	✓
Tertiary filtration	—	Cloth disc filtration (5 µm)	Cloth disc filtration (5 µm)
Disinfection	UV	UV	UV
Role in study	Benchmark (2° vs 3° effluent particulate phosphorus)	Primary study site	Primary study site

Plant W is a full-scale activated sludge WWTP that provides primary, secondary, and disinfection treatment but does not employ tertiary filtration. After passing through screening and grit removal, wastewater undergoes chemical coagulation with ferric sulfate [$Fe_2(SO_4)_3$] followed by primary clarification. The clarified effluent is directed to aeration tanks for biological treatment, after which $Fe_2(SO_4)_3$ is applied again before secondary clarification. Final effluent is disinfected using ultraviolet irradiation before discharge.

Plant K is a full-scale activated sludge WWTP that incorporates tertiary filtration. Incoming wastewater passes through screening and grit removal, then primary clarification. Ferric chloride ($FeCl_3$) is dosed upstream of the primary clarifiers, and ferrous chloride ($FeCl_2$) is added downstream as part of the plant's chemical phosphorus removal strategy. Primary effluent flows to aeration tanks, followed by secondary clarification. The secondary effluent is further treated by cloth disc filtration before UV disinfection and final discharge.

Plant G is a full-scale activated sludge facility with a treatment train similar to Plant K but with a distinct chemical dosing strategy. Wastewater undergoes screening, grit removal, and primary clarification, with $FeCl_3$ added upstream of the primary clarifiers. Primary effluent is treated in aeration tanks, where $FeCl_3$ is also dosed directly to the effluent channels before secondary clarification. Secondary effluent is polished through the same type of cloth disc filters used at Plant K, with a nominal pore size of 5 µm, prior to UV disinfection and discharge.

3.2.2 Sampling design

The experimental design enabled characterization of effluent phosphorus fractions and assessment of the release potential of secondary and tertiary effluent solids. Aqueous samples were collected from secondary and tertiary effluents of Plants K and G, while solids samples were obtained from secondary and tertiary effluents of Plant K and secondary effluent of Plant W. A total of 40 aqueous effluent samples were collected, comprising 10 samples each from the secondary and tertiary effluents of Plants K and G. These samples were used to evaluate phosphorus speciation before and after tertiary treatment.

Suspended solids were collected to assess particulate phosphorus release potential. Secondary effluent solids from Plant W and secondary and tertiary effluent solids from Plant K were collected using the continuous-flow centrifugation method described in Chapter 2. This approach enabled recovery of sufficient mass of fine suspended solids from large volumes of effluent for laboratory release experiments.

3.2.3 Phosphorus fractionation

Several fractionation approaches exist for operationally defining dissolved and particulate phosphorus fractions. Here, the phosphorus fractions measured directly included total phosphorus (TP), total dissolved phosphorus (TDP), total reactive phosphorus (TRP), and soluble reactive phosphorus (SRP), as a measurement of orthophosphate using HACH Method 8048, adapted from APHA (APHA, 2023) and accepted by USEPA for wastewater analyses. The remaining phosphorus fractions were determined by difference.

The phosphorus fractionation scheme used in this study is shown in Figure 3.1. Dissolved organic phosphorus and condensed phosphates (DOCP) were calculated as the difference between TDP and SRP. Total particulate phosphorus (TPP) was calculated as the difference between TP and TDP. Particulate reactive phosphorus (PRP) was calculated as the difference between TRP and SRP. Particulate organic phosphorus and condensed phosphates (POCP) were calculated by difference from the remaining particulate phosphorus pool.

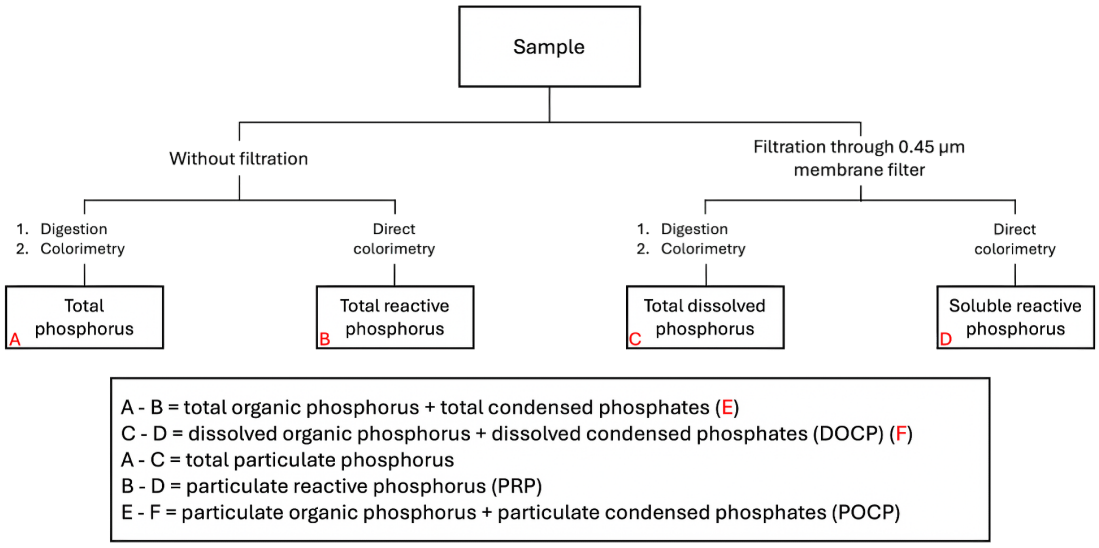


Figure 3.1: Phosphorus fractionation scheme used in this study, showing measured pools and derived fractions. Total phosphorus, total reactive phosphorus, soluble reactive phosphorus, and total dissolved phosphorus were directly measured, while dissolved organic phosphorus and condensed phosphates, total particulate phosphorus, particulate reactive phosphorus, and particulate organic phosphorus and condensed phosphates were obtained from differences between measured pools.

3.2.4 Evaluation of phosphorus release potential from wastewater solids

Wastewater solids contribute to bioavailable phosphorus in receiving waters because they contain particulate phosphorus (Søndergaard et al., 2003). Recent work has shown that the particulate phosphorus contained in wastewater effluent solids is predominantly bioavailable (i.e., NAIP rich) (Vianini et al., 2025; Chapter 2). Commonly used to evaluate phosphorus release potential for freshwater solids, the equilibrium phosphate concentration (EPC_0) can also provide insight into phosphorus release potential for wastewater solids. EPC_0 represents the aquatic system SRP concentration at which there is no net phosphorus exchange between solids and the surrounding water. When ambient SRP is lower than EPC_0, solids tend to release phosphorus to the water column; when ambient SRP is greater than EPC_0, solids tend to adsorb phosphorus.

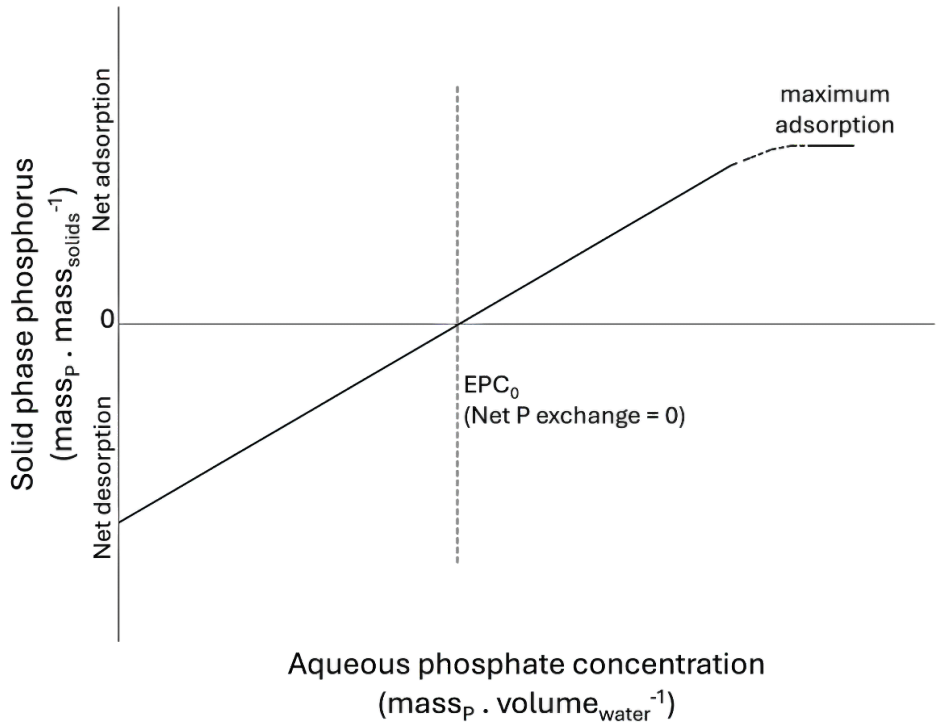


Figure 3.2: Schematic of EPC_0 analysis for assessing phosphorus release potential from solids in an aquatic system. Net phosphorus adsorption or release by solids is plotted against aqueous SRP concentration. The x-intercept represents the EPC_0, where no net exchange occurs. When ambient SRP is below EPC_0, solids release phosphorus to the water column, acting as a source; when ambient SRP exceeds EPC_0, solids act as a sink and adsorb phosphorus.

To estimate phosphorus release potential from effluent suspended solids, a method described by Emelko et al. (2016) for analysis of riverine sediments was used. Specifically, 0.25 g of effluent solids oven-dried at 105 °C for 18 h and ground with a ceramic mortar

and pestle was mixed with 25 mL of the background water matrix in 50 mL centrifuge tubes. Each phosphate treatment was prepared in triplicate and placed on an orbital shaker at approximately 100 rpm for 18 h at room temperature, approximately 20 °C. Samples were then centrifuged, and the supernatant was analyzed for SRP. The incubation period is consistent with the duration commonly used for natural sediments. Because the wastewater-derived solids examined in this study were dominated by the NAIP fraction, equilibrium was expected relatively rapidly, as previous kinetic studies have shown that phosphorus exchange in NAIP-rich materials occurs predominantly within the early stages of incubation (Xu et al., 2015; Zeng et al., 2019). The experiments were designed to provide mechanistic insights, not specific environmental conditions.

Preliminary tests using Milli-Q^{TM} water established a baseline for phosphorus release potential, with four levels of phosphate addition: 0, 50, 150, and 450 µg P L^{-1} for secondary effluent solids from Plants W and K, and 0, 50, 150, and 500 µg P L^{-1} for tertiary solids from Plant K. To assess release potential under environmentally relevant conditions, receiving water was collected upstream of Plant W's outfall, filtered through a 0.45 µm glass-fiber membrane, and amended with phosphate (intended to represent environmentally relevant receiving water conditions). The receiving water incubations compared secondary effluent solids from Plant W with tertiary effluent solids from Plant K.

3.2.5 Data analysis

Concentrations of the various phosphorus fractions in the secondary and tertiary effluents collected from Plants K and G were obtained using the fractionation scheme shown in

Figure 3.1. Descriptive statistics, including means, standard deviations, and proportional contributions to total phosphorus, were used to summarize the distribution of phosphorus in each effluent type. Differences in phosphorus fraction concentrations between secondary and tertiary effluents were assessed using two-tailed t-tests. Where variance assumptions were not met, Welch's t-test was used.

Phosphorus release potential was evaluated by plotting net phosphorus adsorption or release against initial SRP concentration. Linear regression was used to estimate the relationship between SRP and net phosphorus exchange. Differences in slopes were evaluated within an ANCOVA framework by testing the SRP $\times$ treatment interaction using ANOVA on nested linear models in R. When slopes were not significantly different, differences in intercepts were evaluated to compare baseline release potential among solids types. Statistical interpretation emphasized consistency of observed patterns and effect sizes in addition to p-values.

3.3 Results and Discussion

3.3.1 Assessing TP reduction and composition

TP removal in Plants K and G

While TP remains a central metric in wastewater treatment monitoring, assessing treatment performance based solely on TP concentrations can be misleading. Figure 3.3 depicts the concentrations of TP in secondary and tertiary effluents and the various phosphorus

fractions composing it.

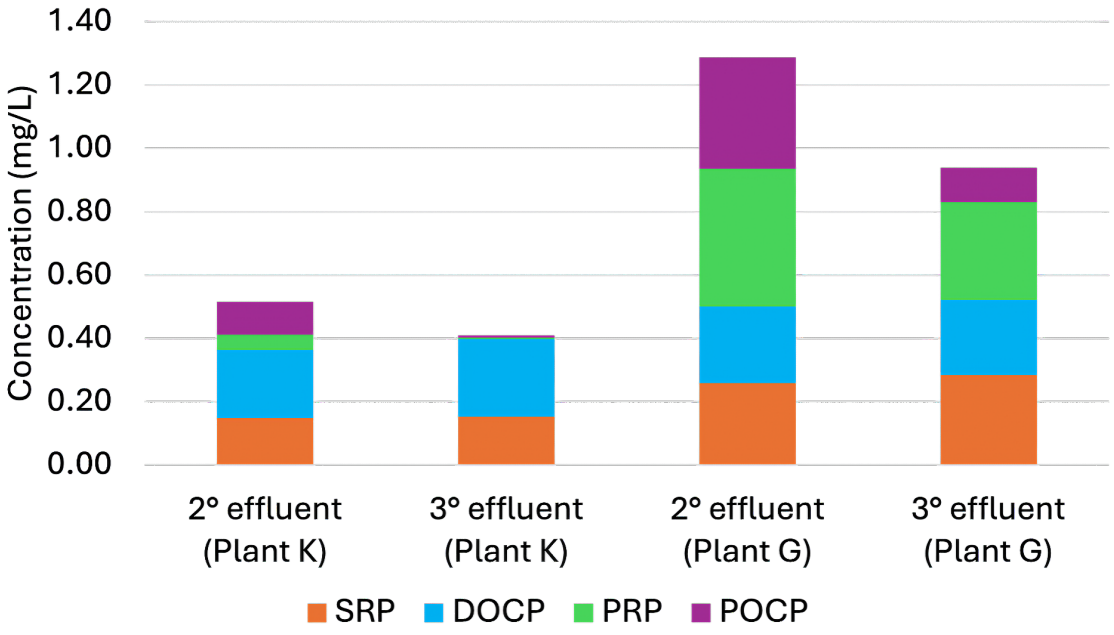


Figure 3.3: Average concentrations of TP and fractions that compose it in 2° and 3° effluents: soluble reactive phosphorus (SRP), dissolved organic phosphorus and condensed phosphates (DOCP), particulate reactive phosphorus (PRP), and particulate organic phosphorus and condensed phosphates (POCP).

Increasingly stringent phosphorus regulations have driven the adoption of treatment technologies capable of achieving low TP concentrations, typically targeting <1 mg P L^{-1} (Alibardi et al., 2021; Murujew et al., 2025). In practice, chemically dosed secondary treatment generally produces effluent TP concentrations in the range of 0.8–1.2 mg P L^{-1} (Comber et al., 2015), while tertiary processes such as cloth filtration can reliably reduce TP to approximately 0.5 mg P L^{-1} (Murujew et al., 2025). Consistent with this expectation,

tertiary cloth filtration reduced TP concentrations at both Plants K and G.

At both plants, TP reduction was driven primarily by removal of particulate phosphorus fractions, particularly POCP, whereas reductions in PRP were smaller, especially at Plant G (Figure 3.3). Consequently, tertiary treatment reduced bulk phosphorus concentrations more effectively than it reduced readily bioavailable phosphorus fractions. Accordingly, TP reduction and bioavailable phosphorus reduction were not equivalent treatment outcomes.

TP composition and removal of TP fractions in Plants K and G

The concentrations of each phosphorus fraction analyzed in effluent samples from Plants K and G are depicted in Figure 3.4. The box-and-whisker plots illustrate the distribution, central tendency, and variability of each phosphorus fraction across the sampled datasets, providing a visual comparison of concentration ranges and potential differences between the two treatment plants. Negative calculated concentrations arise when analytical uncertainty associated with independently measured variables is propagated through difference calculations, particularly when the true concentration is near zero. These values are retained in the statistical analysis to prevent artificially reducing–and thereby biasing–the variance.

