

Bioavailable phosphorus in runoff suspended sediment  
in rivers flowing through contrasting land uses  
(流域の土地利用が対照的な河川の浮遊懸濁物質中の  
生物利用可能態リン)

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## Abstract

Eutrophication in aquatic ecosystems is intimately linked with the increase in the concentrations of nitrogen (N), phosphorus (P), and carbon (C); though P is the main limiting nutrient for primary production in freshwaters. While considerable information in recent years has pointed to the importance of considering bioavailability in water quality restoration programs, established target P load reduction guidelines are still based on total phosphorus (TP). River water P is usually separated into particulate P (PP) and dissolved P (DP), and the forms of P that support algal growth are termed bioavailable. Dissolved P is mostly available for algal uptake, while PP which consists of P associated with sediment and organic material eroded during runoff, contributes a variable but long-term legacy source of bioavailable PP. Therefore, none of the commonly measured P fractions are accurate measures of bioavailable phosphorus (BAP). In general, PP is much more variable than dissolved P, and storm events are extremely important for PP dynamics because large portions of river PP loads can be transported attached to sediment and organic matter during only a few major high flow events. The fraction of PP that is potentially bioavailable (PBAP), may increase if P is bound to clay minerals and degradable organic matter in suspended sediments (SS). It is still unclear how particulate organic carbon (POC) and particulate organic nitrogen (PON), which are important components of particulate organic matter in rivers influence the potential availability of PBAP. Furthermore, much is less known about the relationship between PBAP, and POC and PON stoichiometry despite the spike in SS during high flow events.

The wide variability in PBAP suggests that both river-flow characteristics and land use patterns in the river catchment may be important in addition to POC and PON concentration. Since PP is usually transported to rivers bound to SS, the quantity and type of sediment in runoff will influence the concentration of BAP by varying the relative amounts of DP and PP entering the river. It is poorly understood how different land-use types influence PBAP in river runoff, and few studies have estimated the amount PBAP during low flow conditions. Besides, there is uncertainty regarding the relationship between PBAP and particulate organic matter constituents under different hydrological conditions in urban and agricultural rivers. In this thesis, we investigated the variation in SS, DP, PP, PBAP, BAP, POC and PON in rivers draining through contrasting land uses. The objectives of the study were: i) to estimate PBAP in runoff from agricultural and urban rivers in order to assess whether the PBAP content was markedly different in the rivers; ii) to determine the BAP proportion in river runoff, and to clarify its relationship with TP in the rivers; and iii) to examine the relationship between PBAP, POC and PON, and to relate this to the elemental composition of SS from the rivers.

Here, a new procedure that involves ultrasonic treatment was used to allow for rapid extraction of PBAP from SS samples. A strong statistical relationship was observed between PBAP and SS in the river classed as agricultural ( $r^2 = 0.69$ ), in contrast to the urban one where no correlation was observed, implying that the particle size and composition of SS in both rivers was markedly different. PP was the dominant fraction of TP at high flow and between 6 to 79% of PP was estimated to be bioavailable. A strong correlation was observed between BAP and TP in the urban river ( $r^2 = 0.84$ ), indicating that merely using TP as a proxy for BAP is questionable as this overestimates the eutrophication potential of some P sources. The BAP and TP relationship in the agricultural river revealed that elevated PP concentration at high flow may not translate into higher BAP in the runoff, implying that quantification of BAP in SS is critical for effective watershed management programs. Besides, elevated POC and PON concentrations in both rivers were associated with low flow. POC and PON concentrations in both rivers declined at high flow presumably due to the mixing effects of water from different sources in the watershed which could have altered the particulate organic matter composition. A significant correlation existed between POC and SS in both rivers, and POC to PON ratios of SS from the rivers point to the change in the particulate organic matter at varying flow conditions. PBAP exhibited a positive relationship with POC and PON concentration in both rivers possibly an indication that particulate organic matter contributes to BAP in the rivers. Iron (Fe) was the dominant element measured in SS from both rivers, and the PBAP concentration in the agricultural river was positively correlated with the Fe to POC ratio unlike in the urban river.

Overall, this study shows that it is important to quantify BAP in SS since TP includes complex P forms that may not be available to algae. Moreover, the origin of SS under changing flows could be different, with subsurface sediment pathways linked to low flow and contribution from surface runoff associated with rain events, and particulate organic matter constituents and sediment elemental content could greatly impact BAP in river runoff.

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## List of abbreviations and symbols

N	nitrogen
P	phosphorus
C	carbon
TP	total phosphorus
PP	particulate phosphorus
DP	dissolved phosphorus
BAP	bioavailable phosphorus
SS	suspended sediment
PBAP	particulate bioavailable phosphorus
OM	organic matter
POC	particulate organic carbon
PON	particulate organic nitrogen
NaOH	sodium hydroxide
M	mol/L
Fe	iron
Ca	calcium
Mg	magnesium
Na	sodium



# Chapter 1      General introduction

## 1.1 The context phosphorus as a mineral resource

### *1.1.1 Why conduct research on phosphorus?*

Phosphorus, like nitrogen and potassium, is a plant nutrient essential to all life that therefore cannot be replaced in food production (Vaccari, 2009). It is a major constituent of DNA and RNA which are critical carriers of genetic information. Phosphorus is also a major component of adenosine triphosphate (ATP) which are intracellular energy molecules that store energy that is generated during photosynthesis and respiration so that it can be used in other cellular processes that require energy such as biosynthetic reactions (Mackey et al., 2019). Phosphorus (P) also comprises phospholipids which aid in cell membrane formation, hence enabling the physiological and biological functioning of all animals, plants and microorganisms (Bundy et al., 2005; Cordell and White, 2014; Sharpley et al., 2018). Being a vital component of bones and teeth in all vertebrates, P minerals keep us in a good physical shape and allow us to chew our food (Oelkers and Valsami-Jones, 2008). Approximately 20% of the human skeleton and teeth are made up of calcium phosphate; the human body needs at least 0.7 grams of P per day (Childers et al., 2011). Phosphorus also plays a key role in controlling the primary productivity of terrestrial and aquatic ecosystems (Carpenter et al., 1998; Correll, 1998).

In spite of its biological importance, P is only the 11<sup>th</sup> most abundant element in the lithosphere, occurring only in small quantities (0.10% - 0.12% on a weight basis) (Filippelli, 2008) and is rarely found in its elemental form. Although P has a number of potential oxidation state (from -3 to +5), it occurs almost exclusively in its most oxidized form as orthophosphate ( $\text{PO}_4^{3-}$ ), whether P is dissolved or particulate, organic or inorganic (Bennett and Schipanski, 2013). Besides other critical bio-nutrients, such as carbon (C) and nitrogen (N), P has no stable atmospheric gas phases and its propagation in the ecosystem, is almost entirely dependent on its aqueous and solid transfer (Chapra, 2008).