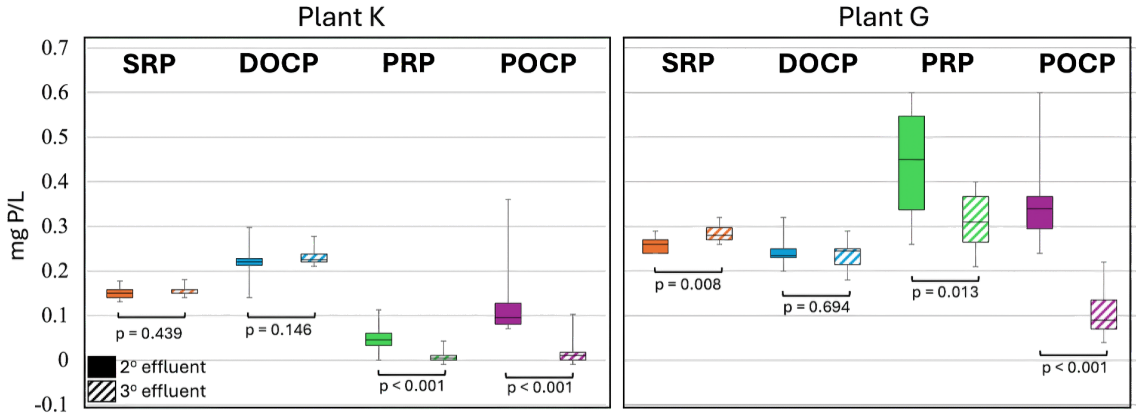


Figure 3.4: Concentrations of phosphorus fractions in 2° and 3° effluents of Plants K and G. Each box-and-whisker plot represents ten observations ($n = 10$). The boxes represent the interquartile range, with the horizontal line inside the box indicating the median and the whiskers showing the minimum and maximum values.

Phosphorus fraction concentrations varied between the two plants; this was expected because treatment conditions, including coagulant type, coagulant dose, and influent wastewater quality, affect final effluent phosphorus characteristics. Notably, despite an overall decrease in TP, SRP, the most readily bioavailable fraction, increased slightly in the tertiary effluent at Plant G, with mean concentrations rising from 0.26 to 0.29 mg P L^{-1} ($p = 0.007$) and median concentrations from 0.26 to 0.28 mg P L^{-1}. At Plant K, SRP remained approximately 0.15 mg P L^{-1} after tertiary treatment.

Although both plants employ activated sludge treatment, utilize tertiary cloth filtration, and apply chemical dosing for phosphorus removal, albeit with different coagulant types and dosing strategies, the phosphorus speciation observed in Plant K differed from that

in Plant G. While Plant G showed a significant reduction in total PP following tertiary filtration (POCP: $p < 0.001$; PRP: $p = 0.013$), the removal of these fractions was not proportional; non-reactive PP, represented by POCP, was removed more effectively than PRP. This indicates that tertiary cloth filtration preferentially removed some particulate fractions while leaving a residual reactive phosphorus pool in the final effluent.

The relative abundance of dissolved phosphorus fractions in tertiary effluent TP was consistent across both plants, reinforcing the trend that treated effluents tend to become predominantly composed of phosphorus forms that are more bioavailable, despite differences in treatment design and performance (Millier & Hooda, 2011). The concentrations of DOCP increased slightly in Plant K, from approximately 0.21 mg P L^{-1} in secondary effluent to 0.24 mg P L^{-1} following tertiary treatment, but this change was not statistically significant ($p = 0.146$). At Plant G, DOCP remained approximately 0.24 mg P L^{-1} across secondary and tertiary effluents. These results indicate that tertiary filtration primarily altered the particulate component of TP, while dissolved phosphorus fractions persisted.

3.3.2 Effect of tertiary treatment on phosphorus release potential from wastewater solids

The effect of tertiary treatment on phosphorus release potential from wastewater suspended solids was first evaluated under standardized aqueous conditions using Milli-Q^{TM} water (Figure 3.5). This comparison provided a controlled and conservative basis for assessing differences among solids collected from secondary and tertiary effluents by minimizing the influence of background water chemistry. In this matrix, differences in release behaviour

can be interpreted primarily as reflecting intrinsic differences in the solids rather than receiving water chemistry.

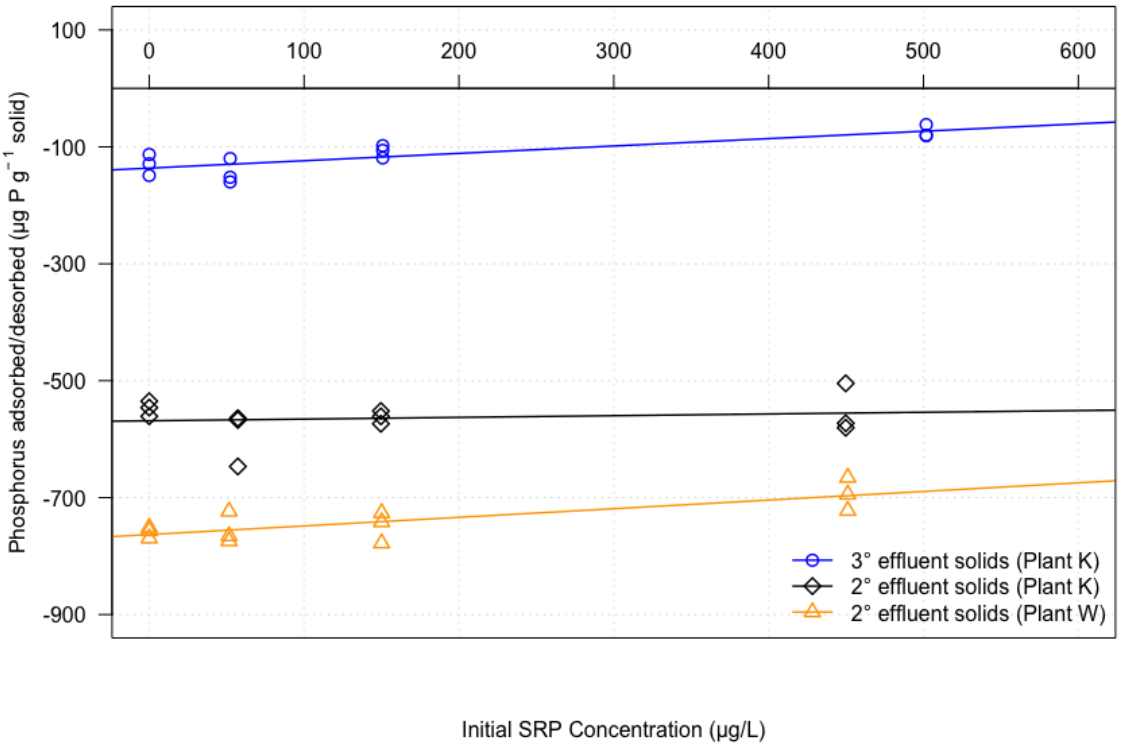


Figure 3.5: Phosphorus release potential from suspended solids collected from secondary and tertiary effluents from Plants W and K as a function of initial SRP concentration. Experiments were conducted in Milli-Q^{TM} water. Negative values on the y-axis indicate phosphorus release, or desorption, from solids to the water column.

In the Milli-Q^{TM} experiments, regression slopes did not differ significantly among treatments (SRP $\times$ treatment interaction, $p = 0.125$; pairwise comparisons $p > 0.05$), indicating that the response of phosphorus release to increasing SRP was not statistically distinguish-

able across solids types (Figure 3.5). In contrast, regression intercepts differed significantly in all cases ($p < 0.001$). Secondary effluent solids exhibited substantially greater baseline phosphorus release than tertiary effluent solids, indicating that tertiary treatment reduced the releasable phosphorus pool associated with residual suspended solids.

The collected effluent solids were introduced into aqueous solutions spanning a broad range of phosphate concentrations, up to 560 µg L^{-1}. Evaluation of EPC_0 typically involves the use of SRP concentrations that exceed EPC_0 so that fitted regressions exhibit Langmuir-type sorption behaviour at non-saturating SRP conditions, where phosphorus exchange is approximately linear and extrapolation of EPC_0 within the tested concentration range is enabled (Cyr et al., 2009). In the present study, SRP concentrations were selected to span environmentally relevant ranges and provide insight into relative phosphorus release behaviour among solids types. Therefore, the results should be interpreted as comparative release potential rather than absolute equilibrium descriptors.

To contextualize the standardized comparison under more environmentally realistic conditions, phosphorus release from final secondary effluent solids from Plant W was also compared with final tertiary effluent solids from Plant K in receiving waters amended with phosphate (Figure 3.6). Because Plant K secondary solids were not available for the receiving water incubations, this comparison should not be interpreted as a strictly paired treatment-stage contrast. Instead, it provides receiving water context for comparing solids from a secondary-only plant with residual solids after tertiary treatment.

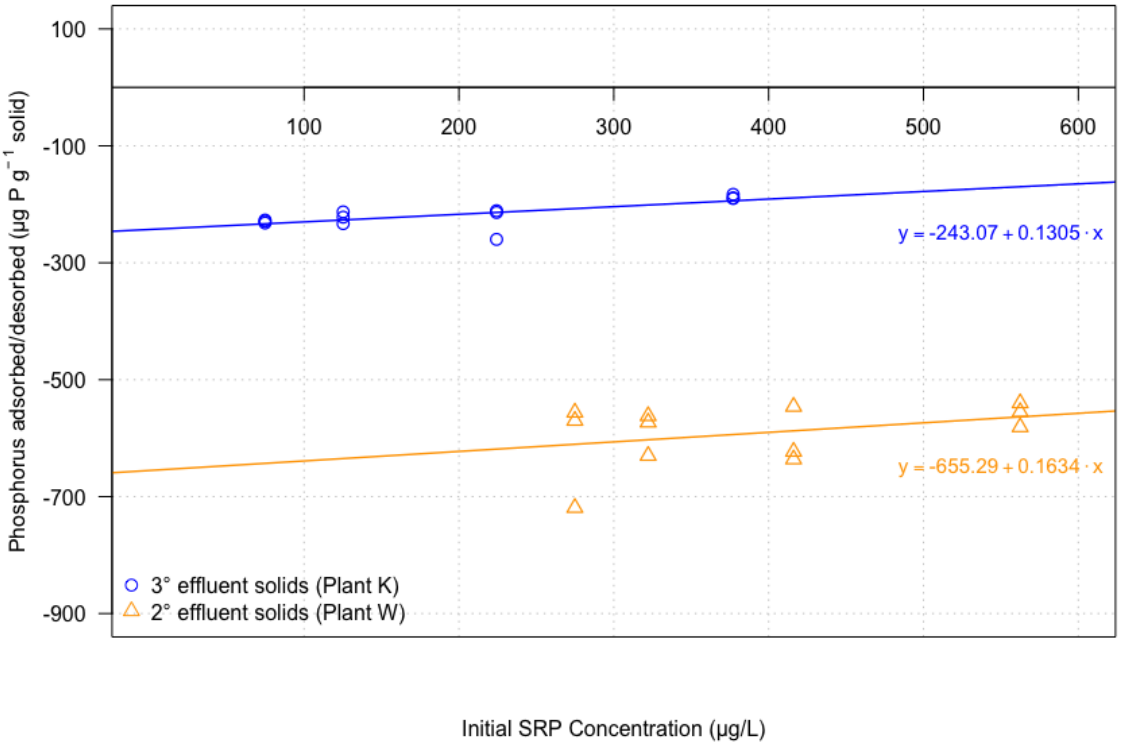


Figure 3.6: Phosphorus release potential from effluent solids collected at a WWTP with secondary treatment only, Plant W, compared to a WWTP with tertiary treatment, Plant K. Collected solids were added to receiving waters amended with phosphate so that SRP concentrations ranged from approximately 275–560 µg L^{-1} for the secondary effluent solids and 75–375 µg L^{-1} for the tertiary effluent solids. The different initial concentrations and ranges reflect SRP at the time of receiving water collection and amendment.

The receiving water incubations showed a similar overall pattern to the standardized Milli-Q^{TM} experiments. Regression slopes were not significantly different between the secondary and tertiary solids (SRP × treatment interaction, $p = 0.813$), suggesting similar

desorption responses to increasing SRP across these solids types. However, regression intercepts differed significantly ($p < 0.001$), with secondary effluent solids exhibiting a more negative intercept than tertiary solids, -655.29 versus -243.07 µg P g^{-1} solids, respectively. This indicates that secondary solids had greater baseline phosphorus release potential than tertiary solids under receiving water conditions.

These findings indicate that WWTPs can influence phosphorus dynamics not only through dissolved phosphorus inputs, but also through the discharge of fine suspended solids with measurable phosphorus release potential. This mechanism is distinct from, but complementary to, the sediment buffering framework synthesized by Simpson et al. (2021), which evaluated streambed sediment EPC_0 and stream-water SRP under baseflow conditions using phosphate exchange potential. Their analysis emphasizes the role of streambed sediments in regulating dissolved phosphorus availability. In contrast, the present results show that wastewater-derived suspended solids can introduce a distinct, mobile, and reactive particulate phosphorus pool that may contribute to bioavailable phosphorus after discharge.

3.3.3 Limitations of inter-plant comparisons and the need for site-specific assessment

The objective of this work was not to establish universal treatment behaviour across all WWTPs, but rather to evaluate how phosphorus speciation and release potential can differ before and after tertiary treatment with cloth filtration under full-scale operational conditions. Inter-plant comparisons should therefore be interpreted cautiously. Differences in

coagulant type and dose, solids retention, biological phosphorus removal performance, influent composition, and hydraulic operation can still influence phosphorus speciation in the final effluent. Accordingly, some of the differences observed between Plants K and G likely reflect operational and treatment-specific variation within chemically assisted phosphorus removal systems rather than fundamentally different phosphorus removal technologies.

3.3.4 Improving phosphorus management beyond TP removal

When effluent TP is treated as a single bulk parameter, important differences in phosphorus speciation may remain undetected, potentially leading to underestimation or overestimation of the ecological implications of WWTP discharges. In the present study, the persistence of SRP and PRP in final effluents indicated limited removal of phosphorus fractions with greater immediate bioavailability, despite substantial reductions in TP. Incorporating phosphorus speciation into routine monitoring and treatment assessment would improve the ability to distinguish between reductions in bulk phosphorus and reductions in eutrophication-relevant phosphorus.

Tertiary treatment is increasingly adopted to achieve stringent TP discharge targets that are often unattainable through conventional secondary treatment alone (Bashar et al., 2018). However, different tertiary treatment technologies alter phosphorus speciation differently and may therefore vary in their effectiveness at reducing eutrophication-relevant phosphorus fractions (Bashar et al., 2018; Gu et al., 2011; Remy et al., 2014). Here, while tertiary cloth media filtration effectively reduced TP and particulate phosphorus, it did not necessarily reduce dissolved bioavailable phosphorus. Therefore, treatment evaluation

based solely on TP may not fully capture the capacity of tertiary filtration to reduce downstream eutrophication potential.

Improving phosphorus management requires moving beyond TP-based metrics toward explicit consideration of phosphorus speciation and bioavailability. Optimizing upstream processes such as coagulation, alongside tertiary treatment, is critical to reducing bioavailable phosphorus, including SRP and reactive particulate fractions such as NAIP, that more directly governs ecological response. This distinction becomes particularly consequential when considering the broader role of WWTPs in receiving water quality and its relationship to human and ecosystem health. Cyanobacterial and algal responses depend not only on phosphorus concentration but also on the form and timing of phosphorus delivery, hydrology, residence time, background nutrient status, and biological demand.

It is important to note that, although the persistence of dissolved and reactive phosphorus fractions indicates that TP reductions alone may not fully represent eutrophication-relevant treatment performance, ecological response cannot be inferred directly from phosphorus concentrations or release potential alone. Biological response is not governed by a universal SRP threshold but by the interaction among phosphorus availability, hydrology, residence time, background nutrient status, and biological demand (Dadi et al., 2023; Dodds, 2003; Reynolds & Davies, 2001). Therefore, reductions or increases in bioavailable phosphorus fractions here are interpreted as changes in eutrophication potential rather than direct predictors of ecological response, as further addressed in Chapter 5.

3.4 Conclusions

This study demonstrated that evaluating phosphorus removal based solely on TP can obscure critical changes in effluent composition that govern eutrophication potential. While tertiary cloth filtration consistently reduced TP and particulate phosphorus fractions, it also altered phosphorus speciation, resulting in effluents dominated by dissolved, more readily bioavailable forms. As such, reductions in TP do not necessarily translate into proportional reductions in eutrophication-relevant phosphorus fractions. When treatment processes preferentially remove less immediately bioavailable fractions while dissolved and reactive fractions persist, TP-based assessment can overestimate the ecological benefit of treatment.

Differences between secondary and tertiary effluents were primarily driven by changes in particulate phosphorus composition and behaviour. Secondary effluent solids exhibited greater phosphorus release potential, whereas tertiary treatment reduced this pool by removing particulate fractions, including some potentially bioavailable and transformable phosphorus. However, the residual phosphorus in tertiary effluent remained largely bioavailable, and in some cases, treatment coincided with increases in SRP. Although several mechanisms could contribute to the observed SRP increase—including transformation of particulate phosphorus, operational variability, or analytical variability—the present study was not designed to distinguish among these processes. The underlying mechanism remains uncertain and warrants further investigation, as even modest changes in SRP warrant consideration when concentrations are already environmentally relevant. Collectively, these findings indicate that tertiary cloth filtration may primarily alter phosphorus partitioning

between particulate and dissolved phases, while exerting limited, if any, reduction in overall effluent bioavailable phosphorus fractions.