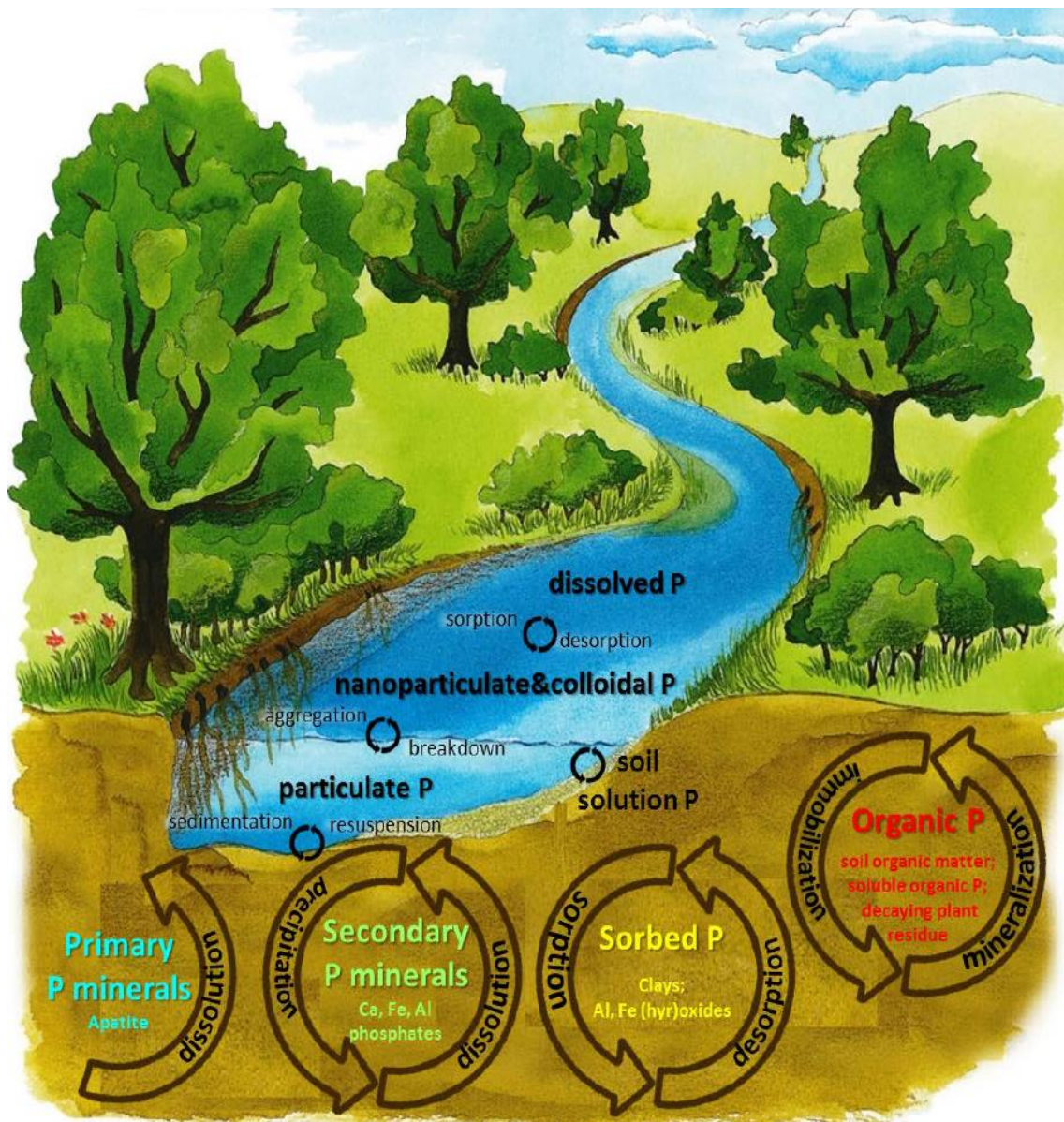


As the P cycle on earth is one of the slowest biogeochemical cycles, that is; on a geological time scale, P is considered to be a non-renewable resource on a human time scale. The P in the bedrock has taken millions of years to form, beginning as remains of aquatic life on the seafloor that was transferred to the lithosphere over millions of years through mineralization and tectonic uplift (Sutton et al., 2014).

### *1.1.2 Phosphorus cycling processes in the ecosystem*

The P cycle encompasses numerous living and non-living environmental reservoirs and various transport pathways. In tracing the movement of P in the environment, the interplay between physical and biological processes becomes apparent (Mackey et al., 2019). Besides acting as reservoirs of P in the environment, microbes contribute to the P transformation processes within other reservoirs such as in soil or aquatic environments. Phosphorus occurs in the ecosystem as inorganic and organic P compounds. Inorganic P compounds include phosphate, pyrophosphate, and polyphosphate, with organisms directly utilizing phosphate ( $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$ ) at a suitable pH range of most natural ecosystems. Organic P compounds have a link to carbon (C), and include orthophosphate monoesters [e.g., glucose 6-phosphate and myo-inositol hexakiphosphate (phytate)]; orthophosphate diesters (e.g., nucleic acids, phospholipids); phosphonates (e.g., aminoethyl phosphonate), and biological polyphosphates (e.g., ATP) (Chapra, 2008; Cade-Menun et al., 2019).

In terrestrial and aquatic ecosystems, P cycles geochemically and biologically (**Figure 1.1**). Geochemical processes include adsorption/desorption of organic and inorganic P compounds with mineral particles, and precipitation with cations in solution. In biological cycling, phosphate is consumed by organisms and transformed into organic P forms such as nucleic acids or is stored in cells as phytate or polyphosphate (Cade-Menun et al., 2019). This P can be released by secretion or after cell death, and converted back to phosphate by mineralization process which is aided by phosphatase enzymes (Baldwin, 2013; Karl, 2014; Orihel et al., 2017). There are similarities and differences regarding P cycling in terrestrial and aquatic ecosystems. Most soils contain a relatively low amount of total P, and only a small fraction of the total P is available to plants.



**Figure 1.1:** Phosphorus pools in soil and stream water and the processes determining the P addition to and release from the respective pools (adapted according to Dietz and Strock, 2016)

Most P compounds in soils have low water solubility, and once in the soil solution, soluble P moves mainly by diffusion (Dietz and Strock, 2016). Terrestrial organisms derive phosphate for their use from the pool that is dissolved in the soil solution, in the space between the solid components of soil (minerals and organic matter) (Shen et al., 2011; Cade-Menun et al., 2019).

In this case, P availability is mostly limited by soil moisture. Labile (easily-obtained) phosphate is taken up from the soil solution, then replenished by desorption, dissolution, or mineralization. As terrestrial plants are fixed in place, strategies have evolved to facilitate their P acquisition. This includes changes in rooting structure or associations with rhizosphere microbes and symbionts, which can enhance access to phosphate or production of phosphatases or organic acids to desorb P compounds from mineral surfaces (Richardson et al., 2011; Shen et al., 2011). In pristine environments, plants growing on juvenile substrates rely on P supply from primary minerals, such as apatite released from the parent material (**Figure 1.1**) (Vitousek et al., 2010; Walker and Syers, 1976).

Apatite is the most abundant group of phosphate minerals, comprising of hydroxyapatite, fluorapatite, and chlorapatite (**Table 1.1**). These three forms of apatite share nearly identical crystalline structures, but differ in their relative proportions of hydroxide, fluoride, and chloride, each being named for the anion that is most abundant in the mineral (Mackey et al., 2019). Phosphate minerals generally form in the environment through precipitation from solution (which may be microbially-mediated), and the chemical composition of the minerals depends on the ion or ions present in solution at the time of precipitation.

**Table 1.1:** Phosphate minerals and their chemical compositions. Apatite is the general term for the three minerals hydroxylapatite, fluorapatite, and chlorapatite (adapted from Mackey et al., 2019)

<i>Apatite</i>	$Ca_5(PO_4)_3(F,Cl,OH)$
Hydroxylapatite	$Ca_5(PO_4)_3OH$
Fluorapatite	$Ca_5(PO_4)_3F$
Chlorapatite	$Ca_5(PO_4)_3Cl$
Frankolite	$Ca_{10-a-b}Na_aMg_b(PO_4)_6-x(CO_3)_x-y-z(CO_3F)_y(SO_4)_zF_2$
Lazulite	$(Mg,Fe)Al_2(PO_4)_2(OH)_2$
Monazite	$(Ce,La,Y,Th)PO_4$
Pyromorphite	$Pb_5(PO_4)_3Cl$
Strengite	$FePO_4 \cdot 2H_2O$
Triphylite	$Li(Fe,Mn)PO_4$
Turquoise	$CuAl_6(PO_4)_4(OH)_8 \cdot 5H_2O$
Variscite	$AlPO_4 \cdot 2H_2O$
Vauxite	$FeAl_2(PO_4)_2(OH)_2 \cdot 6H_2O$
Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$
Wavellite	$Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$

Progressing ecosystem and soil development causes the depletion of rocks and primary minerals as a direct source of P for the biota but at the same time mineral nutrients become increasingly incorporated into biomass (Gottselig and Klumpp, 2016). Through the organic matter accumulation during soil formation, an increasing portion of nutrients in a terrestrial ecosystem, including P, is organically bound (Darch et al., 2014; Egli et al., 2012; Walker and Syers, 1976).

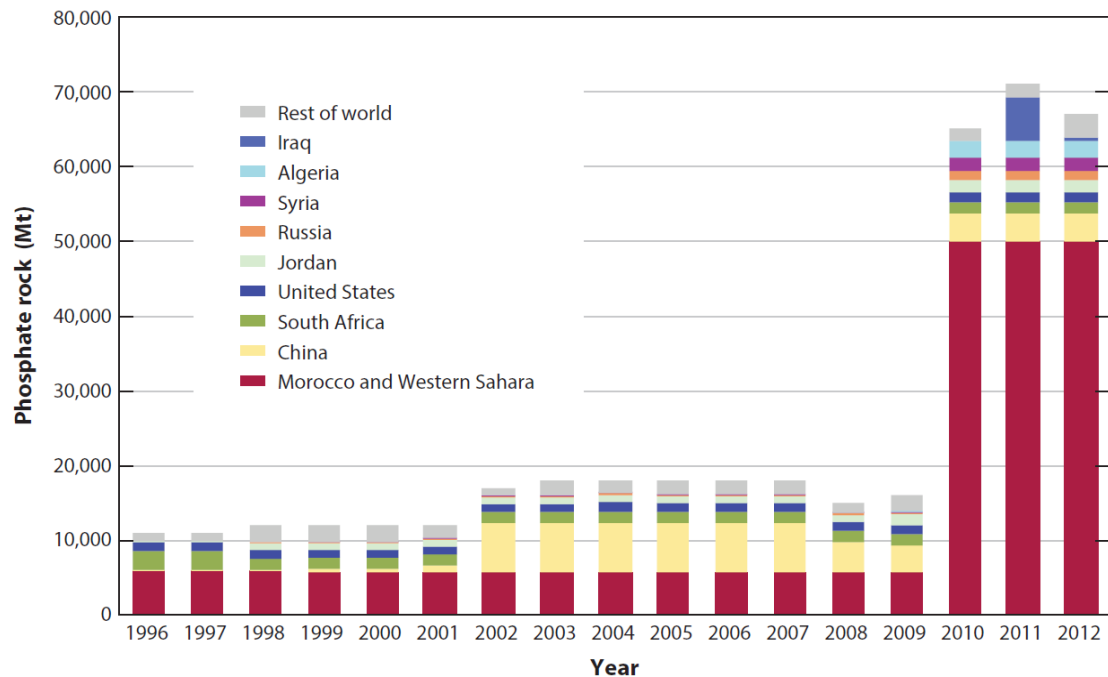
In a progressed ecosystem, organophosphorus compounds ( $\text{PO}_4^{3-}$  bound to organic C through ester bond) make up a considerable portion of total P in the ecosystem and thus P supply for organisms is largely based on these compounds (Gottselig and Klumpp, 2016). Next to organic P (**Figure 1.1**), further P species develop during soil aging (Williams and Walker, 1969) and undergo loss factors, limiting the biological productivity of the ecosystem. Phosphorus can form reactive secondary minerals such as Ca-, Fe- or Al-phosphates (Anderson, 1988; Egli et al., 2007) or also be sorbed to aluminosilicate minerals or Al- or Fe-(hydr)oxides (Walker and Syers, 1976) (**Figure 1.1**). Soil P pools interact with the soil solution, achieve increased mobility and can therefore also be found in aquatic ecosystems such as rivers where their excessive presence leads to deleterious consequences.