This work emphasizes that phosphorus speciation provides a more meaningful basis for assessing WWTP treatment performance and downstream risk. Incorporating measures of bioavailable phosphorus, including SRP and reactive particulate fractions such as NAIP, into monitoring, performance demonstration, and regulatory frameworks is therefore essential to ensure that measured reductions in phosphorus discharged correspond to actual reductions in eutrophication potential.

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Chapter 4

Assessing the Conformity of Wastewater Effluent Solids to Established Paradigms of Phosphorus Desorption in Aquatic Systems

Summary

Effluent-derived particulate phosphorus can contain reactive and potentially bioavailable fractions, and previous results showed that tertiary filtration can reduce particulate phosphorus and lower the release potential of wastewater solids while leaving dissolved bioavailable phosphorus forms in the final effluent. Building on this evidence, phosphorus release from effluent-derived solids was evaluated under receiving water conditions to determine whether their behaviour follows assumptions commonly derived from sediment phosphorus paradigms. Batch experiments evaluated phosphorus desorption across gradients in initial soluble reactive phosphorus, pH, temperature, and receiving water matrix. Effluent solids released phosphorus under environmentally relevant conditions, with release behaviour influenced by ambient phosphorus concentration and environmental controls, particularly lower pH and higher temperature. Although some responses were consistent with sediment-based expectations, wastewater-derived solids exhibited distinct release behaviour that reflected their treatment-derived composition and phosphorus speciation. These findings indicate that effluent solids should not be treated as interchangeable with natural sediments in receiving water assessments, and that their phosphorus release potential should be independently quantified when evaluating wastewater contributions to downstream bioavailable phosphorus.

4.1 Introduction

Phosphorus enrichment remains a central driver of freshwater eutrophication and its resulting harmful algal and cyanobacterial blooms, ecosystem degradation, and drinking-water treatment challenges (Correll, 1998; Elser et al., 2007; Sadegh et al., 2021). Management strategies have therefore focused primarily on reducing total phosphorus (TP) loads to receiving waters. However, ecological response is not controlled by TP alone, but by the chemical form, mobility, persistence, and bioavailability of phosphorus after discharge (Chapter 3) (Boström et al., 1988; Read et al., 2014; Reynolds & Davies, 2001; Vianini et al., 2025). Particulate phosphorus (PP) is especially important because fine solids can transport phosphorus downstream, deposit in receiving environments, and release dissolved bioavailable phosphorus under favourable physicochemical conditions, a phenomenon known as internal phosphorus loading (Boström, 1984; Nurnberg, 2009; Stone & English, 1993).

Phosphorus exchange between particulate material and the water column has been studied extensively for freshwater sediments and suspended solids derived from agricultural, forested, and urban landscapes (Simpson et al., 2021). Sediment phosphorus exchange is influenced by interacting controls, including ambient soluble reactive phosphorus (SRP), pH, temperature, redox conditions, mineralogy, and particle composition (Holdren & Armstrong, 1980; House, 2003; Huang et al., 2021; Kim et al., 2003; Rydin et al., 2011; Simpson et al., 2021; Torrent et al., 2007; Watt et al., 2021; H. Zhang et al., 2022). Concepts such as the equilibrium phosphorus concentration (EPC_0) are commonly used to describe the SRP concentration at which net phosphorus exchange approaches zero and to

infer whether sediments are likely to behave as phosphorus sources or sinks under given water column conditions (Simpson et al., 2021).

The transferability of these sediment-based phosphorus exchange concepts to wastewater effluent solids is not self-evident. Unlike many natural sediments, wastewater-derived particulates are recently formed, biologically and chemically conditioned during treatment, and may contain elevated proportions of reactive iron- or aluminum-associated phosphorus and non-apatite inorganic phosphorus (NAIP), a readily bioavailable phosphorus fraction (Emelko et al., 2016; Vianini et al., 2025). Treatment processes such as coagulation, secondary clarification, and tertiary treatment can further alter the amount and composition of bioavailable phosphorus associated with suspended solids discharged to receiving waters (Vianini et al., 2025). Consequently, wastewater effluent solids may share some qualitative behaviours with natural sediments while differing substantially in release magnitude, apparent exchange thresholds, and sensitivity to receiving water chemistry.

Despite growing recognition that treated wastewater effluents can contribute bioavailable phosphorus to rivers (Carey & Migliaccio, 2009; Jarvie et al., 2006), the environmental controls on phosphorus release from effluent-derived solids remain insufficiently characterized. In particular, it remains unclear whether common sediment phosphorus exchange behaviours, that is, responses to ambient SRP, pH, and temperature, adequately describe wastewater particulates following discharge. This study addresses that gap by evaluating phosphorus release from secondary and tertiary wastewater effluent solids under controlled receiving water conditions. The objectives were to: (1) determine whether effluent solids behave as phosphorus sources or sinks across environmentally relevant SRP gradients; (2) compare extrapolated EPC_0 behaviour between secondary and tertiary effluent solids; (3)

evaluate short-term phosphorus release responses to pH and temperature; and (4) assess where sediment-based exchange concepts are qualitatively useful or quantitatively limited for interpreting wastewater-derived particulate phosphorus.

4.2 Methodology

This study evaluated whether phosphorus exchange behaviours commonly reported for freshwater sediments adequately describe wastewater effluent solids under environmentally relevant conditions. Bench-scale batch experiments were conducted using secondary and tertiary effluent solids to evaluate phosphorus exchange responses across gradients of ambient SRP, pH, and temperature. The experimental design was informed by commonly used sediment phosphorus exchange methodologies (Emelko et al., 2016) to evaluate apparent EPC_0 behaviour and sediment–water phosphorus interactions.

4.2.1 Study Sites and Effluent Solids Sampling

Effluent solids were collected from two full-scale WWTPs in southern Ontario, Canada, referred to as Plant W and Plant K. Both facilities employ primary clarification, activated sludge biological treatment, secondary clarification, chemical coagulation, and ultraviolet disinfection. Plant K additionally incorporates tertiary cloth-disc filtration prior to disinfection. Treatment configurations are summarized in Table 4.1.

Table 4.1: Summary of treatment processes at the sampling sites.

Feature / Process	*Plant W*	*Plant K*
Treatment level	Primary + Secondary	Primary + Secondary + Tertiary
Screening & grit removal	✓	✓
Primary clarification	✓	✓
Primary coagulant dosing	Ferric sulphate	Ferric chloride
Biological treatment	Activated sludge (aeration tanks)	Activated sludge (aeration tanks)
Secondary coagulant dosing	Ferric sulphate	Ferrous chloride
Secondary clarification	✓	✓
Tertiary filtration	—	Cloth disc filtration (5 µm)
Effluent suspended solids concentration	~5-6 mg/L	~1-2 mg/L
Disinfection	UV	UV
Role in study	Primary study site	Additional sampling location to evaluate the effects of level of treatment

Effluent suspended solids were collected during winter 2024 using continuous-flow centrifugation as described by Vianini et al. (2025). Samples were collected from the final effluent at Plant W and from the tertiary filter outflow at Plant K. Wet solids were oven-dried at 105 °C for 24 h and composited across multiple sampling days to obtain sufficient dry mass for experimentation. Although drying may alter some redox-sensitive phosphorus associations, this approach has commonly been used for standardized inter-sample comparison and EPC_0-style analyses with other particulate sources and water matrices (House & Denison, 2000; Jensen et al., 1992).

River water was collected upstream of discharge locations and used as the experimental matrix to approximate receiving water conditions following effluent discharge. Samples were filtered through 0.45 µm glass fibre filters (Whatman®, USA) prior to use to minimize interference from ambient suspended solids (APHA, 2023).

4.2.2 Batch Desorption Experiments

Batch desorption experiments were conducted using river water and oven-dried effluent solids to evaluate phosphorus exchange responses under controlled SRP, pH, and temperature conditions. For SRP gradient experiments, initial SRP concentrations ranged from 275 to 560 µg P L^{-1} for secondary effluent solids and from 75 to 380 µg P L^{-1} for tertiary effluent solids. Differences in concentration range reflected differences in initial river-water SRP concentrations between collection events. The temperature was maintained at 20 °C, and the initial pH was approximately 7.

For pH experiments, initial solution pH was adjusted to 5, 6, 7, 8, 9, or 10 using

sulfuric acid or potassium hydroxide. Temperature was maintained at 20 °C and SRP at approximately 100 µg P L^{-1}. For temperature experiments, incubation was conducted at 5, 15, 20, and 35 °C with initial SRP maintained near 70 µg P L^{-1} and pH near 7.

Batch tests were performed in 50 mL centrifuge tubes containing 0.25 g of dry solids and 25 mL of solution, corresponding to a solids-to-solution ratio of 1:100. Tubes were incubated for 18 h in a temperature-controlled orbital shaker at 100 rpm (Emelko et al., 2016). Each treatment condition was evaluated in triplicate.

4.2.3 Analytical Methods

Following incubation, samples were filtered through 0.45 µm polyethersulfone syringe filters (Pall Corporation, USA). Filtrates were diluted approximately 20-fold prior to analysis to ensure concentrations remained within the analytical range. SRP concentrations were measured using a SEAL AutoAnalyzer (SEAL Analytical, USA) following Standard Method 4500-P-E (APHA, 2023). Calibration standards and analytical blanks were included with each run. Calibration curves yielded correlation coefficients >0.999. Net phosphorus exchange was calculated as the difference between final and initial SRP concentrations, normalized to dry solids mass (µg P g^{-1} solids). Negative values indicate net phosphorus release from solids to solution.

4.2.4 Data Analysis

Linear regression was used to evaluate the relationship between initial SRP concentration and net phosphorus exchange. The 95% confidence intervals were calculated for the

fitted mean response. Although phosphorus sorption can exhibit nonlinear, concentration-dependent behaviour depending on sediment properties (Appan & Wang, 2000), linear regression is commonly applied as a simplified method for estimating the net zero-sorption point. Values derived from this approach should therefore be interpreted as approximate, model-dependent indicators of equilibrium behaviour rather than fixed mechanistic constants (Froelich, 1988; House & Denison, 1998; McDowell et al., 2001).

EPC_0 values were estimated by extrapolating fitted regressions to the x-intercept, consistent with sediment phosphorus exchange methodologies commonly used for comparative interpretation of apparent source–sink behaviour (House & Denison, 2000; Tellinghuisen & Bolster, 2010). Because zero net exchange was not reached experimentally, extrapolated EPC_0 values were interpreted as conceptual indicators of apparent exchange behaviour rather than definitive equilibrium concentrations. Regression analyses were therefore used to support comparative interpretation rather than predictive parameterization.

Differences in phosphorus release among circumneutral pH treatments, pH 6–8, were evaluated using Welch's one-way ANOVA (Delacre et al., 2020). Because each treatment condition was only evaluated in triplicate, statistical outcomes were interpreted conservatively and primarily used to assess directional differences among treatments. Differences in regression slopes between treatments were evaluated within an ANCOVA framework by testing the SRP $\times$ treatment interaction term through ANOVA comparisons of nested linear models (Barrett, 2011). A significance level of $p < 0.05$ was adopted for all statistical tests (DiCarlo et al., 2020; Zar, 2010). Residuals from inferential and regression analyses were assessed for approximate normality and homoscedasticity to evaluate whether assumptions were reasonably met. Because the experimental design involved relatively small

sample sizes, and environmental datasets commonly deviate from ideal distributional assumptions (Reimann & Filzmoser, 2000), statistical results were interpreted cautiously and considered alongside the magnitude and directional consistency of observed desorption responses.

4.3 Results and Discussion

4.3.1 Effect of Initial SRP Concentration and EPC_0 Estimation

Phosphorus Release from Secondary and Tertiary Effluent Solids

Phosphorus release from secondary and tertiary effluent solids was evaluated across gradients of initial SRP concentration to assess wastewater-derived PP desorption response to ambient SRP (Figure 4.1). The data presented here were previously reported in the context of tertiary treatment performance and solids-associated phosphorus release potential (Chapter 3). Here, the same dataset is re-examined with a different objective: to evaluate how initial SRP concentration regulates net phosphorus exchange from effluent-derived solids and whether this behaviour is consistent with EPC_0-based source–sink concepts commonly applied to natural freshwater sediments.

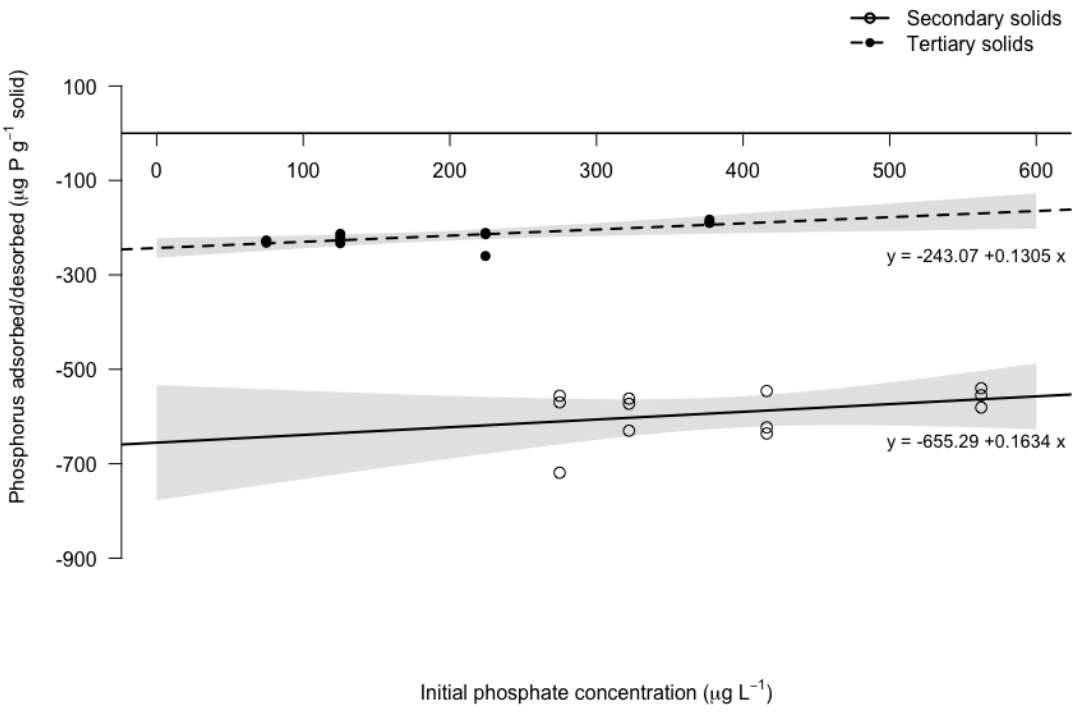


Figure 4.1: Phosphorus release from secondary and tertiary effluent solids under varying initial SRP concentrations in receiving waters. Negative values indicate net phosphorus release from solids to solution. Secondary effluent solids from Plant W were tested across an SRP range of approximately 275–560 µg P L^{-1}, while tertiary effluent solids from Plant K were tested across an SRP range of approximately 75–375 µg P L^{-1}.

Both secondary and tertiary effluent solids released phosphorus across all tested SRP concentrations, and no treatment condition approached net adsorption within the experimental range. Secondary effluent solids from Plant W exhibited the greatest release magnitude, with an average release of approximately 600 µg P g^{-1} solids. The fitted regression between initial SRP and net phosphorus exchange had a positive but non-significant slope

of 0.162 µg P g^{-1} solids per µg P L^{-1} ($p = 0.255$; $R^2 = 0.127$), indicating that variation in initial SRP explained little of the observed release response over the tested concentration range. Thus, secondary effluent solids remained persistent net phosphorus sources even at initial SRP concentrations approaching 560 µg P L^{-1}.

Tertiary effluent solids from Plant K also released phosphorus across all tested SRP concentrations, but release magnitudes were substantially lower than those observed for the secondary solids. The fitted regression slope for tertiary solids was 0.131 µg P g^{-1} solids per µg P L^{-1} and was statistically significant ($p = 0.008$; $R^2 = 0.517$), indicating a more constrained relationship between initial SRP and net phosphorus exchange. Although tertiary treatment reduced the baseline release potential of residual solids, the remaining particulate material continued to function as a net phosphorus source throughout the tested SRP range.

Apparent EPC_0 Estimates and Treatment-level Differences

Because zero net exchange was not reached experimentally, EPC_0 values were estimated by extrapolating the fitted SRP–exchange relationships and should therefore be interpreted as conceptual indicators of relative phosphorus source strength rather than realized equilibrium thresholds. The secondary effluent solids produced an intercept of –655.29 µg P g^{-1} and an extrapolated EPC_0 of approximately 4045 µg P L^{-1}, although the weak regression fit limits quantitative interpretation. Tertiary effluent solids produced a smaller negative intercept of –243.07 µg P g^{-1} and an extrapolated EPC_0 of approximately 1856 µg P L^{-1}, consistent with reduced baseline phosphorus release following tertiary treatment. This es-

timate is better supported statistically than the secondary effluent estimate, but it also lies well beyond the measured SRP range. Thus, even for tertiary solids, the EPC_0 should be treated as a conceptual indicator of source strength rather than a realized equilibrium concentration under typical receiving water conditions.