Aquatic environments include sediments, benthic biofilms, and the water column. In sediments, organic and inorganic P compounds are associated with mineral particles, algal and bacterial biomass (particularly at the sediment-water interface) and organic matter, or occur in aqueous form in pore water. Phosphate and other P fractions can interchange with the water column through adsorption/desorption and precipitation/dissolution, and through uptake and remineralization by organisms in the sediment and in the water column (Cade-Menun et al., 2019). Within the water column, organic and inorganic P compounds can be dissolved, associated with colloids, or associated with larger particulates including plankton (Orihel et al., 2017). Colloidal material has been defined as particles in the size range 1 nm – 1  $\mu\text{m}$  (Buffle and Leppard, 1995), and therefore spans the operationally defined 0.45  $\mu\text{m}$  threshold between dissolved and particulate phases (Haygarth et al., 1997). Colloids act as vectors for phosphorus transport in the ecosystem.

Colloidal inorganic P refers to P bound to iron and manganese oxides, clay minerals, iron hydrous oxides, and products of weathering and soil colloids, e.g. aluminium silicates and kaolinites (Gimbert et al., 2007). Colloidal organic P consists of natural organic matter containing species such as oligosaccharides, lipids, peptides, and refractory organic matter such as humic substances (Gimbert et al., 2007). However, further characterization of colloidal material and associated P is further complicated by its dynamic and unstable nature (Chen and Buffle, 1996; Gottselig et al., 2014). Despite the enormous studies and knowledge amassed in recent decades regarding the P forms in the environment, P anomalies still exist where by P concentrations are excessive in some aquatic ecosystems resulting in eutrophication, while they are deficient in some environments such as in agricultural soils.

### ***1.1.3 The current concerns regarding phosphorus sustainability***

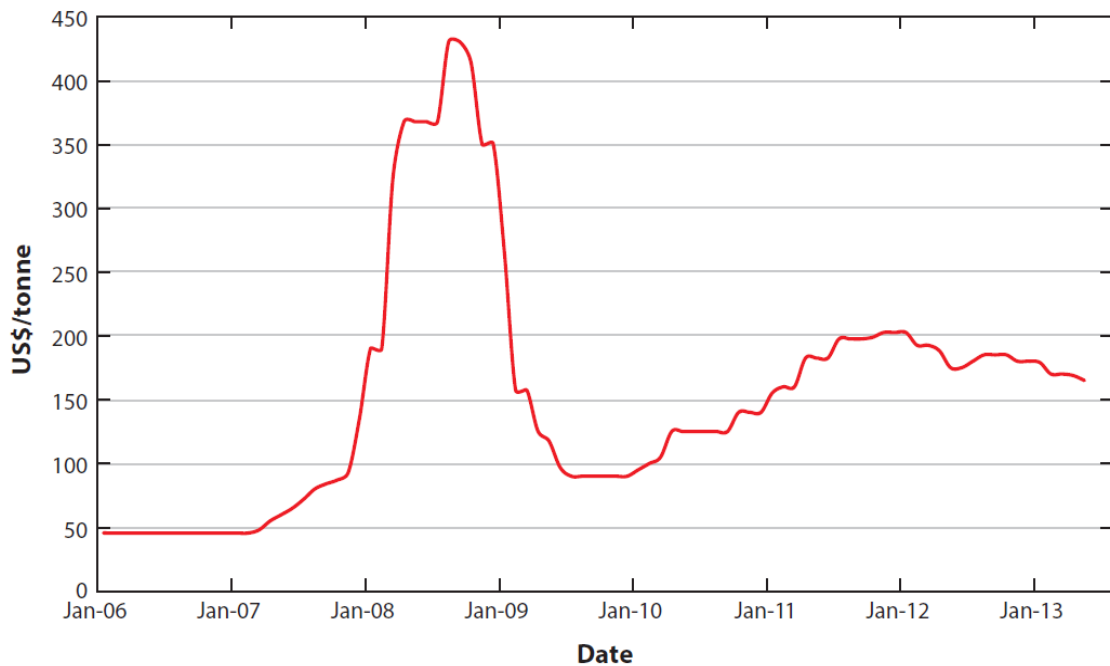
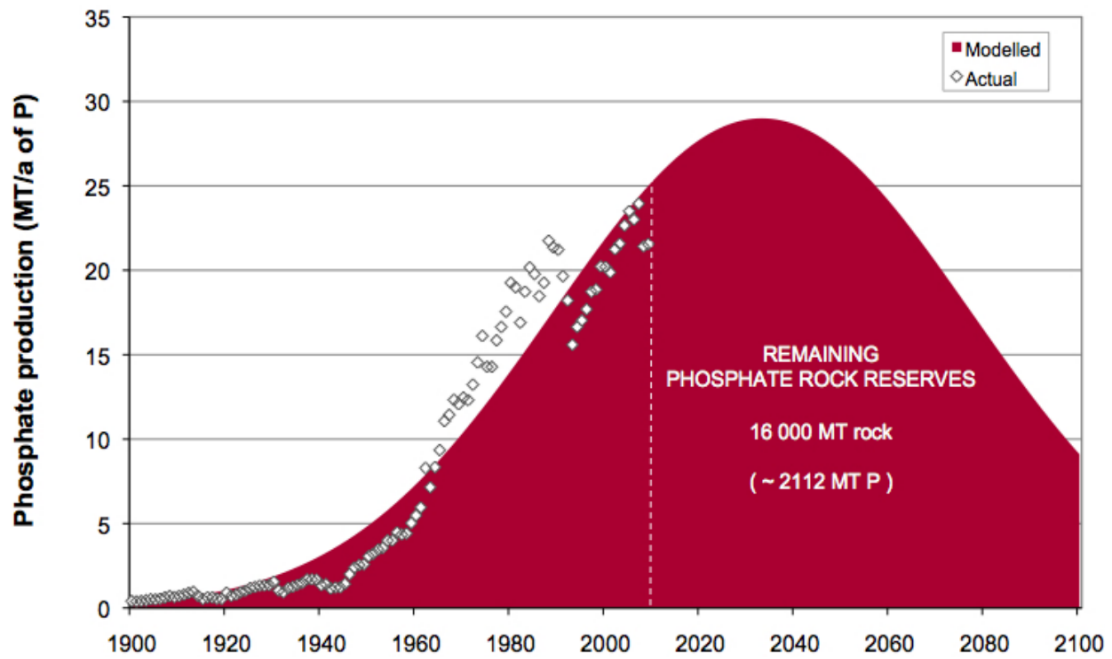
Humans acquire P by consuming plant-and animal-based food. Livestock obtain phosphorus from feed, fodder, grazing, and supplements. Plants in turn obtain phosphorus from soil - their roots draw dissolved phosphorus from soil solution (Johnston, 2000). Soil phosphorus is either naturally derived from weathered bedrock or is added through fertilizers, manures, and organic residues. Growing concern exists regarding avoiding P depletion and mitigating against environmental damage. A finite resource, the world's economically useful P is mainly obtained from geological reserves of phosphate rock. Approximately 80% of these reserves are localized in Morocco and its disputed territory, the Western Sahara (Cordell et al., 2009) (**Figure 1.2**). Other important reserves are in South Africa, Syria, Algeria, Jordan, USA and China (Syers et al., 2011). Due to the lack of an atmospheric component in the P cycle, the availability of P in a terrestrial ecosystem depends almost exclusively on the original soil P content and anthropogenic inputs (Delmas et al., 2015). Large amounts of P contained in fertilizers have been mobilized to raise soil fertility in support of the Green revolution. During the last 75 years, agricultural demand has increased global P mobilization by roughly fourfold (Falkowski et al., 2000; Villalba et al., 2008). A sizable amount of P has ended up in natural waters, causing costly eutrophication problems (Bennett, 2001; Smith and Schindler, 2009).



**Figure 1.2:** Breakdown of phosphorus rock reserves by country, indicating both market concentration and how reported estimates have changed over time. In 2013, most reported reserves were controlled by Morocco, China, Algeria, Syria, Jordan, and South Africa. Data source: USGS Phosphate Rock Mineral Commodity. Summaries 1996–2013 ([http://minerals.usgs.gov/minerals/pubs/commodity/phosphate\\_rock](http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock)). After Cordell and White, 2014

The mined P is used predominately to produce P fertilizers, with the remaining being used in cattle-feed supplements, food preservatives, detergent additives and industrial cleaning agents (Elser and Bennett, 2011).