Comparison of regression parameters provides the clearest secondary versus tertiary treatment interpretation. The slopes for secondary and tertiary solids were not significantly different ($p = 0.83$), suggesting that background SRP exerted a similar directional influence on phosphorus exchange for both solids types. Although the regression for secondary solids was not statistically significant, comparing slope estimates remains useful for evaluating whether treatment level can fundamentally alter the response to increasing SRP. In contrast, the intercepts differed substantially ($p = 3.8 \times 10^{-7}$), indicating that treatment level primarily affected baseline release potential rather than SRP sensitivity. At equivalent SRP concentrations, the secondary effluent solids released approximately 412 µg P g^{-1} more phosphorus than the tertiary effluent solids.

Comparison with Freshwater Sediment EPC_0 Values

The apparent EPC_0 values estimated for wastewater effluent solids were substantially higher than values commonly reported for freshwater sediments (Table 4.2). Many freshwater sediment EPC_0 values occur within or near ambient riverine SRP ranges, meaning that sediments can shift between source and sink behaviour depending on water-column chemistry. In contrast, the effluent solids tested here remained net sources across the experimental SRP range, and their extrapolated exchange thresholds were far above typical

receiving water SRP concentrations.

Table 4.2: Compilation of reported EPC_0 values for freshwater sediments.

Study	Water matrix for EPC test	EPC_0 (µg L^{-1})	Notes
R. W. McDowell et al. (2018)	Synthetic river water solution	16	Upstream site samples
R. W. McDowell et al. (2018)	Synthetic river water solution	33	Downstream site samples
Peryer-Fursdon et al. (2014)	$CaCl_2$ solution	25	Stream 1
Peryer-Fursdon et al. (2014)	$CaCl_2$ solution	22	Stream 9
Peryer-Fursdon et al. (2014)	$CaCl_2$ solution	10	Pastoral site
Son et al. (2015)	Stream Water	126	Mean value pre-fire disturbance
Son et al. (2015)	Stream Water	782	Mean value post-fire disturbance
Palmer-Felgate et al. (2009)	Stream Water	2.35	Mean value from Welland site, shallow, rapid flow.
Palmer-Felgate et al. (2009)	Stream Water	19.5	Mean value from Avon site, shallow, rapid flow.
Palmer-Felgate et al. (2009)	Stream Water	14	Mean value from Wye site, shallow, rapid flow.
Haggard et al. (2007)	Stream Water	140	Mean value
Pailles & Moody (1992)	$CaCl_2$ solution	20.55	Mean value
Klotz (1991)	Ca solution	1.95	Mean value site 4A
Klotz (1991)	Ca solution	11.3	Mean value site 4F
Klotz (1985)	$CaCl_2$ solution	1.1	Mean value

This contrast indicates that sediment-based EPC_0 concepts are useful for interpreting the direction of phosphorus exchange, but their direct quantitative application to wastewater-derived particulates requires caution owing to the elevated proportions of reactive particulate phosphorus fractions, including NAIP, in wastewater effluent solids (Vianini et al., 2025).

Treatment Implications

Tertiary phosphorus removal is increasingly implemented because conventional primary and secondary treatment alone often cannot consistently achieve compliance with increasingly stringent effluent phosphorus limits (Bashar et al., 2018). However, tertiary treatment technologies differ substantially in their mechanisms of phosphorus removal and therefore in the composition and bioavailability of residual effluent phosphorus (Bashar et al., 2018; Gu et al., 2011; Remy et al., 2014). Tertiary cloth filtration may substantially reduce TP and suspended solids (Chapter 3) and, under the conditions evaluated here, it reduced the baseline phosphorus release potential of effluent solids; however, it did not eliminate the persistence of highly exchangeable phosphorus fractions or elevated EPC_0 values, potentially hindering desired outcomes.

4.3.2 Effect of pH on Phosphorus Release from Secondary Effluent Solids

Phosphorus release from secondary effluent solids differed across the tested pH gradient, with the strongest response observed under acidic conditions (Figure 4.2). Release was

greatest at pH 5, reaching approximately 1000 µg P g^{-1} solids. At pH 6 it was less pronounced and then varied within a narrower range across circumneutral to alkaline conditions. Within the pH range most representative of many receiving waters, pH 6–8, phosphorus release did not differ significantly based on Welch's ANOVA ($p = 0.160$). These results indicate that short-term phosphorus release from secondary effluent solids was enhanced under acidic conditions but comparatively insensitive to modest pH variation near neutrality.

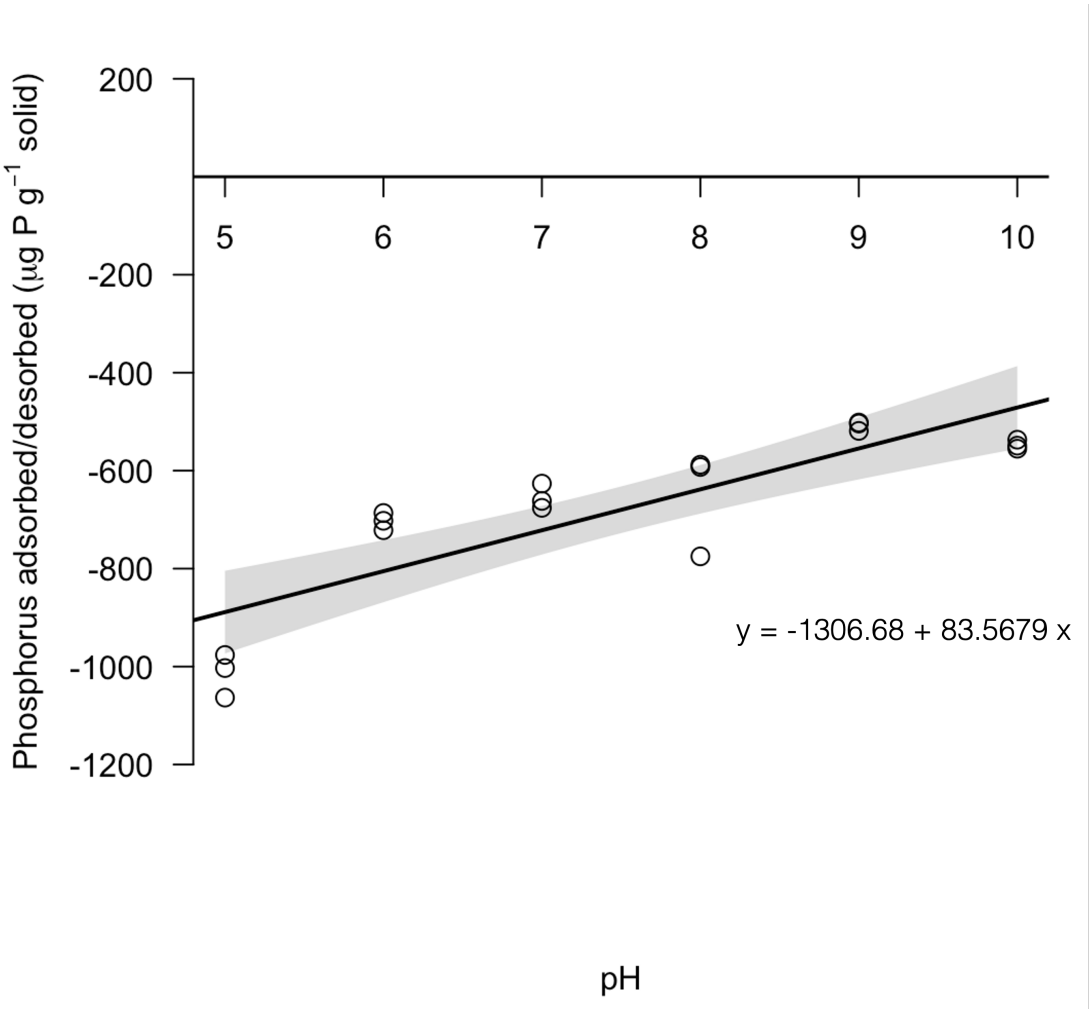


Figure 4.2: Average phosphate released by secondary effluent solids in receiving waters under varying pH. Solution SRP was approximately 100 µg P L^{-1} and temperature was 20 °C. Phosphorus release exhibited a condition-dependent response to pH, with enhanced desorption under acidic conditions and limited variation near circumneutral pH.

This response should not be interpreted as contradicting sediment phosphorus exchange theory. Although phosphate release is often expected to increase at higher pH because hy-

droxyl ions can compete with phosphate for sorption sites on Fe- and Al-associated surfaces, sediment studies also report non-monotonic, matrix-specific, and plateau-like pH responses (Cheng et al., 2020; L. Zhang et al., 2016). This indicates that the pH effect depends on solid-phase composition, mineral stability, redox-sensitive phases, organic coatings, and the relative contribution of rapidly exchangeable phosphorus pools (Froelich, 1988; L. Zhang et al., 2016). The response observed here is therefore better interpreted as evidence that wastewater-derived solids exhibit conditional pH behaviour, similar to natural sediments, rather than a universal monotonic response.

The observed increase in dissolved phosphorus at pH 5 may be more appropriately interpreted as a pH-dependent shift in phosphorus partitioning between particulate and dissolved phases rather than evidence of desorption alone (Zhao et al., 2022). Changes in pH influence the chemical equilibrium governing phosphorus retention by wastewater solids through multiple processes, including alterations in surface charge, mineral stability, and adsorption-desorption equilibria associated with metal-bound phosphorus phases (Li et al., 2021). Consequently, the measured increase in dissolved phosphorus represents the net result of these interacting geochemical processes rather than a direct measurement of a single release mechanism. Given the predominance of the NAIP fraction in the recovered solids (Vianini et al., 2026), the observed response is consistent with changes in the reactivity of metal-associated phosphorus under acidic conditions, although the present study was not designed to distinguish among the individual processes governing phosphorus redistribution.

The short incubation period is also relevant. The 18 h batch tests primarily capture rapid exchange from readily mobilizable phosphorus pools and may not fully resolve slower

transformations involving mineral dissolution, surface restructuring, or redox-mediated reactions. Under this experimental timescale, acidic conditions appeared to enhance the release of labile phosphorus, whereas circumneutral pH changes produced limited differences in net release. Thus, the pH results indicate that phosphorus release from wastewater-derived solids is strongly condition- and solids-dependent.

4.3.3 Particulate Phosphorus Desorption at Different Temperatures

The phosphorus release potential of secondary effluent solids increased consistently with temperature (Figure 4.3). Across the tested range, 5–35 °C, increasing temperature produced progressively greater phosphorus release ($p < 0.0001$; $R^2 = 0.81$), indicating a strong positive relationship between temperature and net phosphorus desorption under the tested conditions.

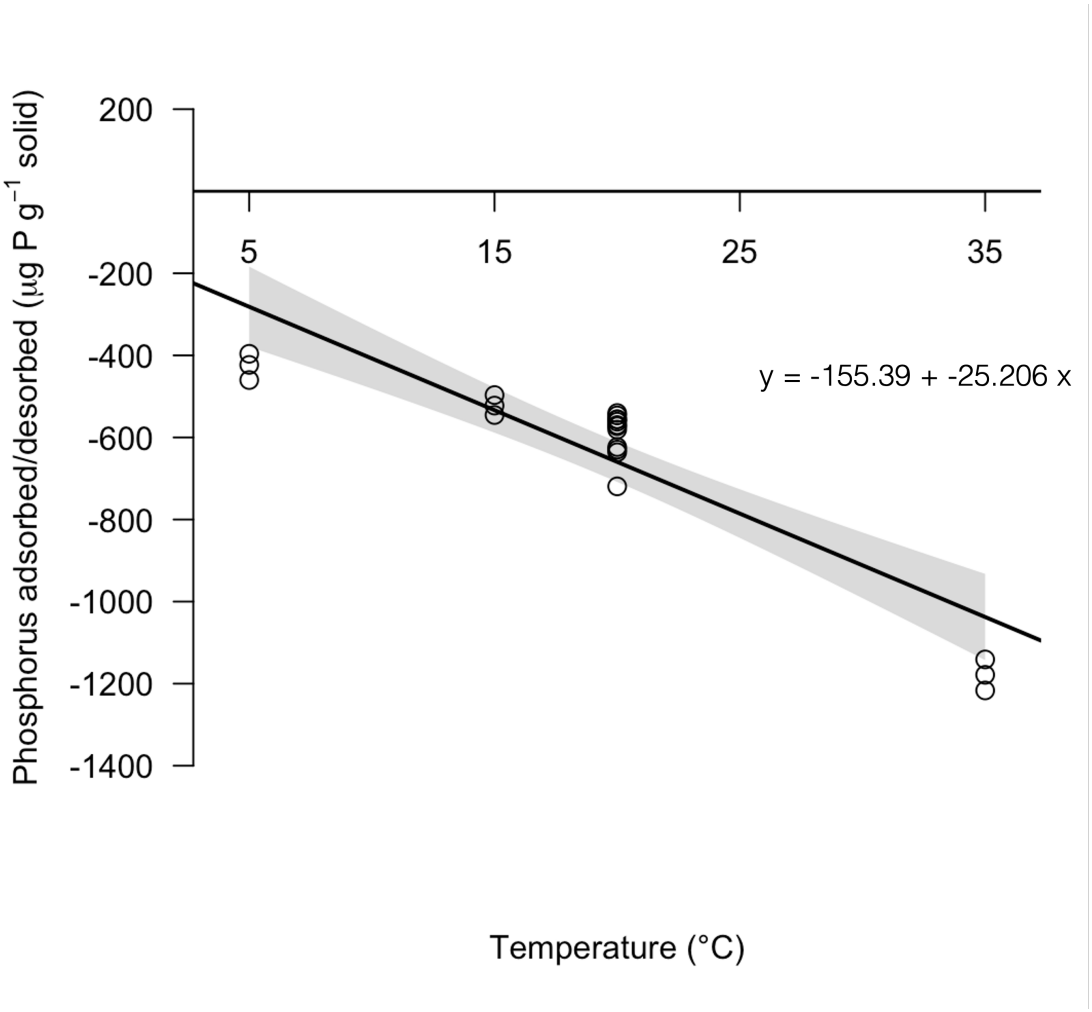


Figure 4.3: Average phosphate release from secondary effluent solids in receiving waters under varying temperatures. Solution SRP was 70 µg P L^{-1} and pH was approximately 7, with increasing temperature consistently enhancing phosphorus release.

This behaviour is directionally consistent with trends commonly reported for freshwater sediments, where elevated temperatures are frequently associated with enhanced phosphorus mobilization. Sediment studies have attributed these responses to interacting

physical, chemical, and biological processes, including increased microbial activity, accelerated diffusion, oxygen depletion, and destabilization of redox-sensitive phosphorus phases (Cheng et al., 2020; Holdren & Armstrong, 1980; Jiang et al., 2008; Kosten et al., 2012). However, the present study was designed to evaluate comparative phosphorus exchange behaviour rather than resolve the specific mechanisms controlling temperature-dependent release from wastewater-derived solids.

Despite this limitation, the observed temperature response suggests that wastewater effluent solids may behave similarly to freshwater sediments with respect to warming-driven increases in phosphorus release. At the same time, the magnitude of release observed here remained substantially greater than values typically reported for many natural sediment systems, consistent with the elevated apparent phosphorus release potential observed throughout this study (Holdren & Armstrong, 1980). These findings indicate that temperature may be an important control on phosphorus mobility from effluent-derived particulates following discharge, particularly during warm, low-flow receiving water conditions.

4.4 Comparative Synthesis with Sediment Phosphorus Exchange Behaviour

Wastewater effluent solids exhibited several phosphorus exchange behaviours qualitatively consistent with freshwater sediments, including condition-dependent responses to pH and increased phosphorus release with temperature. However, the magnitude of phosphorus release and the apparent EPC_0 values observed here were substantially greater than values

commonly reported for natural sediments. Table 4.3 summarizes representative sediment phosphorus exchange behaviours reported under varying pH and temperature conditions and provides context for interpreting similarities and divergences observed for wastewater-derived particulates.

Table 4.3: Comparative synthesis of reported pH- and temperature-dependent phosphorus exchange behaviour in aquatic sediments.

Study	Sample Type	pH effect	Temperature (T) effect	Overall trend summary
Holdren & Armstrong (1980)	Lake sediments	Not studied	↑ P release	T links to microbial activity, oxygen depletion, and reduction of Fe(III) to Fe(II)
Boström (1984)	Lake sediments	Condition-dependent	Not Studied	P release typically redox sensitive and favoured by ↑ pH
House & Denison (2000)	River sediments (hardwater systems)	Sediment-specific	Not studied	pH altered $EPC_{0;}$ direction is sediment-specific
House (2003)	Conceptual + field synthesis	Context-dependent	T acts indirectly	Context-dependent (e.g., bio-geo-chemical cycling)
Christophoridis & Fytianos (2006)	Lake sediments	Non-linear	Not Studied	U-shaped response: lowest release near neutral pH
Jiang et al. (2008)	Shallow lake sediments	Not studied	↑ P release	T-driven
Cheng et al. (2020)	River sediments	No effect	↑ P release	No pH effect around neutrality
He et al. (2023)	Wetlands sediments	Condition-dependent	↑ P release	↓ P concentration with ↑ pH
Kosten et al. (2012)	Global shallow lakes	Context-dependent	↑ P release	High pH ↑ P release in certain conditions
Seitzinger (1991)	Estuarine sediments	↑ P release	Not studied	Recognize multi-factor control
Temporetti et al. (2019)	River sediments	↑ P release	Not studied	Sediment-specific control
Wu et al. (2014)	Lake sediments	Non-linear	↑ P release	↓ P release at neutral pH; ↑ at acidic & alkaline; dissolved oxygen > T > pH
Xia et al. (2023)	River sediments	↓ P release	Not studied	Less pH effect when Fe-rich; redox dominated
L. Zhang et al. (2016)	Riparian sediments	Non-linear	Not studied	Non-linear response
Zhao et al. (2022)	Lake sediments	Condition-dependent	Not studied	Acidic & alkaline conditions favoured release; alkaline more
Zhou et al. (2005)	Lake sediments	No consistent trend	Not studied	Direct pH effect is unclear and cannot be generalized
Simpson et al. (2021)	River sediments	Context-dependent	↑ P release	pH effects strongly context-dependent; surface chemistry supports conditional behaviour

The strongest divergence from conventional sediment behaviour was observed in the SRP gradient experiments. Natural sediments commonly exhibit EPC_0 values within or near environmentally relevant SRP ranges, allowing sediment particles to function as either sources or sinks depending on water-column chemistry. In contrast, both secondary and tertiary effluent solids remained net phosphorus sources across all tested SRP concentrations, and extrapolated EPC_0 values were far above typical riverine SRP concentrations. These results indicate that the effluent solids tested here were not approaching zero net exchange under conditions normally encountered in receiving waters.

This comparison suggests that sediment phosphorus exchange frameworks are conceptually useful but quantitatively incomplete for wastewater-derived particulates. They correctly anticipate that phosphorus exchange is affected by ambient chemistry and temperature, but they may underestimate the mass-normalized release potential of solids produced by wastewater treatment processes. The difference likely reflects the distinct origin and treatment history of effluent solids, including chemical conditioning, biological floc formation, and enrichment in reactive particulate phosphorus fractions (Fan et al., 2008; Stone & Mudroch, 1989; Zhu et al., 2012). Therefore, wastewater effluent solids should not be treated simply as equivalent to natural sediments in nutrient models or receiving water assessments. Instead, sediment frameworks should be used as interpretive reference points, while phosphorus release from effluent solids should be independently quantified and integrated with dissolved phosphorus inputs, effluent solids loading, and receiving water hydrology (Chapter 5).

4.5 Conclusions

This study evaluated whether sediment-based phosphorus exchange behaviours adequately describe phosphorus release from wastewater effluent solids. Across the tested SRP gradients, both secondary and tertiary effluent solids remained net phosphorus sources, with apparent EPC_0 values substantially exceeding those commonly reported for freshwater sediments.

Wastewater-derived particulates exhibited several behaviours qualitatively consistent with natural sediments, including condition-dependent responses to pH and enhanced phosphorus release at higher temperatures. However, the magnitude of phosphorus release observed here indicates that direct quantitative application of sediment phosphorus exchange frameworks may underestimate the release potential of effluent-derived solids.

Collectively, these findings indicate that wastewater effluent solids occupy a distinct phosphorus exchange domain relative to many natural sediments and should therefore be evaluated independently in receiving water assessments and nutrient management frameworks.

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Chapter 5

Toward Multi-Form Phosphorus Accounting of Wastewater Contributions for Describing Dynamic Utilization and Eutrophication

Summary

Building on evidence that wastewater-derived solids contain bioavailable particulate phosphorus and can release phosphorus under environmentally relevant receiving water conditions, the relative influence of dissolved phosphorus and particulate phosphorus release to near-field bioavailable phosphorus availability following discharge was investigated. Experimentally constrained phosphorus speciation and desorption behaviour were integrated with effluent flow, river flow, and background soluble reactive phosphorus conditions to determine when wastewater inputs can materially alter downstream phosphorus availability. The analysis showed that wastewater influence depends strongly on hydrologic context, with the greatest relative contribution occurring under low-flow conditions and in receiving waters with lower background phosphorus concentrations. Direct discharge of soluble reactive phosphorus was the dominant contributor to near-field bioavailable phosphorus availability, while desorption from effluent-derived solids provided an additional bioavailable phosphorus contribution that linked residual particulate phosphorus to downstream exposure. However, concentration increases alone are insufficient to infer eutrophication response because ecological effects depend on site-specific nutrient limitation, hydrology, residence time, biological uptake, light availability, and physical habitat. By connecting wastewater phosphorus speciation with receiving water dilution and the broader conditions that regulate eutrophication, this chapter provides a more context-dependent basis for interpreting the significance of wastewater phosphorus inputs beyond total phosphorus concentrations.

5.1 Introduction

Management of eutrophication in inland waters has largely been focused on controlling nutrient inputs, particularly phosphorus because it commonly limits primary productivity and can stimulate harmful algal and cyanobacterial blooms with consequences for drinking water quality, ecosystem function, and economic activities (Carpenter et al., 1998; Emelko et al., 2011; Paerl et al., 2016). Despite decades of management efforts, a fundamental question remains unresolved: what maximum concentration of total phosphorus (TP) is sufficiently protective of receiving waters? Although guidelines and reference values exist (Chambers et al., 2012), no universally accepted threshold distinguishes acceptable from harmful phosphorus concentrations. This reflects the complex and system-specific nature of eutrophication responses (Zeng et al., 2016). A major limitation of TP is that it aggregates phosphorus fractions with fundamentally different bioavailability and ecological relevance (Vianini et al., 2026b; Chapter 3).

Among the phosphorus sources contributing to surface waters, municipal wastewater treatment plant (WWTP) effluents represent one of the most consistent and controllable point inputs (Carpenter et al., 1998) and can dominate nutrient loading under conditions of limited dilution (Jarvie et al., 2006). Consequently, WWTP discharges are a central focus of nutrient management and regulatory control. However, these controls typically rely heavily on TP and do not explicitly account for bioavailable phosphorus (BAP) fractions (Comber et al., 2015; Kardos et al., 2025; Preisner et al., 2020).

Backed by decades of monitoring data and rigorous regulatory standardization, TP remains a vital and widely accepted metric that owes its universal comparability to its

operational simplicity (Carey & Migliaccio, 2009; Hendriks & Langeveld, 2017; Nair et al., 2022). Effluent TP comprises both dissolved and particulate phosphorus (PP) forms with differing bioavailability (Chapter 3). Particular attention has been given to soluble reactive phosphorus (SRP), which is immediately bioavailable, and non-apatite inorganic phosphorus (NAIP), a particulate form that is often predominant in effluent solids and can act as a secondary source of dissolved phosphorus because it can readily desorb following discharge (Vianini et al., 2025; Chapters 2 and 3). Owing to its nuanced composition, equivalent TP concentrations may produce substantially different ecological responses; thus, TP alone cannot distinguish among immediately bioavailable, potentially bioavailable, and relatively inert phosphorus pools (Comber et al., 2015; Li & Brett, 2013).

The influence of WWTP phosphorus discharges on receiving waters is therefore not solely a function of bulk phosphorus loads. Following discharge, effluent-derived phosphorus is diluted, transported, and transformed through processes that determine its resulting concentration and bioavailability (Carey & Migliaccio, 2009). Under low-flow conditions, effluent represents a larger fraction of total flow and has increased relative influence on downstream phosphorus concentrations, whereas other diffuse phosphorus sources typically dominate at higher flows (Bowes et al., 2008). An additional complexity is that SRP, although considered immediately bioavailable, does not correspond to a single ecological response at a given concentration (Li & Brett, 2013). Its uptake and utilization depend on environmental conditions and biological demand, making its ecological significance inherently dynamic.

These phosphorus dynamics may become increasingly important under climate-driven hydrologic shifts associated with more frequent and prolonged low-flow conditions (Paerl

& Paul, 2012), particularly under conditions where treated wastewater comprises an increasingly large fraction of downstream flow, and the implications of them go beyond eutrophication threats. In many water systems, treated wastewater can comprise a substantial fraction of downstream flow, creating conditions associated with de facto water reuse (National Research Council et al., 2012). Under these circumstances, wastewater-derived nutrients may exert greater influence on downstream water quality and can affect systems used for drinking water supply, recreation, and ecological protection (Westerhoff et al., 2025). These conditions reinforce the need for integrated "One Water" perspectives, where wastewater discharges, receiving water quality, ecosystem protection, and downstream water use are increasingly interconnected (Pokhrel et al., 2022). Consequently, there is a growing need for decision support methods capable of identifying when wastewater effluent exerts a meaningful influence on downstream water quality.

Although detailed water quality models such as QUAL2K and WASP simulate nutrient dynamics through representations of hydrodynamic and biogeochemical processes, they require extensive data inputs and calibration and are typically applied to site-specific analyses (Mbuh et al., 2019; Zehra et al., 2023). Existing simplified approaches, in contrast, often focus primarily on TP loading (Bowes et al., 2008) and do not explicitly distinguish between the different pathways through which dissolved and particulate phosphorus, particularly BAP, can contribute to phosphorus loading. As a result, there is currently no simple and transferable (i.e., able to be applied across systems using site-specific inputs) assessment method for identifying the conditions under which WWTP discharges can materially influence downstream bioavailable phosphorus across systems.

Recent work has demonstrated that wastewater PP differs substantially from conven-

tional representations of natural suspended sediments and may contain a large proportion of readily bioavailable NAIP fractions (Vianini et al., 2025; Chapter 2). Additional investigations showed that tertiary treatment can substantially alter phosphorus partitioning without necessarily proportionally reducing bioavailable phosphorus contributions (Chapter 3), while phosphorus desorption experiments demonstrated that effluent-derived solids can exhibit release behaviour distinct from established freshwater sediment paradigms (Chapter 4). Collectively, these findings highlight the need to integrate phosphorus speciation, bioavailability, and dynamics of the receiving environment when evaluating WWTP impacts on receiving waters.

The objective of this study was to apply a multi-form phosphorus accounting approach that integrates experimentally constrained wastewater phosphorus speciation and desorption behaviour with flow regime analysis to identify conditions under which WWTP discharges may materially influence BAP concentrations. It also considered the extent to which these concentration-based estimates can be used to infer eutrophication relevance within receiving waters. By integrating dissolved phosphorus inputs with desorbable particulate phosphorus contributions, this approach links treatment performance, phosphorus speciation, and hydrologic regimes within a unified basis for interpreting receiving water phosphorus exposure. Receiving water exposure is defined here as the magnitude and significance of wastewater-derived BAP inputs to which a receiving water is subjected. Rather than directly predicting algal proliferation or eutrophication responses, this study focuses on quantifying how wastewater-derived bioavailable phosphorus is expressed post discharge, thereby serving as a mechanistic input layer for more complex ecological or watershed assessments.

5.2 Methodology

This section presents the development of the proposed assessment methodology for evaluating the exposure of receiving waters to wastewater-derived bioavailable phosphorus. The conceptual basis and governing equations are first introduced, followed by the assumptions underlying the near-field mixing representation within the initial mixing zone. The methodology then describes the scenario-based parameterization approach, dimensionless relationships, and threshold metrics used to characterize system response.

5.2.1 Structural Design and Approach

The methodology herein was developed to evaluate how WWTP effluent influences downstream BAP under varying hydrologic conditions. It represents a near-field, fully mixed control volume immediately downstream of discharge and integrates two pathways of phosphorus contribution: (i) directly discharged SRP, and (ii) phosphorus released from effluent-derived suspended solids following discharge. The released phosphorus is assumed to be fully bioavailable and is accounted for as SRP; it reflects experimentally observed desorption behaviour associated with NAIP-rich wastewater solids identified in previous studies (Vianini et al., 2025; Chapters 2–4). Downstream BAP was represented as the final SRP concentration following mixing and particulate phosphorus release:

$$SRP_{final} = \frac{Q_w SRP_w + Q_r SRP_r + Q_w SS_w R_d}{Q_w + Q_r} \tag{5.1}$$

where Q_w and Q_r are the wastewater effluent and river flow rates, SRP_w and SRP_r are

the corresponding SRP concentrations, SS_w is the effluent suspended solids concentration, and R_d is the phosphorus rate of desorption, or release potential, which represents the contribution of phosphorus released from effluent-derived solids. This formulation requires a limited set of inputs describing effluent quality and receiving water conditions, enabling direct evaluation of the relative importance of dissolved and particulate-derived phosphorus contributions across hydrologic regimes.

The total effluent-derived bioavailable phosphorus concentration (P_e) was defined as the sum of dissolved SRP and phosphorus released from effluent solids. The term $SS_w R_d$ converts the suspended solids concentration (mg solids L^{-1}) into an equivalent phosphorus concentration (µg P L^{-1}), accounting for the short-term phosphorus release potential per unit of solids mass (mg P g^{-1} solids).

$$P_e = SRP_w + SS_w R_d \tag{5.2}$$

To provide a dimensionless representation of hydrologic influence, the effluent fraction (EF) was calculated as the ratio of effluent flow to total flow:

$$EF = \frac{Q_w}{Q_w + Q_r} \tag{5.3}$$

The wastewater discharge contribution to BAP, expressed as a percentage, and the contribution from solids only were estimated using Equations 5.4 and 5.5, respectively:

$$Contribution_{total} = \frac{Q_w P_e}{Q_w P_e + Q_r SRP_r} \times 100 \tag{5.4}$$

$$Contribution_{solids} = \frac{Q_w SS_w R_d}{Q_w P_e + Q_r SRP_r} \times 100 \tag{5.5}$$

5.2.2 Output Application and Evaluation

Outcomes were evaluated using two main complementary metrics: (i) the relative contribution of effluent-derived phosphorus to downstream SRP, based on Equation 5.4, and (ii) a dimensionless responsiveness metric referred to as the SRP augmentation factor (Equation 5.6). These metrics enable assessment of both relative system influence potential and absolute changes in bioavailable phosphorus concentrations. Results were visualized using flow-response curves, augmentation factor–effluent fraction relationships, and two-dimensional heatmaps depicting downstream response across combinations of effluent flow (Q_w) and river flow (Q_r). The SRP augmentation factor (AF) was introduced to facilitate comparison across scenarios and aid interpretation of exposure to BAP loads. The AF was defined as:

$$AF = \frac{SRP_{final} - SRP_r}{SRP_r} \tag{5.6}$$

The AF informs the relative increase in BAP attributable to WWTP discharge, normalized to background river conditions. Values approaching zero indicate minimal impact, whereas increasing values indicate greater contribution potential of effluent inputs to receiving water. Because the AF is normalized to background SRP, it provides a transferable metric that enables comparison across systems with different baseline nutrient conditions

and hydrologic regimes. An AF value of 0.10 corresponds to a 10% increase in downstream SRP relative to background conditions.

5.2.3 Threshold Analysis

Threshold conditions were defined as the river flow (Q_r) at which wastewater effluent contributes a specified fraction to downstream BAP. These thresholds were expressed in terms of the percentage contribution of effluent-derived phosphorus to the total downstream SRP concentration. Equation 5.7 was obtained by rearranging Equation 5.4 to solve for the river flow required to produce a specified contribution level.

$$Q_r = \frac{Q_w P_e (1 - \phi)}{\phi \times SRP_r} \tag{5.7}$$

where ϕ represents the selected fractional contribution threshold (e.g., $0.1 = 10\%$ contribution of effluent-derived phosphorus to downstream BAP). Threshold levels of 10%, 25%, and 50% were selected to represent increasing degrees of effluent influence on downstream conditions. For each threshold level, combinations of effluent flow (Q_w) and river flow (Q_r) corresponding to that threshold were identified and plotted. These thresholds represent the hydrologic conditions under which wastewater-derived phosphorus reaches a defined fraction of downstream BAP, providing a quantitative basis for identifying transitions between low- and high-influence regimes.

5.2.4 Assumptions and Scope

This assessment approach is intentionally streamlined to isolate the dominant hydrologic and phosphorus-speciation controls governing near-field receiving water response. It represents conditions immediately downstream of discharge where dilution and initial phosphorus exchange processes dominate. Complete and instantaneous mixing between effluent and upstream river water is assumed. Background river SRP concentrations are treated as quasi-equilibrium conditions such that additional sorption or desorption from ambient sediments is negligible over the spatial and temporal scale considered. These assumptions are consistent with a near-field control volume representation commonly used in initial dilution modelling, where physical mixing dominates over biogeochemical transformations at short spatial and temporal scales (Hetland, 2010).