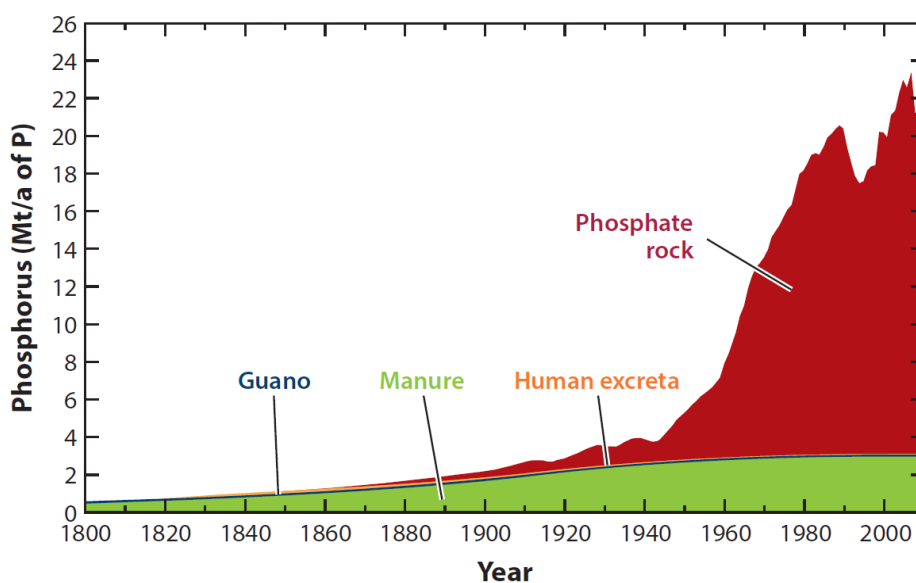
Owing to the increased demand for food and changing diets; which is likely to include more animal products, the demand for P fertilizers is expected to accelerate in the near future (Matsubae et al., 2011; Neset and Cordell, 2012). Cordell et al. (2009) predicted a phosphorus peak in approximately 2033, based on the P reserve estimates by the United States Geological Survey (USGS) in 2009 (**Figure 1.3 top**). Due to the rapid depletion of the known P reserves with easy accessibility and high grade (Cordell and White, 2011), the future P resources will certainly be more costly to extract and of lower quality. This will lead to geopolitical stresses and have remarkable implications for farmers and food security, such as the 800% price spike (**Figure 1.3 bottom**), for phosphate rock and other fertilizer products in 2008 (Cordell and White, 2014).



**Figure 1.3: (top)** Predicted peak in Phosphorus production by 2033, derived from US Geological Survey and industry data. Source: Cordell and White (2011). **(bottom)** Phosphate rock commodity price for the period 2006 – 2013, indicating the 2008 price spike at US\$431/tonne. From Cordell and White, 2014. The price of a tonne of phosphate rock averaged at around US\$105 in June 2019

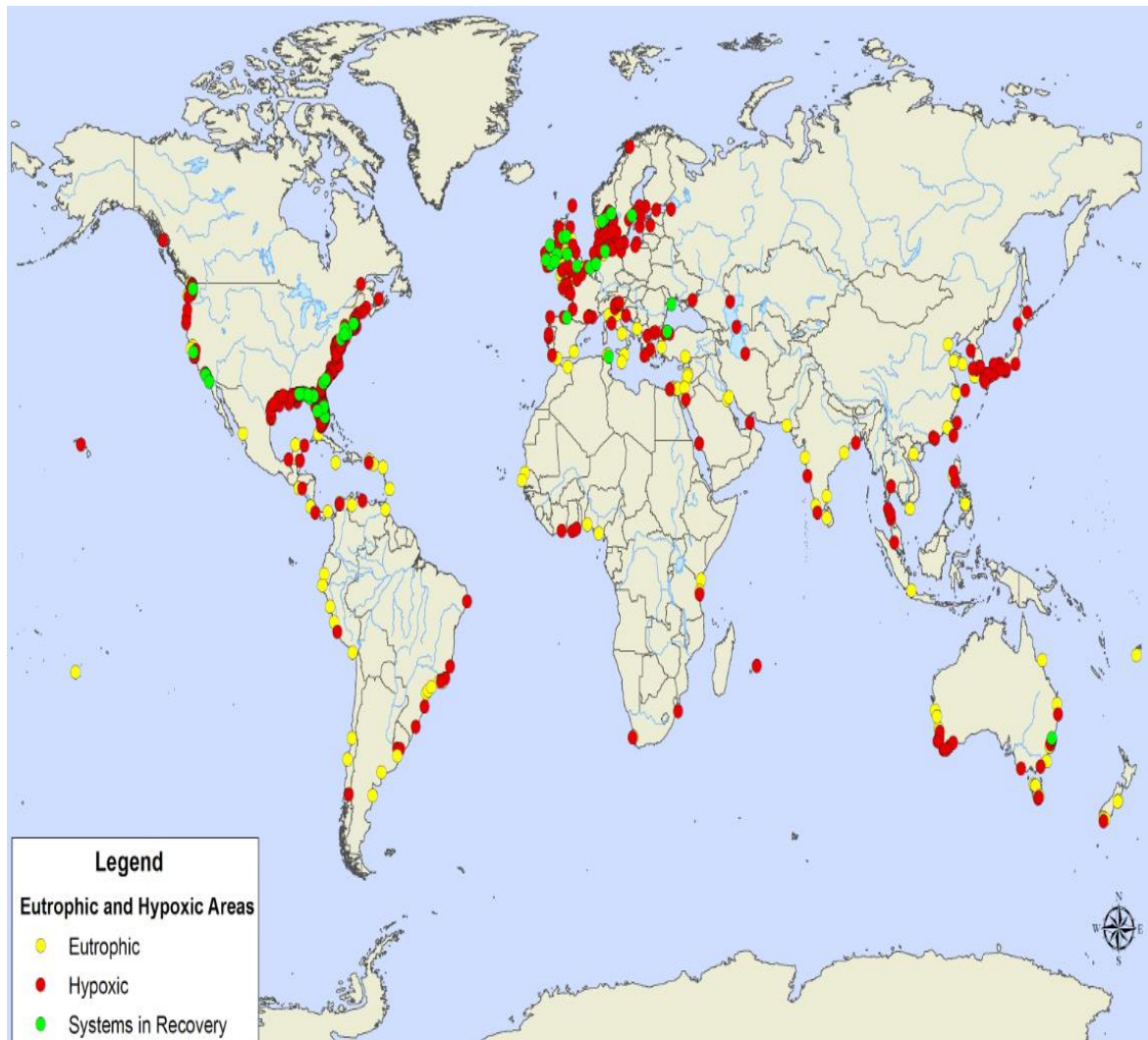
The average price of the ore was 2.34 times higher in 2009 than it was in 1993 (Matsubae et al., 2011). In response to growing phosphate demand, several producing countries have taken measures to restrict the export of phosphate rock in order to ensure sufficient availability of phosphate to meet their own future needs. For example, China shocked the world in 2008 by suddenly imposing a 135% export tariff on phosphate rock to discourage exports and protect domestic supplies (Fertil. Week., 2008).

The United States and China are each estimated to have a 30-year domestic supply of minable phosphate (NSF, 2015). Thus, in 2050, the world’s two largest economies and military powers are both projected to be running short of affordable supplies of domestic P for fertilizer and internal food production going by the current trend of P extraction and consumption (**Figure 1.3 top; Figure 1.4**). Competition for exports of North African phosphate is then expected to become quite significant (Cordell et al., 2009; Cordell and White, 2014). As Europe, just like Japan (Matsubae et al., 2011), does not have significant minable deposits of phosphate rock and has recently labeled this substance a “critical material” (EC, 2014), it too will be competing for the dwindling supply of this resource (Cordell et al., 2009). Imagining a future in which a resource so critical to the survival of billions of people could be disrupted has prompted increased attention to ensuring P sustainability (NSF, 2015).



**Figure 1.4:** Historical sources of phosphorus for global fertilizer use, including guano, excreta, manure, and phosphate rock (1800–2010). Cordell and White, 2014





**Figure 1.5:** World hypoxic and eutrophic coastal areas (WRI, 2008). This map identified 415 eutrophic and hypoxic coastal systems worldwide. Of these, 169 were categorized as hypoxic areas, 233 were areas of concern and 13 were systems in recovery. According to the Millennium Ecosystem Assessment, over the past 50 years, nitrogen flux had doubled and phosphorus had tripled, and these cumulative changes were and are still devastating coastal areas around the world (WRI, 2008)