In-stream processes such as biological uptake, sediment–water exchange, settling, or long-term transformation of phosphorus species are not explicitly accounted for. Although these processes govern phosphorus dynamics over longer spatiotemporal scales, this methodology focuses on the critical initial mixing phase, offering a refined BAP loading foundation that enhances the accuracy of broader, system-specific assessments.

5.2.5 Scenario Design and Parameter Selection

Input parameters (Q_w, Q_r, SRP_w, SRP_r, SS_w, R_d) were defined using a scenario-based approach spanning low, intermediate, and high values representative of realistic wastewater and receiving water conditions. Where available, parameter values were obtained from the experimental findings of Chapters 2–4, including measurements of phosphorus speciation,

bioavailability, and particulate phosphorus release potential (Vianini et al., 2025). These results supplied the mechanistic information required to evaluate dissolved and particulate-derived phosphorus contributions within a common receiving water accounting approach. Additional values were selected to bracket plausible system behaviour. This bracketing approach was useful because phosphorus fate and transformation dynamics can be dependent on solids composition and receiving water chemistry, including ambient SRP, pH, and temperature that can directly influence PP release potential (Chapter 4). Therefore, these inputs are treated here as operational scenario parameters used to evaluate receiving water exposure and identify threshold-like transitions in the relative influence of effluent-derived phosphorus on downstream BAP concentrations, as well as to evaluate treatment performance effects.

The scenarios were designed to isolate the influence of hydrologic dilution capacity and background nutrient conditions on downstream response. Scenarios 2–5 represent directional contrasts around the central condition (Scenario 1), enabling independent evaluation of low versus high effluent flow and low versus high background SRP conditions. The scenario matrix consisted of a $6 \times 5 \times 5$ factorial design, comprising six WWTP configurations, five river flow conditions, and five combined effluent-flow/background-SRP scenarios. The latter corresponded to the four corner points and centre point of a 3×3 factorial space defined by effluent flow and background SRP. The scenario structure and input values are summarized in Table 5.1.

Table 5.1: Scenario input matrix and representative WWTP configurations.

Effluent characteristics				
WWTP	**SRP_w ($\mu g\ L^{-1}$)**	**SS_w ($mg\ L^{-1}$)**	**PP R_d ($mg\ P\ g^{-1}$ solids)**	**Notes**
Plant 1	400	8	0.8	Conservative, upper-end case
Plant 2	300	7	0.7	Final effluent representing moderate SRP reduction and limited solids removal
Plant 3	200	6	0.6	Secondary effluent with improved SRP removal
Plant 4	200	2	0.2	Tertiary effluent with improved SRP reduction and solids removal
Plant 5	100	1	0.1	Well-performing low-P, low-TSS tertiary effluent
Plant 6	50	0.8	0.1	Best, lower-bound case

Hydrologic and receiving water conditions	
Parameter	**Values**
Effluent flow (Q_w, $m^3\ s^{-1}$)	0.05, 0.5, 2
River flow (Q_r, $m^3\ s^{-1}$)	1, 3, 10, 30, 100
Background SRP (SRP_r, $\mu g\ L^{-1}$)	10, 50, 150

Scenario definitions	
Scenario	**Description**
1	Central/baseline conditions
2	Low Q_w / High SRP_r
3	High Q_w / Low SRP_r
4	High Q_w / High SRP_r
5	Low Q_w / Low SRP_r

5.2.6 Method Development and Scientific Basis

The scenario-based analysis was designed to characterize the primary hydrologic and chemical factors driving near-field bioavailable phosphorus behaviour. Rather than serving as a site-specific predictive ecosystem model, it provides a mathematically constrained structure to identify the specific hydrologic and effluent quality thresholds under which WWTP effluents become environmentally influential.

The parameters used are grounded in experimentally constrained phosphorus characteristics and behaviours (Vianini et al., 2025; Chapters 2–4). Specifically, these studies newly demonstrated that effluent-derived solids are enriched in readily desorbable NAIP, establishing a dynamic bioavailable phosphorus source rather than an inert particulate fraction. Additionally, they provide phosphorus fraction characterization across treatment systems and phosphorus release behaviour from effluent-derived solids under varying receiving water conditions. These empirical relationships dictate the dissolved (SRP_w) and particulate phosphorus desorption (R_d) terms used herein.

5.3 Results

5.3.1 Effluent Contribution as a Function of Hydrologic Conditions

Effluent contribution to downstream bioavailable phosphorus (computed using Equations 5.4 and 5.5) exhibited a consistent nonlinear dependence on river flow across all scenarios (Fig-

ure 5.1). This behaviour provides a mechanistic basis for identifying low-dilution conditions under which effluent-derived BAP contributions become more pronounced. Although six representative plants were evaluated, four are shown here to capture the full envelope of system behaviour without redundancy. The remaining plants fall within these bounds and do not introduce additional response patterns.

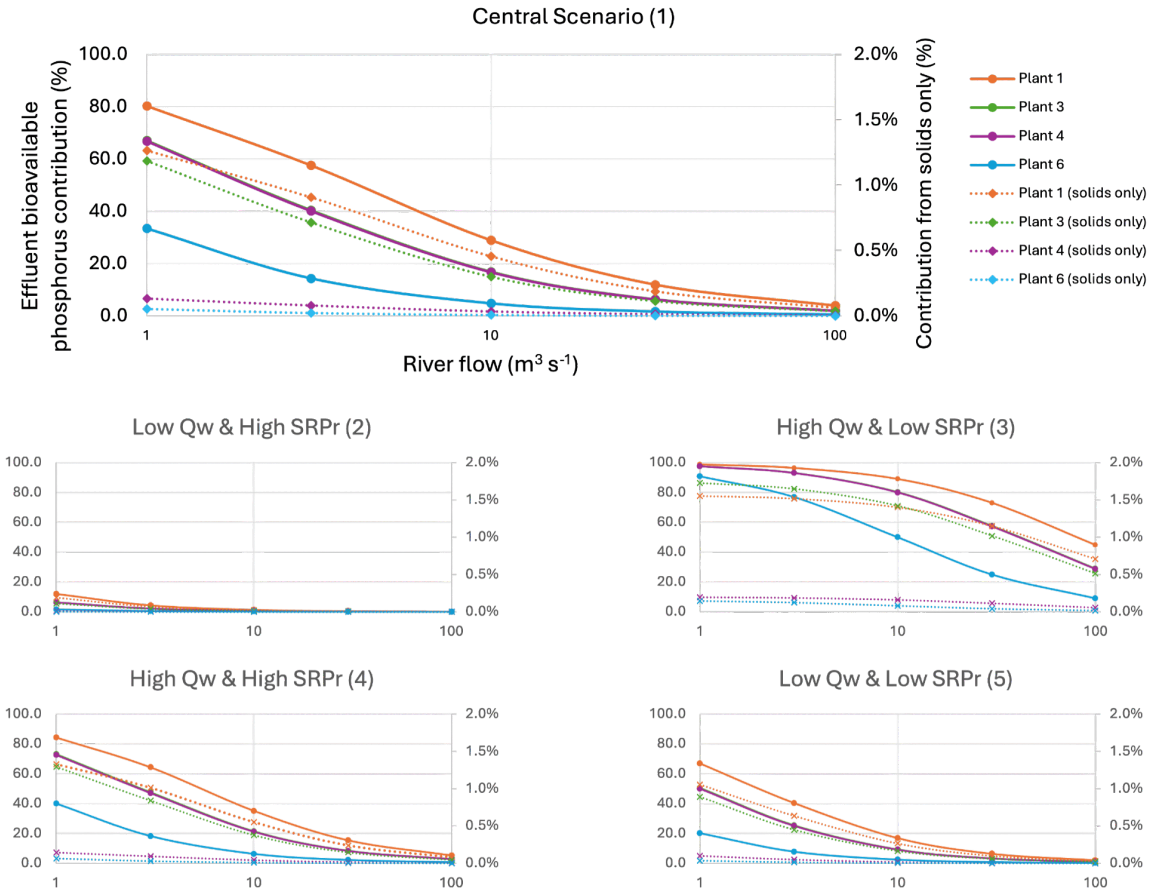


Figure 5.1: Percentage contribution of wastewater effluent to BAP post discharge as a function of river flow (Q_r) across generated scenarios. Solid lines represent total effluent contributions, dissolved plus desorption from solids, while dashed lines represent contributions from effluent solids only. The nonlinear decline reflects a dilution-driven response, in which effluent contributions scale with the ratio of Q_w to Q_r rather than absolute flow values.

Although Equation 5.5 reports the relative contribution of particulate-derived phospho-

rus, the same particulate-release term was also expressed as an absolute downstream SRP concentration increase (µg L^{-1}). Because this calculation does not depend on background river SRP concentration (SRP_r), scenarios differing only in SRP_r produced identical results and are therefore represented by overlapping curves in Figure 5.2. The resulting SRP increases remained comparatively low across all conditions, with values confined to a narrow range and declining rapidly with increasing flow. Minimal separation between plants at moderate to high flows indicates limited influence of particulate phosphorus on short-term downstream SRP under the conditions evaluated.

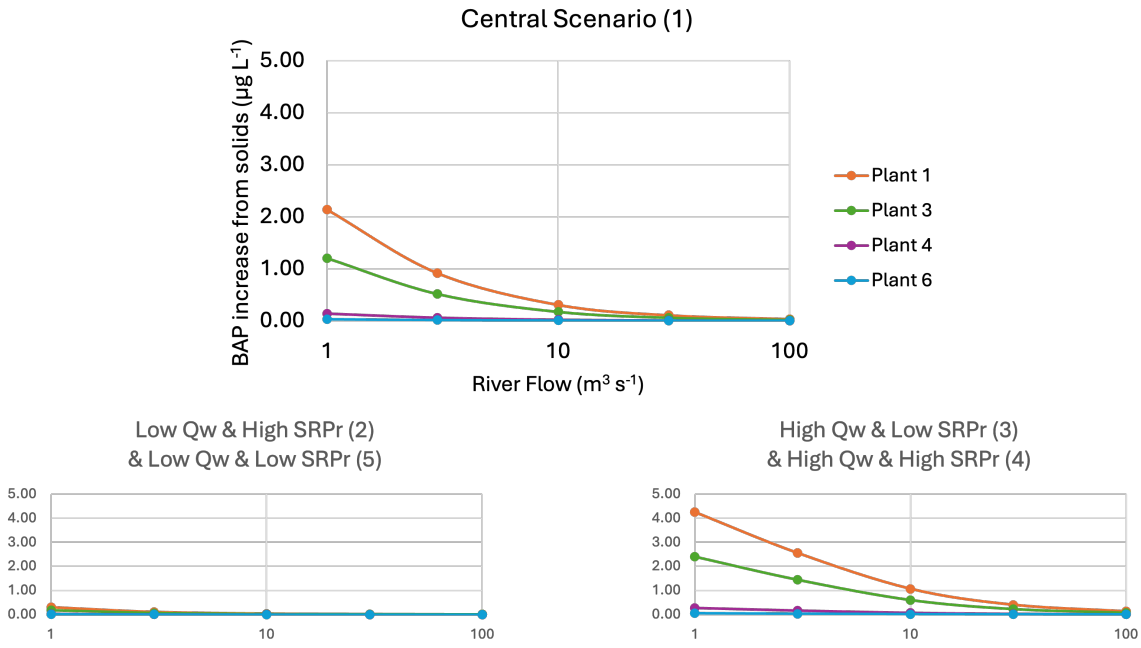


Figure 5.2: Absolute increase in downstream SRP attributable solely to phosphorus desorption from effluent-derived solids. The limited magnitude of the solids contribution reflects its dependence on both suspended solids concentration and release rate, which together form a secondary source term relative to direct dissolved inputs. As a result, PP desorption is a secondary, less pronounced source of short-term increases in downstream SRP under the conditions evaluated.

Plants 3 and 4 produced nearly identical total contribution curves (Figure 5.1). Because these effluents were intentionally similar except for the improved suspended solids and particulate phosphorus removal achieved in Plant 4, this comparison effectively isolates the influence of solids-associated phosphorus. Differences between the plants emerged only when particulate-derived contributions were examined separately (Figure 5.2), where Plant

4 consistently exhibited lower solids-associated SRP increases.

5.3.2 Effluent Fraction and SRP Augmentation Factor

To evaluate whether receiving water response could be described independently of absolute flow magnitudes, downstream exposure was expressed as a function of effluent fraction (EF), defined as the proportion of total post-discharge flow composed of wastewater effluent. Under the mixing assumptions of the model, the SRP augmentation factor is determined entirely by EF and the relative phosphorus concentrations of the effluent and receiving water. As a result, disparate flow scenarios converge onto a common relationship between EF and downstream response (Figure 5.3).

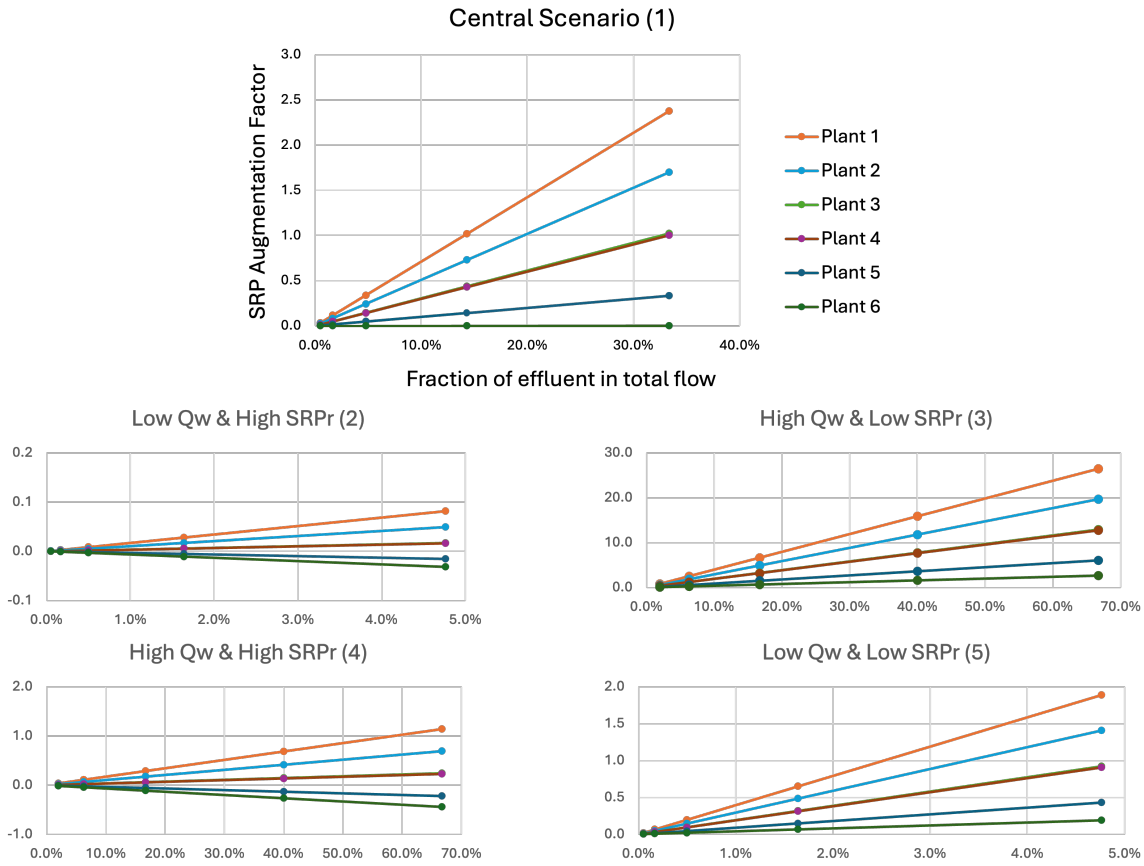


Figure 5.3: SRP augmentation factor (Equation 5.6) plotted against effluent fraction (EF) across all scenarios. Axes were adapted for improved visual interpretation. Points represent individual scenario combinations of effluent and river flow conditions, while connecting curves illustrate the continuous flow-conditioned relationship between increasing effluent fraction and downstream response. Increasing AF values indicate progressively greater downstream susceptibility to WWTP discharge relative to background SRP conditions.

Despite differences in magnitude among scenarios, the overall relationship between AF

and effluent fraction remained highly consistent, demonstrating that effluent fraction provides a practical and transferable descriptor of receiving water exposure to BAP increases. Rather than evaluating wastewater impacts solely through absolute discharge concentrations or loads, this protocol identifies how the relative hydrologic influence of effluent governs downstream effects across systems.

5.3.3 Threshold Flow Conditions for Downstream BAP Responses

To mechanistically map the hydrologic conditions under which WWTP discharges dominate receiving water chemistry, system responses were projected across a continuous matrix of effluent flow (Q_w) and river flow (Q_r). The resulting response surfaces (Equation 5.4) and threshold curves (Equation 5.7) depicted in Figure 5.4 reveal that effluent influence is not merely a function of hydrologic dilution but is deeply coupled with background river chemistry (SRP_r). To illustrate system behaviour, Plant 4 was selected as a representative case, which fixes P_e from Equation 5.7 at 200.4 µg/L.

SRPr = 10 µg/L					
Qw\Qr	1	3	10	30	100
0.05	50.0%	25.0%	9.1%	3.2%	1.0%
0.1	66.7%	40.0%	16.7%	6.3%	2.0%
0.25	83.4%	62.5%	33.4%	14.3%	4.8%
0.5	90.9%	77.0%	50.0%	25.0%	9.1%
1	95.2%	87.0%	66.7%	40.0%	16.7%
2	97.6%	93.0%	80.0%	57.2%	28.6%
3	98.4%	95.2%	85.7%	66.7%	37.5%

SRPr = 50 µg/L					
Qw\Qr	1	3	10	30	100
0.05	16.7%	6.3%	2.0%	0.7%	0.2%
0.1	28.6%	11.8%	3.9%	1.3%	0.4%
0.25	50.0%	25.0%	9.1%	3.2%	1.0%
0.5	66.7%	40.0%	16.7%	6.3%	2.0%
1	80.0%	57.2%	28.6%	11.8%	3.9%
2	88.9%	72.8%	44.5%	21.1%	7.4%
3	92.3%	80.0%	54.6%	28.6%	10.7%

SRPr = 150 µg/L					
Qw\Qr	1	3	10	30	100
0.05	6.3%	2.2%	0.7%	0.2%	0.1%
0.1	11.8%	4.3%	1.3%	0.4%	0.1%
0.25	25.0%	10.0%	3.2%	1.1%	0.3%
0.5	40.0%	18.2%	6.3%	2.2%	0.7%
1	57.2%	30.8%	11.8%	4.3%	1.3%
2	72.8%	47.1%	21.1%	8.2%	2.6%
3	80.0%	57.2%	28.6%	11.8%	3.9%

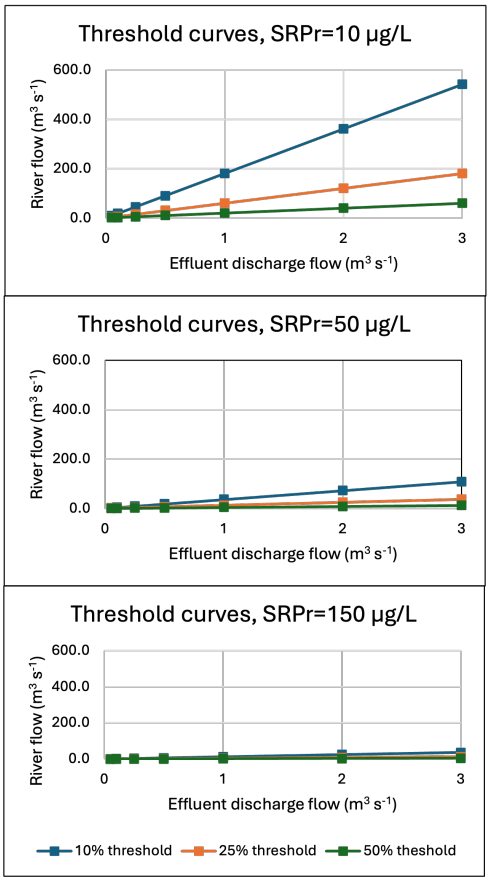


Figure 5.4: Response surfaces illustrating downstream bioavailable phosphorus influence potential across combinations of effluent discharge and river flow under different background SRP conditions for Plant 4. Threshold curves, 10%, 25%, and 50%, identify combinations of wastewater discharge and receiving water flow associated with progressively increasing effluent influence on downstream bioavailable phosphorus.

Across all scenarios, the expected gradient of increasing effluent contribution is observed as the system shifts toward low river flow and high effluent influence. However, the spatial extent of these exposure potential zones exhibits a pronounced compression effect as back-

ground river concentrations rise from 10 µg L^{-1} to 150 µg L^{-1}. In environments with low background SRP (SRP_r = 10 µg L^{-1}), the receiving water is highly influenced by effluent inputs. Under these conditions, the 10% contribution threshold extends broadly across the hydrologic spectrum. Conversely, at higher background SRP conditions (SRP_r = 150 µg L^{-1}), the ambient river loading effectively masks the effluent signature. This suppresses the effluent's relative impact, compressing the 10% threshold curve toward near-field zones where river flow is low.

5.3.4 Generalized Threshold Envelopes

To evaluate whether threshold behaviour depended strongly on plant-specific effluent characteristics, threshold relationships were compared across all representative WWTP configurations. Threshold curves from all evaluated plants converged into relatively narrow envelopes (Figure 5.5). With SRP_r fixed at 50 µg L^{-1}, differences among plants are represented primarily through variation in P_e (Equation 5.7). Consequently, plant-specific phosphorus concentrations shift the absolute location of the threshold curves while preserving their overall geometric form.

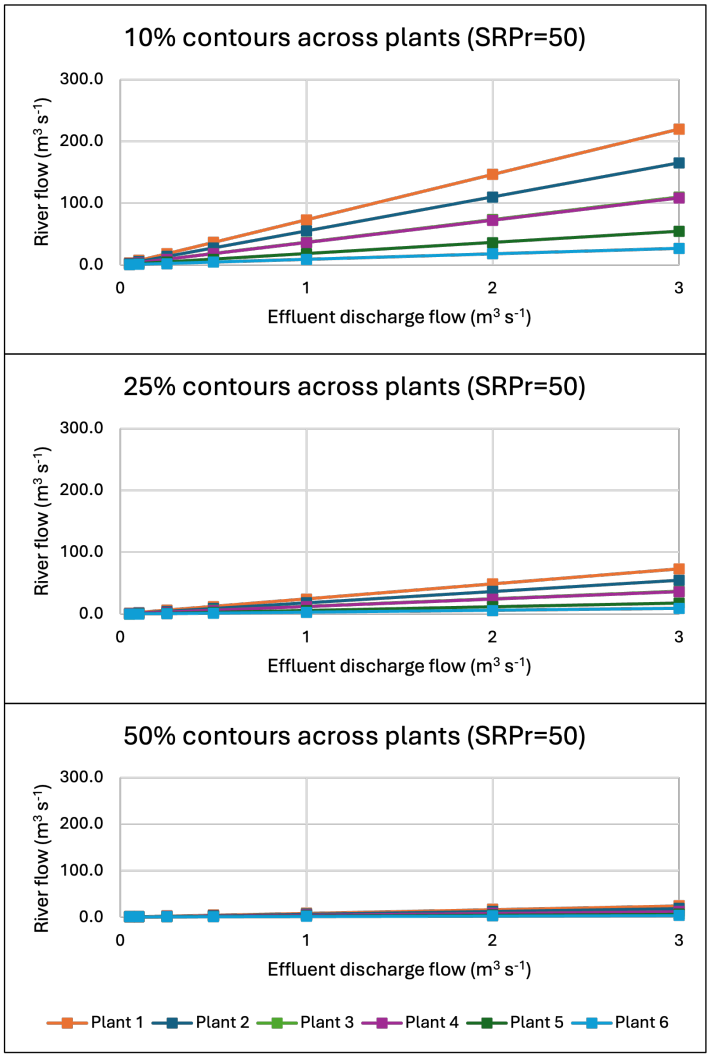


Figure 5.5: Generalized threshold envelopes across plants at $SRP_r = 50$ µg L^{-1}. Variation among plants, represented through differences in P_e (Equation 5.7), shifts the absolute position of the threshold curves but has little effect on their overall geometry.

These results indicate that threshold behaviour is controlled principally by the interaction between dilution capacity and background nutrient conditions, with effluent BAP

concentrations acting primarily as a scaling factor on threshold magnitude. Importantly, BAP increases can be estimated using a unified approach despite substantial differences in treatment performance and effluent composition.

5.4 Discussion

5.4.1 System-level Controls and Emergent Behaviour

Downstream bioavailable phosphorus exhibited consistent flow-conditioned behaviour across all scenarios, with system response organized by the interaction between effluent discharge, receiving water flow, and background SRP (Figures 5.1, 5.2, and 5.3). Differences among scenarios and plants were expressed primarily as shifts in response magnitude rather than changes in functional behaviour. Despite substantial variation in effluent characteristics, all scenarios converged toward similar response structures (Figure 5.3). Within the parameter space evaluated here, hydrologic mixing conditions exerted stronger control on short-term downstream response structure than variation in plant-specific effluent composition alone.

5.4.2 Mechanistic Drivers of Assessment Response

SRP Augmentation Factor and Effluent Fraction

Expressing system response through effluent fraction provides a mechanistically interpretable basis for comparing systems that would otherwise appear dissimilar when evaluated solely using conventional concentration-based metrics. Under this representation,

the receiving water is conceptualized not simply as a dilution medium, but as a dynamic mixing environment in which the relative contribution of wastewater-derived phosphorus determines the extent to which effluent characteristics are manifested downstream. Consequently, the augmentation factor provides a transferable basis for evaluating receiving water exposure potential across systems with differing baseline nutrient conditions and treatment performance, even without requiring site-specific calibration.

Dissolved vs. Particulate Phosphorus Contributions

The separation of dissolved and particulate phosphorus contributions reveals that direct SRP inputs dominate short-term downstream bioavailable phosphorus. While effluent-derived solids contribute measurable phosphorus through desorption, their contribution to short-term downstream SRP remained comparatively limited within the near-field conditions and parameter ranges evaluated here (Figures 5.1 and 5.2). This reflects the relative magnitudes of the two mechanisms: dissolved SRP is immediately available and scales directly with effluent loading, whereas particulate-derived phosphorus is constrained by solids concentration and release rates.

The contribution of particulate-derived phosphorus represents an additional BAP source that, while smaller in magnitude than direct SRP in the near-field, is not captured when wastewater phosphorus is represented solely as dissolved phosphorus. Importantly, the comparatively limited short-term contribution observed for particulate-derived phosphorus should not be interpreted as inconsequential. Rather, the results demonstrate that quantifying phosphorus speciation and desorption behaviour is necessary to determine

when particulate phosphorus release becomes environmentally relevant and when dissolved phosphorus governs receiving water response. The ability to make these distinctions depends on the collection and characterization of effluent-derived suspended solids, as enabled by the sampling approach developed in Chapter 2. Even comparatively small changes in bioavailable phosphorus loading may remain ecologically relevant where receiving waters are already nutrient-sensitive, approaching trophic thresholds, or subject to cumulative downstream loading effects (Jarvie et al., 2004). Consequently, quantifying short-term phosphorus contribution should not be interpreted as equivalent to directly quantifying ecosystem-scale impact.

5.4.3 Threshold Behaviour and Response

Threshold-like response regions are most clearly illustrated by plotting downstream response across combinations of effluent flow and river flow (Figures 5.4 and 5.5). Although downstream response varies continuously across the flow domain, the curves representing fixed contribution levels (e.g., 10%, 25%, and 50%) delineate combinations of effluent and river flow associated with equivalent receiving water exposure.

The similar shape and alignment of the threshold contours across plants and background SRP conditions indicate that threshold behaviour is primarily governed by the underlying mixing relationships, while phosphorus concentrations influence the absolute location of the curves. Importantly, these thresholds should not be interpreted as ecological tipping points. Rather, they represent hydrologic and phosphorus-loading conditions under which wastewater-derived bioavailable phosphorus becomes increasingly capable of influencing

downstream water quality and ecosystem response.

5.4.4 Treatment Effects and Dissolved vs Particulate BAP Contributions

Under the near-field hydrologic and phosphorus conditions evaluated here, reductions in particulate-associated phosphorus reduced the solids-derived contribution, but did not necessarily reduce total near-field BAP exposure proportionally when dissolved SRP remained the dominant effluent contribution. This behaviour is particularly evident when comparing Plants 3 and 4, which produced nearly identical total contribution patterns despite substantial reductions in suspended solids concentration and phosphorus release potential associated with tertiary treatment via filtration. The primary distinction between these plants emerged only when isolating solids-derived contributions to absolute SRP increases, where tertiary treatment reduced particulate-derived impacts without substantially altering overall short-term downstream response. This does not suggest tertiary treatment is ineffective but rather highlights that for systems specifically targeting immediate reduction in BAP loads, phosphorus removal strategies may need to prioritize dissolved-phase removal alongside solids separation.

5.4.5 Interpreting BAP Exposure: Why SRP Matters but Does Not Equate Eutrophication Response

The analysis could stop at estimating post-dilution concentration increases; however, defining eutrophication strictly by nutrient levels and excess availability is scientifically flawed because it ignores the physical characteristics of the water body and confuses the cause of the problem with the actual ecological repercussions (van Beusekom, 2018). Thus, the estimations for downstream SRP concentrations should be interpreted as indicators of near-field bioavailable phosphorus exposure and not direct indicators of eutrophication response. In this context, SRP represents the immediately bioavailable dissolved phosphorus fraction and therefore provides a practical operational metric for evaluating the direct contribution of WWTP effluent to receiving waters. The inclusion of phosphorus released from effluent-derived suspended solids extends this estimate by incorporating an additional short-term particulate-derived phosphorus source that would not be captured by conventional methods.

Ambient SRP concentration, however, is not equivalent to total bioavailable phosphorus, nor is it a fixed ecological endpoint (Li & Brett, 2013; Reynolds & Davies, 2001). In aquatic systems, SRP reflects a transient balance among external loading, biological uptake, sediment exchange, internal loading, hydrologic variability, and transformations among phosphorus pools that can fluctuate on daily and seasonal scales, driven by ever-changing biological and chemical processes (Dadi et al., 2023; Reynolds & Davies, 2001). Rapid biological assimilation can maintain low ambient SRP concentrations even in enriched systems, while elevated SRP does not necessarily produce the same ecological re-

sponse across different water bodies. Therefore, a single water quality snapshot fails to inform eutrophication dynamics because it provides a static measurement of highly dynamic variables. Thus, fluctuations in SRP should be interpreted as changes in exposure potential, not as universal predictors of algal response or ecosystem impairment (Dodds, 2003).

To contextualize the limitations of interpreting SRP concentration as a direct indicator of eutrophication risk, reported SRP concentrations associated with eutrophication-related responses were compiled across diverse aquatic systems (Table 5.2). This synthesis demonstrates that eutrophication responses are not associated with a single universal SRP threshold, but instead reflect system-specific interactions among phosphorus availability, biological uptake, hydrology, internal loading, and ecological sensitivity.

Table 5.2: Reported SRP/BAP concentrations associated with eutrophication indicators and context-dependent threshold interpretations across freshwater systems.

SRP/BAP (µg L^{-1})	Study Site(s)	Evidence of Eutrophication Response	Significance of observations	Reference
3-123	11 water bodies (China)	Chlorophyll *a*, algal biomass, TP, trophic state index, SRP, sediment EPC_0, phosphorus adsorption parameters, and cyanobacterial organic matter	Reported SRP across lakes. Surprisingly, **SRP was negatively correlated** with eutrophication indicators. Notes that low SRP can be both a cause and consequence of cyanobacterial dominance because cyanobacteria rapidly deplete SRP while sediment processes replenish it at low concentrations.	Wang et al. (2023)
>8	Green Bay (Lake Michigan)	Regions with phytoplankton growth saturation and insensitive to further phosphorus increases	Trophic-state boundaries established based on phytoplankton physiology: oligotrophic: 0.5–1.2 µg SRP L^{-1}, mesotrophic: 1.2–8.0 µg SRP L^{-1}, eutrophic: >8.0 µg SRP L^{-1}. **"Thresholds" can represent physiological saturation points, not ecological tipping points.** Once SRP exceeds ~8 µg L^{-1} in this framework, further SRP increases may not produce proportional algal-growth responses.	Auer et al. (1986)
19	Chaohu Lake (China)	Measured chlorophyll *a*	**Direct threshold study**, in which chlorophyll a response showed two regression regions intersecting at 19 µg SRP L-1, interpreted as the growth threshold.	Yin et al. (1992)
30	Taihu Lake (China)	Chlorophyll *a*, phytoplankton microscopy, *Microcystis* dominance, nutrient dilution/enrichment bioassays, and field observations	30 µg SRP L^{-1} saturated growth, but **bloom control required translating dissolved nutrient responses into TP and total nitrogen targets, and chlorophyll *a* endpoints**.	Xu et al. (2015)
30-83	River Thames (UK)	Periphyton growth	Phosphorus limitation became apparent at 83 µg SRP L^{-1}, and change in algal community occurred at 30 µg SRP L^{-1}. Points out that **lowering SRP does not automatically reduce algal biomass** unless concentrations cross the system-specific phosphorus-limiting concentration. Hydrology, residence time, light, and habitat structure can mediate the biological response.	Bowes et al. (2012)
<40	Miyun Drinking Water Reservoir (China)	Measured chlorophyll *a*	Nitrogen thresholds also reported. Phosphorus thresholds can interact with nitrogen form. Ammonium + P produced stronger stimulation than nitrate + P, so **SRP alone may not fully predict bloom response**.	Zeng et al. (2016)
100	River Thames (UK)	Measured chlorophyll *a*	Annual average; indicative, **not a strict presence/absence threshold**.	Kinniburgh et al. (1997)
100	River Thames (UK)	Measured chlorophyll *a*	**After P-removal investments at WWTPs, observed BAP reductions still exceeded concentrations thought to limit algal growth. Yet, chlorophyll *a* concentrations declined**	Kinniburgh & Barnett (2010)

Table 5.2 continued.