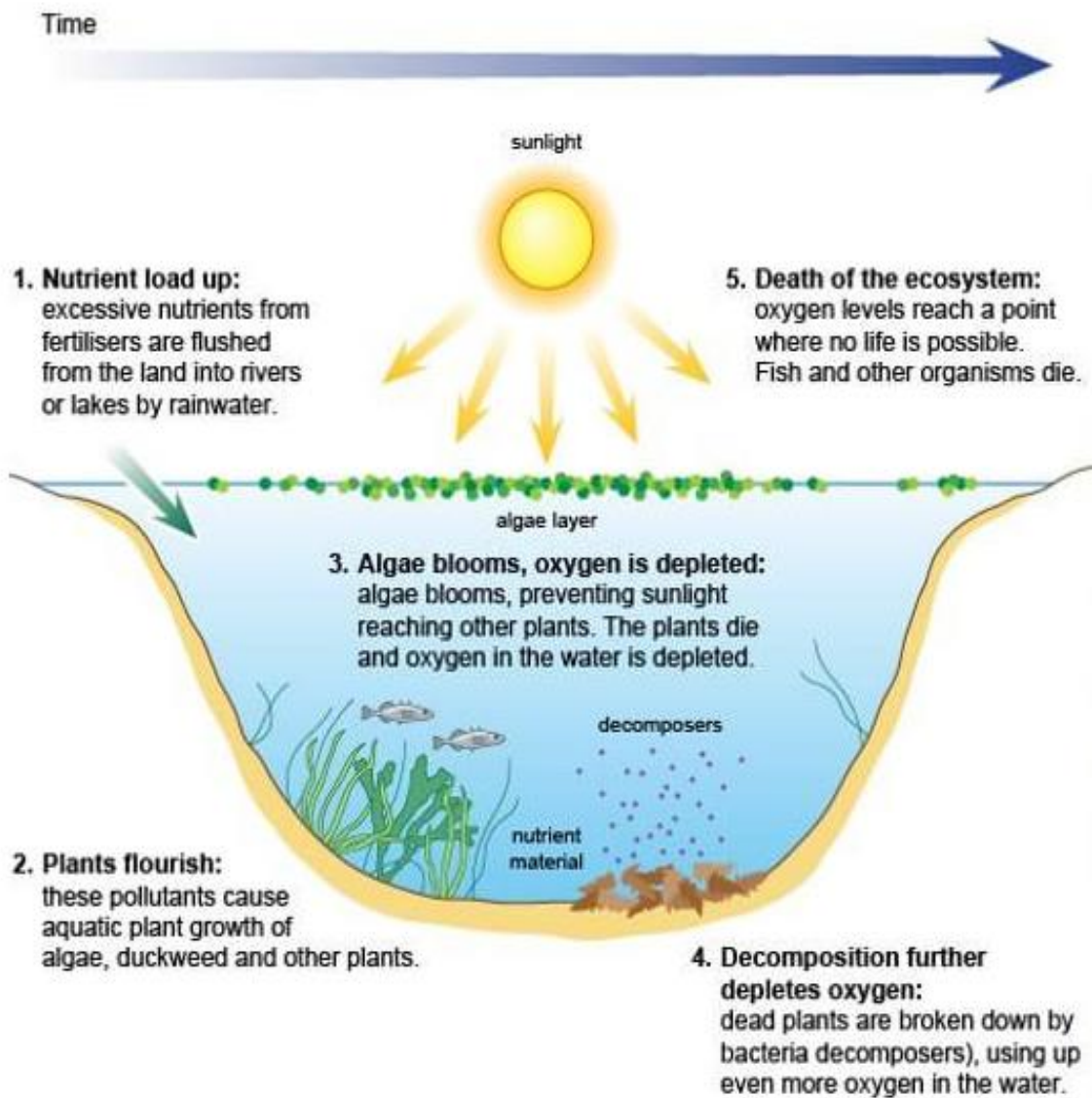
Generally, while the concept of “peak phosphorus” is still controversial, with time estimates varying from decades to centuries, the undisputed central and strategic role for P in food security calls for accelerated innovation in how P is acquired, deployed, and cycled in the human environment (Syers et al., 2011). It is important to note that concerns about P sustainability are not confined to issues of continued supply.

Sustainability concerns are growing increasingly acute because the discharge of P from point (municipal wastewaters) and non-point (agricultural sources including fertilizer leaching, soil erosion, and manure leaching) sources deliver large, unwanted quantities of this nutrient to inland and coastal waters. Once there, this anthropogenic P contributes to algal blooms (eutrophication) and exacerbates the spread of dead zones (Diaz and Rosenberg, 2008) (**Figure 1.5**).

## **1.2 A brief history of eutrophication in water bodies**

Eutrophication is a scientific term that describes algal blooms and associated problems that are caused by the response of natural waters to excessive inputs of nutrients (Schindler et al., 2016). **Figure 1.6** depicts the sequences resulting in eutrophic waters. Impaired water quality as a result of nuisance algae blooms is a global and growing problem, limiting water resources for drinking, domestic use, food production and recreation, as well as harming ecosystems. Eutrophication and climate change are one of the greatest challenges facing humanity. The effects of higher water temperatures under global warming act in concert with increasing nutrients, to paint a bleak future for a problem that is already extreme (Schindler et al., 2001). The scientific study of algal blooms dates from the earliest days of limnology (the study of inland waters), where by Limnologists used quantitative methods to observe increases in the size and duration of algal blooms in Lake Zurich, Switzerland as early as 1890 (Schindler and Vallentyne, 2008). The term eutrophic, derived from Greek meaning rich in food, was first applied to lakes with algal blooms by reknown Swedish botanist and limnologist; Einar Naumann in the early years of the 20<sup>th</sup> century (Schindler et al., 2016). The term eutrophication was coined to describe the process by which lakes become nutrient enriched, which was believed to occur naturally as lakes slowly filled with sediment, concentrating nutrients in less and less water (Schindler et al., 2016).

The causes of eutrophication were still a mystery until the mid-20<sup>th</sup> century. Public concern regarding the deterioration in recreational and drinking water quality, as a consequence of culturally accelerated eutrophication prompted several studies (Pearsall, 1921).



**Figure 1.6: The process of eutrophication**

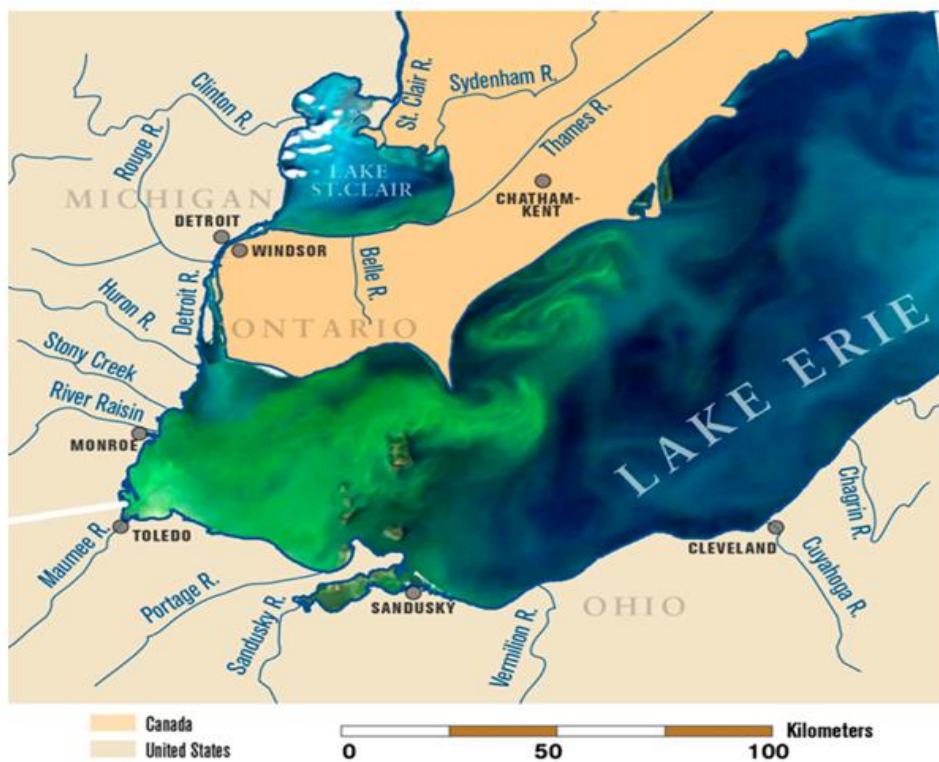
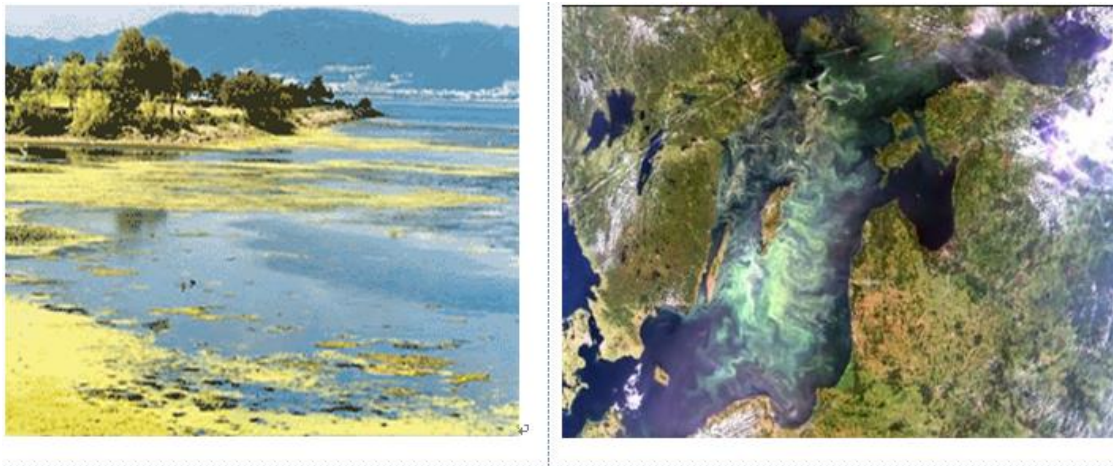
<https://www.pmfias.com/water-pollution-biological-oxygen-demand/> (accessed on 22 July 2019)

This led to the development of a number of quantitative relationships, between selected indices of the respondent plant biomass and selected representations of the availability of nutrients to primary producers, including studies by Sakamoto (1966), Lund (1970), Dillon and Rigler (1974).

By relating the chemical composition of algae with water chemistry, limnologists were able to conclude that the problem had something to do with nutrient enrichment (Vollenweider, 1968).

The nutrients with the highest ratio of concentration in algae relative to concentration in lake water were suspected to be the main drivers, which led to an early focus on P, C and N (Schindler et al., 2016). Later studies suggested that the abundance of trace elements, and even major ions also might play a role (Beeton, 1965; Chapra et al., 2012). In 1971, the International Joint Commission (IJC) recommended control of phosphorus input as the most likely way to decrease eutrophication in the Great Lakes (IJC, 1971). This recommendation was subsequently adopted for reducing eutrophication in other lakes in Europe, North America, and other developed countries. This early choice of P regulation was based largely on; the extensive review of the eutrophication problem by Richard Vollenweider (Vollenweider, 1968), findings from whole lake experiments (Schindler, 1974) and the reported restoration of Lake Washington (Edmondson, 1970).

Despite the noted recovery of several lakes from eutrophication owing to stringent measures undertaken to reduce the TP loads over the years to the set limits, algae blooms have re-emerged in some lakes, most notably in Lake Erie, USA and Lake Winnipeg, Canada (Michalak et al., 2013; Baker et al., 2014). **Figure 1.7** shows the extent of algal blooms in selected areas around the world. During a previous bloom in 2014, 500,000 people living near Lake Erie were ordered not to drink domestic tap water, because it contained levels of hepatotoxins produced by the cyanobacterium *Microcystis* that were 2.5 times higher than the World Health Organization's safe standard (Michalak, 2016; Wilson, 2014). Lake Winnipeg has experienced a steady increase of blue-green algae growth over the past 30 years. These blooms affect around 5.5 million people that rely on the health of the lake. It also affects the tourist and fishing industries of the lake, which combined account for \$125 million per year (Environment Canada, 2011). The Lake Winnipeg algal blooms are considered the worst algae problem of any large freshwater lake in the world. In Europe, the Baltic Sea receives an excessive amount of P and N from surrounding regions, which manifests itself in nuisance algal blooms, turbidity and oxygen depletion in bottom waters. The gulf of Finland is one of the most heavily loaded sub-basins in the Baltic Sea, with the area-specific N and P loads being two to three times higher than those of the entire Baltic Sea (HELCOM, 2015).



**Figure 1.7: (top left):** Lake Biwa, the largest lake in Japan during summer time showing overgrowth of aquatic plants. Source: Newsletter and Technical Publications: Lakes and Reservoirs vol. 3; Water Quality: The Impact of Eutrophication: Water Quality management and Eutrophication in Some Lakes Around The World; Lake Biwa. United Nations Environmental Program; **(top right):** Extensive surface blooms of cyanobacteria in the Baltic Sea (credit: NASA, GES Distributed Active Center, MODIS 2005-07-11, processed by the Oceanography unit); **(bottom):** MODIS satellite Image of Lake Erie on September 3, 2011, overlaid over map of Lake Erie tributaries. This image shows the bloom about 6 weeks after its initiation in the western basin. On this date, it covers the entire western basin and is beginning to expand into the central basin, where it will continue to grow until October. Michalak et al., 2013 adapted according to NOAA coast watch

Algae blooms have also been persistent in Lake Biwa, Japan's largest freshwater lake especially during summer, and red tides are also common in coastal areas of Japan occurring to a great extent in Mikawa bay (Suzuki, 2001).

### **1.3 Phosphorus: A tale of deficiency and excess**

Globally, water and food security depend upon sustainable P management (Elser and Bennett, 2011). The river catchment scale provides an ideal unit of focus for studying sustainable P practices, and analytical developments in in-field measurements have promoted interest in short-term temporal dynamics (Haygarth et al., 2012). In many cases, intended reductions in catchment P fluxes have not occurred as immediately or desired by catchment and water quality managers. This is increasingly recognized to result from the legacy effect which is associated with the build-up of P in the topsoil, and the complex release patterns in river catchments (Sharpley et al., 2013). Accurate quantification of these effects in response to human intervention at catchment scale is currently a big challenge (Jarvie et al., 2013).

Fertilizer use has increased at unprecedented rates following the Second World War, to meet the food demands of a rapidly growing population, with P a vital element for agricultural productivity globally (Haygarth et al., 2014). Over the past decades, the fertilizer industry, governmental institutes, and research organizations have actively supported more efficient fertilizer application practices including recycling of organic matter containing P, and using organic farming techniques to optimize soil conditions to increase soil P availability for plants (FAO, 2008). Nonetheless, much of the world's cropland especially in developed nations, is still subjected to P surpluses above local needs, due to the historical over-application of P onto soil (MacDonald et al., 2011). This has led to P-impairment of surface waters through soil erosion and leaching, and yet areas of P deficit limiting production abound (Haygarth et al., 2014). The excessive presence of bioavailable P in aquatic ecosystems due to human acceleration of the P cycle has deleterious consequences for these ecosystems, because P together with nitrogen and to some extent carbon stimulates the growth of phytoplankton, algae and aquatic plants; resulting in eutrophication (Smith and Schindler, 2009).

Currently, there is a general consensus that P is the limiting nutrient for eutrophication in freshwater ecosystems (Schindler et al., 2008; Schindler et al., 2016), while the coastal water eutrophication is limited by nitrogen (Paerl et al., 2016). It is thus vital to limit P losses to waters, so as not only to prevent the future P crisis by keeping the P cycling in the terrestrial ecosystem but also to secure human and aquatic ecosystem health by mitigating the eutrophication of water bodies.

#### **1.4 Pathways of P to surface waters**

Phosphorus is discharged to the aquatic ecosystem from essentially two sources classified as; point and non-point (diffuse) sources (**Figure 1.8**). Point sources derive from urban and industrial wastewater treatment plants, and diffuse sources mostly from agricultural landscapes, either through erosion of P-rich soil particles during overland flow, or P leaching during drainage and subsurface water flow (Chardon and Schoumans, 2007; Heathwaite et al., 2005). The implementation of targeted measures such as; complete exclusion of P in detergents, precipitating P in sewage water treatment plants, has resulted in the reduction of P losses from point sources in many developed countries (Collins et al., 2014).

However, eutrophication is still occurring in many lakes and estuaries in these countries, indicating a permanent contribution from diffuse sources that transfer P from agricultural soils to surface waters (Jarvie et al., 2017; Scavia et al., 2014; Schoumann et al., 2014). Managing agricultural diffuse P loss is difficult because of the large spatio-temporal variations in water pathways and soil erosion processes and the complexity of P forms in both soils and waters; that is dissolved organic and inorganic P, colloidal P, and particulate P. It is estimated that agricultural P loss contributes greater than 50% of the TP load to coastal waters in several developed countries (Alexander et al., 2008). Cases of extreme impairment often lead to disproportionate human and ecosystem impacts. The costs can be huge, it is estimated that more than US\$4 billion are lost each year in the United States alone as a result of harmful algal blooms (Kudela et al., 2015).



**Figure 1.8:** Diffuse sources of phosphorus. **(a):** Wastewater treatment plant. **(b):** Runoff from agricultural fields and entrained soil discharged to rivers

## 1.5 Phosphorus in soils and sediments

### *1.5.1 Phosphorus in soils*

The primary P mineral in most young soils is apatite (calcium phosphate), which is slowly weathered and transformed into secondary P minerals and organic P forms during soil development (Tiessen et al., 1984; Walker and Syers, 1976). Secondary P minerals in non-calcareous soils are associated with aluminium (Al) or iron (Fe), whereas secondary calcium (Ca) phosphates dominate in calcareous soils (Smeck, 1985). The P content of a typical soil profile is relatively high in the surface horizons (Ap in agricultural soils) and decreases to a profile minimum in the subsurface (B) horizon (Peltovuori, 2007). In agricultural soils, fertiliser and manure applications, when associated with long-term positive P balances, increase the P content in the Ap horizon (Baker et al., 2017). The P surplus is mainly recovered in the fractions of Al- and Fe-bound and organic P (Peltovuori, 2007). Negligible amounts of readily soluble P are found in subsoil horizons, indicating plant uptake from the B horizon, but vertical stratification of soil P results in leaching of P to ground water and also in surface runoff (Baker et al., 2017; Kleinman et al., 2011).

Most easily soluble P added to soil as fertiliser or manure is rapidly adsorbed by soil particles. Transformation of Fe and Al into oxides, hydroxides or oxyhydroxides creates new functional groups for P adsorption.



Phosphorus is bound to short-range-ordered (hydr)oxides of Al and Fe, to the edges of clay minerals, and in Al and Fe complexes of organic matter (Walker and Syers, 1976). Most importantly, a specific ligand-exchange reaction happens on the (hydr)oxide surfaces, in which  $-\text{OH}$  or  $-\text{OH}_2$  coordinated with a metal cation in the solid phase is replaced by phosphate ion ( $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ) (Laakso et al., 2016). The maximum number of phosphate ions that may be retained is limited by the number of sorption sites responsible for maintaining equilibrium between soil pore water P and solid phase P in fertilised soils (Barrow, 1983).