SRP/BAP (µg L^{-1})	Study Site(s)	Evidence of Eutrophication Response	Significance of observations	Reference
182-570	Maninjau Lake (Indonesia)	Eutrophication inferred from phosphorus concentrations exceedance, greenish lake colour, and historic chlorophyll *a* values	Refer to common 20 µg TP L^{-1} and TP range was 265-603 µg L^{-1}. Points out that **how eutrophication is expressed depends on depth, dissolved oxygen, pH, and temperature**, for instance.	Komala et al. (2020)
210-840	Chaohu Lake (China)	Algal bloom occurrences	Surface-water SRP ranged by lake region. **Eutrophication status was site-based**; algal blooms occurred more frequently and intensely in the western lake.	Jin et al. (2019)
280-330	Dianchi Lake (China) **simulated lake microcosm with Dianchi sediment*	Measured *M. aeruginosa* growth	Reported BAP is post sediment release. Notes that **BAP can be regenerated internally from sediments and sustain cyanobacterial growth.**	Liu et al. (2016)
Specific concentration linked to eutrophication response not specified	Lakes Qingling & Yandong (China)	Chlorophyll *a*, trophic state index, algal/macrophyte regime classification, surface/interstitial SRP, sediment P fractions, EPC_0, enzymatic activities, and phosphorus-solubilizing bacteria.	In the algal-dominated basin, SRP in surface and interstitial water was the highest among all studied sites and supported algal blooms. In transitional basins, blooms could occur even where surface SRP was limited because P regeneration pathways differed. **Bloom response depends not only on SRP concentration, but on system regime and dominant phosphorus supply pathway**: exogenous input, Fe-bound P desorption, organic P hydrolysis, or macrophyte blocking of sediment-water P transfer.	H. Li et al. (2021)
Specific concentration linked to eutrophication response not specified	Dianchi Lake (China) **in situ enclosure experiment during cyanobacterial bloom decline*	Measured chlorophyll *a*	BAP increase from 101 to 633 µg L^{-1}, accounting for 96.7% of the TP increase in water and 67.8% of TP reduction from algae. Points out that **BAP can increase after bloom collapse, be adsorbed by sediment, and later support new cyanobacterial growth**, creating an internal phosphorus feedback loop.	Zhang et al. (2018)

5.4.6 Interpretive Scope and Ecological Relevance

Within this scope, SRP is used as the operational proxy for the immediately bioavailable dissolved phosphorus fraction because it represents the most direct and rapidly available source by which WWTP effluent can influence receiving water phosphorus conditions. The inclusion of phosphorus released from effluent-derived suspended solids extends this exposure estimate beyond dissolved inputs alone by accounting for an additional particulate-derived contribution. However, computed downstream SRP concentrations should be interpreted as approximate near-field concentration estimates. Owing to the dynamic nature of phosphorus cycling, observable SRP concentrations may not scale linearly with eutrophication response, and low ambient SRP does not necessarily indicate low phosphorus pressure if rapid assimilation or internal cycling is occurring (Dodds, 2003); thus, elevated SRP does not translate into a universal ecological response threshold because system sensitivity varies according to specific conditions across rivers, lakes, reservoirs, and estuarine systems.

This distinction is important for interpreting the outputs herein as initial exposure conditions created when WWTP-derived SRP and desorbable particulate phosphorus enter a receiving water are isolated. This allows for estimation of when effluent-derived BAP is likely to become proportionally important before subsequent biological or sediment-mediated processes modify the signal (i.e., when WWTP inputs create a potentially important near-field BAP exposure and loading, not how that contribution will propagate throughout the aquatic ecosystem).

The simplified structure also supports transferability across treatment and receiving water scenarios. Because this assessment is based on quantifiable parameters such as ef-

fluent flow, river flow, upstream SRP, effluent SRP, suspended solids concentration, and particulate phosphorus release potential, it can be parameterized for different WWTPs and receiving waters. The use of effluent fraction and relative contribution metrics further allows comparison among systems with different absolute flow magnitudes. This streamlined approach, therefore, defines this protocol's appropriate use: exposure potential, scenario comparison, and identifying conditions where more detailed site-specific assessment is warranted.

5.4.7 Management Implications and Future Development

The analyses indicate that wastewater phosphorus impacts should not be evaluated from effluent concentration, treatment type, or annual loading alone. The same effluent composition can produce substantially different near-field BAP exposure depending on river flow, upstream SRP concentration, and the resulting effluent fraction of the mixed flow. Management approaches based only on average effluent quality may therefore overlook periods when WWTP influence becomes proportionally more important, particularly during low-flow conditions or in nutrient-sensitive receiving waters with limited dilution capacity.

From a treatment-evaluation perspective, the outputs here highlight the importance of distinguishing between dissolved and particulate-associated phosphorus contributions. Treatment strategies aimed specifically at reducing immediate bioavailable phosphorus exposure should consider whether performance improvements arise from reductions in dissolved phosphorus, particulate phosphorus release, or both.

The results can also support broader water quality assessment by providing hydro-

logically conditioned estimates of WWTP-derived BAP loading. Process-based models such as CE-QUAL-W2, WASP, SWAT, MIKE, and AQUATOX can represent downstream hydrodynamic, biogeochemical, and ecological processes, including sediment interactions, biological uptake, trophic response, and watershed-scale transport. However, these models often require extensive site-specific calibration and may rely on phosphorus inputs that do not resolve WWTP-specific bioavailable fractions, particulate reactivity, or short-term desorption behaviour (Gil et al., 2026). The work presented here can help bridge this gap by translating effluent speciation and release potential (Vianini et al., 2025; Chapters 2–4) into flow-dependent BAP inputs that can be used for contribution conditions or incorporated into more detailed downstream assessments.

Future development should extend this approach beyond single-discharge applications by incorporating multiple WWTPs within a watershed, flow-duration data, seasonal variation in upstream SRP, and site-specific effluent speciation datasets. This would allow cumulative point-source effects to be evaluated under realistic hydrologic conditions rather than treating each discharge in isolation. Coupling this approach with downstream water quality or ecological response models would provide a stronger basis for evaluating how WWTP-derived BAP inputs translate into biological uptake, algal response, and longer-term ecological outcomes.

5.5 Conclusion

This study developed a multi-form phosphorus accounting approach to identify WWTP-derived bioavailable phosphorus contribution potential to receiving waters. By integrating

experimentally constrained wastewater phosphorus speciation and particulate phosphorus desorption behaviour with hydrologic mixing, this protocol provides a method for evaluating wastewater contributions beyond traditional TP metrics.

The results show that near-field BAP response is governed primarily by hydrologic mixing, particularly the effluent fraction of the receiving water. Dissolved phosphorus dominated short-term downstream BAP exposure, whereas particulate-derived phosphorus made a smaller contribution whose importance depended primarily on treatment performance and phosphorus release potential. The analysis also highlighted threshold-like transitions between low- and high-influence conditions, illustrating that WWTP impacts are not fixed properties of effluent quality alone but emerge from how phosphorus is expressed under specific receiving water conditions.

These findings support a more contextualized interpretation of quantified WWTP phosphorus loads. Small predicted increases in downstream SRP should not be interpreted as evidence of negligible ecological relevance, because SRP is a dynamic concentration shaped by biological uptake, sediment exchange, recycling, and site-specific sensitivity. Rather than directly predicting eutrophication response, this approach complements existing water quality and ecological assessment models by providing mechanistically constrained, hydrologically conditioned wastewater phosphorus inputs. More broadly, it advances multi-form phosphorus accounting as a practical basis for describing dynamic phosphorus utilization, receiving water exposure, and the conditions under which WWTP discharges can have greater potential for eutrophication threats.

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Chapter 6

Conclusions, Implications, and Recommendations

6.1 Conclusions

The key conclusions from this thesis research are presented below.

1. Wastewater effluent solids are not inert residual particles; they can contain measurable reactive and bioavailable phosphorus forms.

2. Continuous-flow centrifugation provided a practical method for collecting and characterizing low-concentration effluent solids.

3. Although tertiary cloth filtration substantially reduced particulate phosphorus and its reactive fraction, it had little effect on immediately bioavailable phosphorus, which remained dominated by SRP in the final effluent.

4. TP reduction alone does not fully describe changes in eutrophication-relevant phosphorus.

5. Effluent-derived solids showed phosphorus release behaviour that was related to, but distinct from, established sediment phosphorus paradigms. Release potential is not fixed but depends on the conditions into which the solids are discharged.

6. The desorption experiments showed that wastewater-derived solids can act as net phosphorus sources across the tested receiving water SRP conditions. Benchmarking these responses against established sediment paradigms demonstrated both the utility and limitations of applying sediment-derived concepts to wastewater solids, whose phosphorus composition and treatment history differ fundamentally from those of natural sediments.

7. Scenario analysis suggested that dissolved phosphorus would generally dominate the short-term pathway for near-field bioavailable phosphorus exposure, while particulate-derived phosphorus represented a smaller but mechanistically important secondary pathway.

8. Receiving water hydrology primarily governs dilution, transport, residence time, and therefore the magnitude and duration of modelled downstream BAP exposure. The ecological consequences of that exposure subsequently depend on phosphorus transformation, biological utilization, and ecosystem-specific responses.

9. Threshold-like transitions were identified where WWTP effluent shifts from a minor to a more prominent contributor to downstream bioavailable phosphorus.

10. A multi-form phosphorus accounting approach provides a more mechanistic basis for interpreting WWTP impacts than TP-based assessment alone.

Taken together, these conclusions demonstrate that wastewater-derived phosphorus is best understood as a mixture of phosphorus forms whose receiving water significance depends on both effluent characteristics and receiving water conditions. Although TP remains an important metric for regulatory and operational assessment, it does not distinguish among phosphorus forms that differ in bioavailability, release potential, or downstream behaviour. Consequently, improvements in treatment performance, as measured by TP removal, do not necessarily translate proportionally into reductions in downstream bioavailable phosphorus concentrations. Tertiary filtration can reduce TP and reactive particulate phosphorus, yet dissolved bioavailable forms may remain the dominant short-term

source after discharge. Effluent solids also represent a distinct secondary source because they can release phosphorus under receiving water conditions and should not be assumed to behave like natural sediments.

More broadly, this thesis provides a mechanistic basis for interpreting WWTP phosphorus contributions. It shows that the relevance of wastewater phosphorus depends on what forms are discharged, how those forms behave after discharge, and the hydrologic conditions that control the magnitude of their contributions. These findings demonstrate that no single phosphorus metric is sufficient for all engineering and environmental decisions. In addition to TP assessments, phosphorus composition provides complementary information regarding phosphorus release behaviour, potential bioavailability, and post-discharge fate. Consequently, phosphorus management should be guided by the management objective, treatment configuration, phosphorus composition, receiving-water hydrology, and the environmental processes governing phosphorus transformation and biological utilization.

6.2 Implications

The findings of this research have important implications for wastewater treatment assessment, receiving water protection, and phosphorus management. First, this work demonstrates that while TP provides an appropriate basis for compliance monitoring and phosphorus loading assessment, it does not fully capture the environmental behaviour of wastewater effluent phosphorus under all management objectives. TP is operationally useful because it is simple, measurable, and embedded in regulatory frameworks. However, the results further confirm that TP can obscure major differences in phosphorus composition.

Two effluents with similar TP concentrations may differ substantially in the distribution of dissolved and particulate phosphorus forms, and therefore in their bioavailability and release potential; thus, a treatment process may reduce TP while leaving a larger proportion of the remaining phosphorus in dissolved or readily bioavailable forms. This does not mean that TP limits are unimportant; rather, it means that the choice of phosphorus metric ultimately depends on the management objective being addressed.

TP remains appropriate for compliance monitoring and loading assessments, whereas phosphorus composition provides additional insight when evaluating treatment performance, downstream exposure, release behaviour, and potential ecological significance. Municipal wastewater phosphorus regulation is fundamentally intended to protect receiving water quality rather than simply evaluate treatment performance. Consequently, permit limits for total phosphorus are commonly established using receiving-water objectives that consider assimilative capacity, expected dilution, designated water uses, and other site-specific characteristics, resulting in different phosphorus limits among wastewater treatment plants. The framework developed in this thesis is therefore intended to complement, rather than replace, this existing regulatory approach. By incorporating phosphorus speciation, treatment configuration, receiving-water hydrology, and post-discharge phosphorus transformation, it provides additional mechanistic information for interpreting downstream phosphorus exposure under conditions where phosphorus composition may influence environmental behaviour. Such information may be particularly valuable where assimilative capacity is limited or environmentally sensitive receiving waters are present.

Treatment performance should increasingly be evaluated using phosphorus speciation alongside conventional concentration-based metrics. Tertiary cloth filtration clearly re-

duced particulate phosphorus including the associated reactive particulate pool, which is an important treatment benefit. However, because dissolved forms persisted, the net effect of treatment on bioavailable phosphorus was more nuanced than TP reductions alone would suggest. If the management objective is to reduce receiving water bioavailable phosphorus, then treatment evaluation should consider whether a physical solid–liquid separation process is enough for bioavailable phosphorus removal. This distinction is particularly important in systems where receiving waters are sensitive to small changes in bioavailable phosphorus or where effluent comprises a substantial fraction of the flow.

Wastewater-derived suspended solids are a distinct source of reactive particulate phosphorus and should be evaluated accordingly. The results demonstrate that characterizing the composition and release behaviour of effluent-derived solids can provide information that is not captured by TP measurements or by treating wastewater particulates as equivalent to natural suspended sediments. Importantly, obtaining this information depends on the ability to collect sufficient quantities of representative effluent solids for direct analysis. The sampling and solids-concentration approach developed in this thesis enabled such characterization and revealed substantial differences in phosphorus composition and release behaviour that would not have been apparent from conventional monitoring alone. These distinctions have implications for nutrient models, monitoring programs, and management decisions that seek to represent particulate phosphorus contributions and downstream phosphorus availability.

A pathway for improving how WWTP phosphorus inputs are represented in receiving water models was provided. A mechanistically constrained phosphorus input evaluation can support model parameterization, scenario development, and interpretation. By sepa-

rating dissolved inputs from particulate phosphorus release, it is possible to identify which effluent characteristics are likely to matter most under specific hydrologic regimes. This is especially useful where managers need to prioritize monitoring, evaluate treatment scenarios, or determine whether more complex modelling is warranted.

Finally, this thesis has broader implications for nutrient management under changing environmental conditions. Low-flow periods, warming temperatures, altered hydrologic regimes, population growth, and increasing pressure on wastewater infrastructure may all affect how effluent phosphorus loading is expressed in receiving waters. As wastewater contributions can represent an increasing proportion of river flow, receiving waters may become progressively more influenced by treated effluent, even where effluent quality remains unchanged. Because the environmental relevance of phosphorus depends not only on load but also on form, transformation, and dilution, nutrient management will require more accurate assessment tools. This thesis supports a shift from static phosphorus accounting toward multi-form phosphorus assessment that better reflects how wastewater-derived phosphorus behaves after discharge.

6.3 Recommendations and Future Directions

The findings of this study are directly applicable to WWTPs that employ chemically assisted phosphorus removal. Future work should extend the methodological and mechanistic basis developed in this thesis by applying phosphorus speciation across a wider range of wastewater treatment configurations and receiving water settings. Effluent monitoring intended to inform receiving water assessment should distinguish, at minimum, TP, SRP, and

reactive particulate phosphorus fractions such as NAIP. This would allow treatment performance to be evaluated not only as bulk phosphorus removal, but also as changes in the forms most relevant to short-term bioavailability. A broader application across biological phosphorus removal systems, chemical dosing regimes, filtration technologies, and seasonal operating conditions is needed to determine the consistency of the patterns observed here.

Further research should also evaluate how the phosphorus release behaviour measured under controlled conditions is expressed under more complex receiving water conditions. The desorption experiments in this thesis quantified release potential across SRP, pH, and temperature gradients, but field-scale expression will also depend on residence time, flow conditions, particle transport, settling, resuspension, and interactions with natural suspended and bed sediments. Longer-term evaluations should also consider repeated sorption–desorption cycles, aging of effluent-derived solids, and transformation of dissolved organic and condensed phosphorus forms.

Finally, the multi-form phosphorus evaluation approach should be tested using paired effluent and receiving water datasets across contrasting flow regimes. Combining effluent speciation with upstream and downstream monitoring would allow predicted SRP and bioavailable phosphorus contributions to be compared with measured near-field patterns. This would improve integration with more detailed water-quality models and help define management-relevant thresholds based on site-specific receiving water objectives rather than generalized phosphorus concentration targets.

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