The number of P sorption sites (Al and Fe (hydr)oxides) already occupied by P is described by the degree of P saturation concept, and indicates the potential desorbability of soil P. The increased saturation of Al and Fe (hydr)oxides due to former farming practices of applying P in surplus have resulted in increased plant availability of P in surface soils, but also increased P loss via leaching (Daniel et al., 1998). This could most likely be the case for some agricultural catchment soils in Japan and other developed countries where intensive agriculture with fertilizer application is prevalent. For example, a recently published large survey of the 35-year trend (1974–2009) in soluble nutrients (of pH 4.65 ammonium acetate-extractable P) in cultivated Finnish soils generally showed increasing concentrations of agronomic soil test P (Keskinen et al., 2016).

Soil weathering causes dissolved phosphate from primary minerals to (i) precipitate with some cations and lead, for example, to the formation of calcium phosphate in alkaline soils (Beck and Sanchez, 1994); (ii) form biologically active organic compounds that remain as organic P in soil (Dodd and Sharpley, 2015). Transformations between inorganic and organic forms of P are governed by factors affecting its mineralization and immobilization (e.g., microbial activity, moisture, physico-chemical and mineralogical soil properties) (Shen et al., 2011). The dissolution of minerals or phosphate fertilizers, and the mineralization of organic components in soils results in the production of different anionic species (Lindsay et al., 1989), that are protonated to a variable extent depending mainly on pH (Hinsinger, 2001). Inorganic P species derived from orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) such as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are preferentially adsorbed by plants (Fink et al., 2016).

The degree to which P is adsorbed, desorbed and mineralized, determines the extent P remains in soil solution (Hinsinger, 2001). Soil test methods that estimate plant availability of soil phosphorus are generally used for relating P in runoff to soil P content. Alternative approaches that reflect soil P release to surface and subsurface runoff include water extractable P, Fe-oxide P and P sorption saturation of the surface 5cm of soil (Kleinman, 2017; Sharpley et al., 1998; Breeuwsma and Silva, 1992). Hedley et al. (1995) presented various tests that have developed in several countries to suit the forms of P present in their agricultural soils. These include; Mehlich, Olsen, Bray 1, and Bray 2 tests. The form of soil P extracted by each test is determined by its solution pH and the reaction of ions present in the extractant with sorbed or mineral P (Kleinman, 2017).

### ***1.5.2 Phosphorus forms in sediments***

Sediment has been defined as any particulate matter/material that can be transported from land to natural waters (Förstner, 2004), and can comprise of clay (< 2 µm), silt (2-60 µm), sand (60 µm – 2 mm), pebbles (2 – 60 mm), cobbles (60 – 256 mm) and even boulders with sizes exceeding 256 mm (Gimbert et al., 2007). Soils are parent materials for suspended particulate matter or suspended sediments (SS) that ends up in recipient freshwater systems. In agricultural catchments, sediments found in adjacent watercourses are comprised of soil material eroded mainly from topsoils of cultivated land, transported by surface and subsurface runoff and finally settled to the bottom of receiving waters. Phosphorus amounts and fractions in the sediment are largely determined by their parent material along with the biogeochemical environment during runoff, settling and during residence in the bottom sediments (Hoffman et al., 2009; Kleinman et al., 2011; Kröger et al., 2013). The vertical distribution of P in lake sediments often shows a decreasing concentration with sediment depth (Holtan et al., 1988). A high P concentration in surface sediment is due to recently settled material and possibly due to a delay in mineralization because of an increased sedimentation rate and reduced biological activity introduced by low oxygen supply (Holtan et al., 1988).

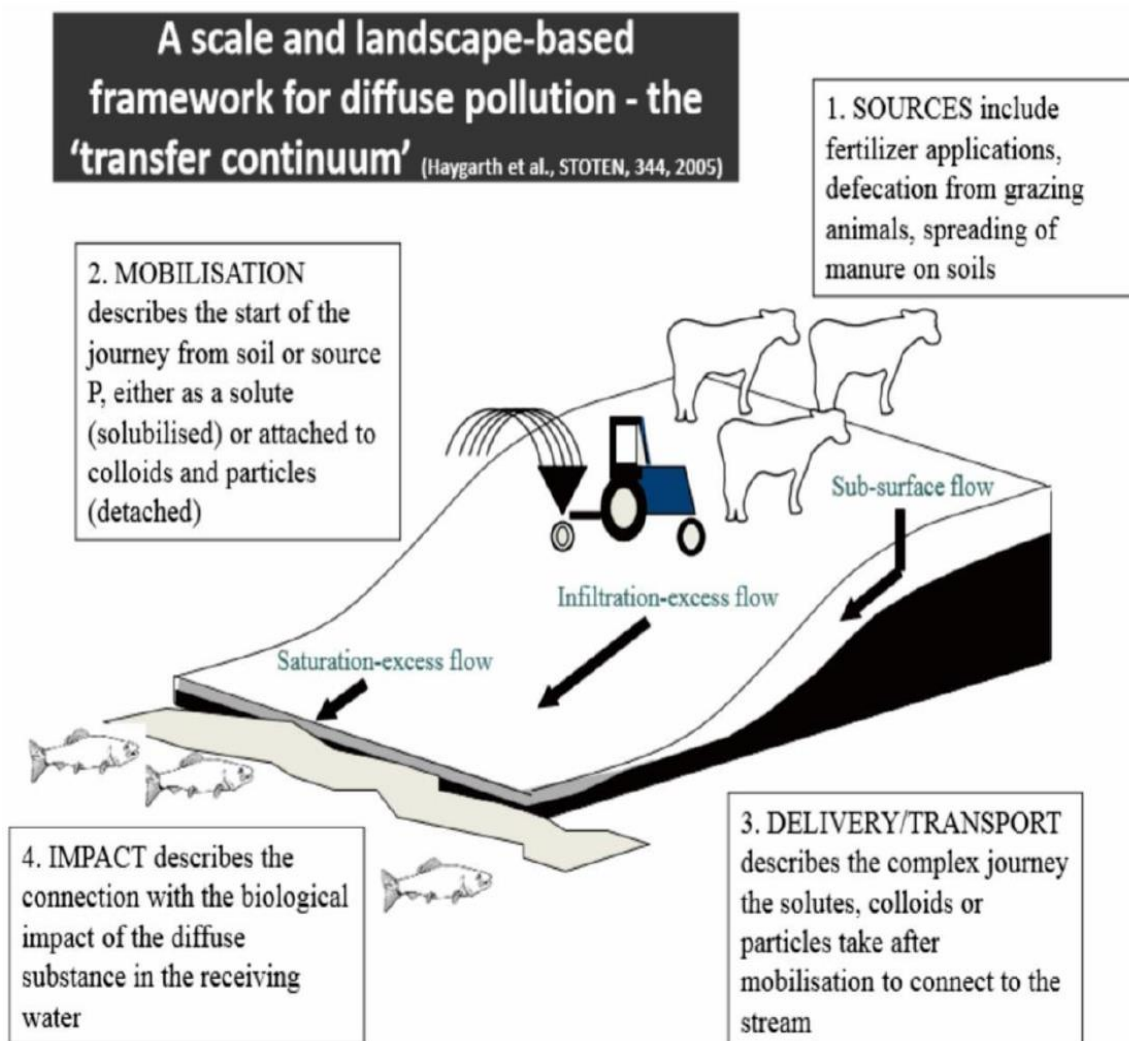
Phosphorus can be held in solid phases through sorption and/or precipitation with mineral phases (Fe, Mn, Al, and Ca phases) as well through sorption and incorporation within organic matter (OM) (Gottselig et al., 2014, 2017; Yan et al., 2016).

The seminal “Mortimer experiments” (Mortimer, 1942) and subsequent field studies have advanced a long-standing paradigm which postulates that P release to the aqueous phase is prevented under oxic conditions, whereas anoxic conditions promote such a release (Hupfer and Lewandowski, 2008). Of the inorganic P fractions, Al-P is highly affected by pH and Fe-P by redox conditions. Calcium bound P is considered rather inert in sediments; nevertheless, the dissolution of an apatite structure occurs by decreased pH owing to CO<sub>2</sub> production generated by OM decomposition (Eckert et al., 1997). The dissolved P from indices of Al and Fe oxides, along with the metal ions itself, tend to diffuse along concentration gradients from deeper sediment layers to the sediment surface and the sediment-water interface, where higher redox potential (Eh) and presence of soluble P favour its binding to metal phosphates (Holtan et al., 1988). Phosphorus cycling in aquatic ecosystems is related to carbon (C), Fe and sulphate (SO<sub>4</sub>), as microbial degradation of OM in anaerobic sediments, such as in constructed wetlands, is coupled to Fe oxides and SO<sub>4</sub> as common electron acceptors (Lehtoranta et al., 2015).

Fe oxides are reduced by two mechanisms; *via* microbial dissimilatory Fe reduction, where microbes use the oxides as electron acceptors in respiration, and *via* chemical reduction by sulphides (H<sub>2</sub>S, HS<sup>-</sup>) formed in microbial SO<sub>4</sub> reduction (Reddy and DeLaune, 2008). Microbial and chemical reductions of Fe have crucially different consequences for Fe cycling. When Fe oxides are directly reduced by microbial dissimilatory reactions, the highly soluble Fe(II) produced is able to diffuse upward in the sediment pore water, and will be oxidised when encountering the oxygenated zone. Newly precipitated Fe oxides will be formed as a result, and are capable of capturing high amounts of dissolved P (Baken et al., 2015). When organic C availability increases due to loading-induced primary production (eutrophication), Fe reduction gives way to SO<sub>4</sub> reduction. The end products; solid Fe sulfides (FeS, FeS<sub>2</sub>), are permanently buried under anoxic conditions, and the ability of sediments to retain P is drastically reduced (Cooper et al., 2015; Lehtoranta et al., 2009; Roden and Edmonds, 1997).

## 1.6 Phosphorus propagation processes in catchments

The P transfer processes in catchments also referred to as the “Phosphorus transfer continuum” highlights the interdisciplinary nature of P transfer science (Haygarth et al., 2005). The P transfer continuum especially in agricultural landscapes assumes that the overall process can be categorized into four steps namely; sources, mobilization, delivery and impact (Figure 1.9).



**Figure 1.9:** Phosphorus transfer continuum in agricultural landscapes. Sourced from Haygarth et al., 2005.

### ***1.6.1 Sources***

The input of P to soil creates the potential for an increase in transfer to the wider environment. The P sources can be of natural (indigenous soil-P mineralization and atmospheric deposition of P-rich micro-particles) or anthropogenic (fertilizers and manure applied to the soils) origins. Because the natural background concentrations of P in soils were generally low to sustain the burgeoning demand of farm produce, humans have applied fertilizers and imported animal feed to counteract the insufficient natural P concentration in soils. This application of P has been excessive in several regions resulting in the accumulation of P in soils, referred to as “legacy phosphorus” (Jarvie et al., 2013a; Sharpley et al., 2013).

### ***1.6.2 Mobilisation***

Mobilisation describes the processes by which P is separated from its sources in the soils, for example by solubilization under the action of chemical/biochemical processes or by the physical detachment of P-rich particles. Strong evidence exists supporting the assertion that the potential of P solubilisation (indicated by the P concentrations in soil solutions) generally increases with the increasing concentration of extractable soil P (McDowell et al., 2001). Owing to this, agronomic P tests which were originally designed to estimate the fertilization requirement of soils, are currently often used in environmental risk assessment tests, as they have the capacity to evaluate the P solubilization potential in soils (Jordan-Meille et al., 2012; Wall et al., 2013). The degree of P saturation (DPS) provides another technique to evaluate the risk of P solubilization in soils, and is currently used as a regulation and management tool in several countries (McDowell et al., 2002; Schoumans and Chardon, 2015). The DPS can be calculated by adsorption isotherms or by chemical extraction of Fe and Al oxides, which are considered as the two main P-sorbing phases in soils (Renneson et al., 2015). The physical detachment of soil P-rich particles is regulated by the susceptibility of soils to be eroded, either via surface runoff or through soil macropore water flows.

### ***1.6.3 Delivery***

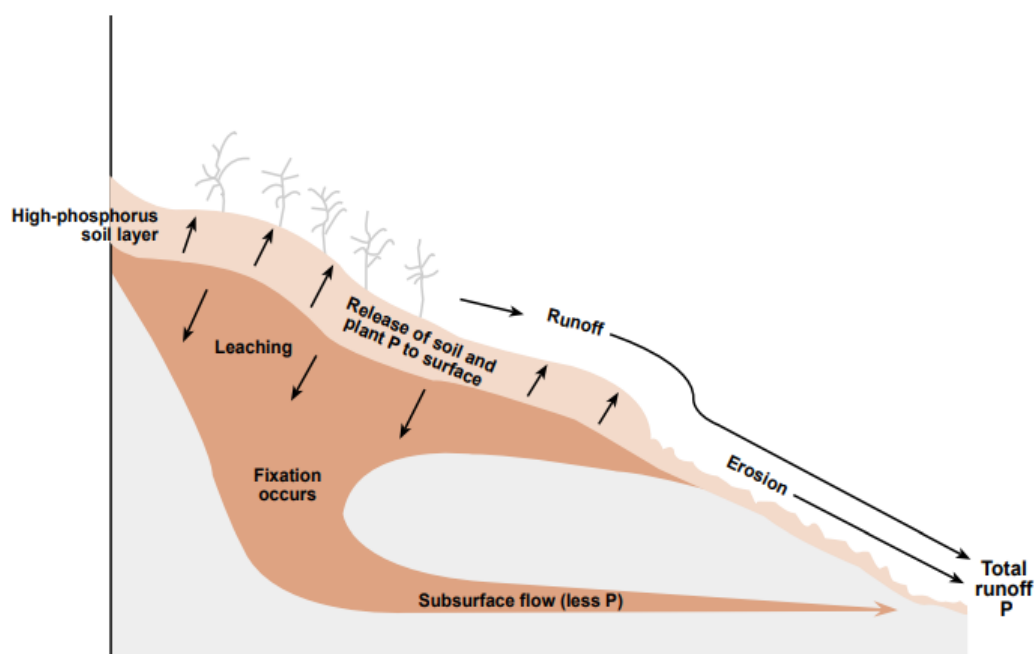
The delivery of the mobilized P to water bodies can only occur if there is hydrological connectivity between the P source in the catchment and the receiving water body. Overland flow caused by saturation excess, a situation generally confined to high-magnitude and high intensity rainfall events, was for long considered as the dominant pathway of P transfer, mobilizing both particulate and dissolved P forms (Boardman, 1990; Fraser et al., 1999). More recently, however, contribution of subsurface transfer (natural or due to artificial drainage) of dissolved and colloidal P was acknowledged to be an important transfer pathway in agricultural catchments (Mellander et al., 2016; van der Salm et al., 2011). The soil properties, groundwater level, the presence of tile drains, and topography are all factors that control this subsurface transfer. These factors vary spatially (field, hillslope, and catchment) and temporally (due to temporal variations in water table levels), hence making the quantification and scaling-up of this P transfer pathway very complex (Haygarth et al., 2012). The complexity is even compounded due to the chemical nature of P, which can be adsorbed onto soil matrix and thus become retained during transport, a process which can strongly vary both in space and time (Haygarth et al., 2005).

### ***1.6.4 Impact***

The impact of P transfer refers to the perturbation that P inputs cause in a receiving water body. Presently, some aspects of the P-associated deterioration of aquatic environment (including eutrophication) can be identified. Nevertheless, more assessment is needed to quantify the exact linkage between source types and locations, transfer processes and pathways and impacts (McDowell et al., 2004). There is an increasing impetus to track P inputs backward, from delivery through mobilization to source locations of P in catchments, to fully link the processes of P release especially from agricultural catchments to the impacts of non-point P losses in water bodies (Haygarth et al., 2005).

## 1.7 Phosphorus transport in runoff water

The term “runoff” encompasses both surface runoff and subsurface flow, which are two dynamic and closely related processes. For example, surface or overland flow can infiltrate into a soil during movement down a slope, move laterally through the soil, and reappear as surface flow. The main factors controlling P loss in agricultural runoff are shown in **Figure 1.10**. The first step in the movement of P in surface runoff is its release from a thin (less than 5cm) surface layer of soil and plant material (McDowell and Sharpley, 2001a). Phosphorus often accumulates to higher levels in this surface soil layer than elsewhere in the soil. The remaining water percolates through the soil, where fixation by P-deficient subsoils generally results in low dissolved P concentrations in ground water. Phosphorus forms associated with P losses by runoff water are usually operationally defined as either dissolved or particulate P by filtering a water sample through filters of different sizes. Dissolved P can be divided into reactive (DRP) and unreactive P (DUP), depending on its reactivity with reduced molybdate reagent.

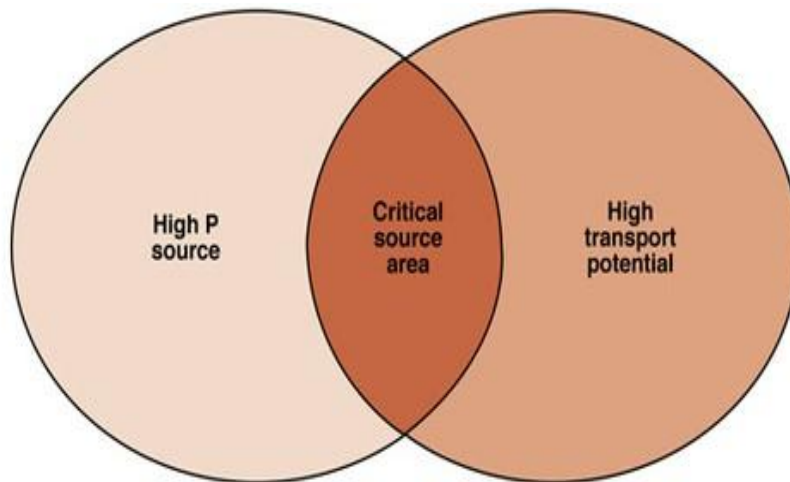


**Figure 1.10:** Phosphorus can be lost by erosion or released from soil and plant material to surface and subsurface runoff water (adapted from Sharpley and Beegle, 2001)

DRP is readily available for biological utilization by algae (Ekholm, 1994) and its role in the eutrophication of receiving waters has been emphasised (Baker et al., 2014). Dissolved unreactive P is thought to primarily contain organic P compounds and soil colloids that are able to pass through the filter (0.45µm pore size), and is also ultimately algal available. Particulate P (PP) is defined as P bound to suspended mineral particles and organic matter in runoff water. The PP fraction likely represents the less refractory part of the total suspended sediment; that is, the more labile organic and inorganic part of the solid phase (e.g plant debris and acid soluble minerals such as the less crystalline iron oxides/hydroxides and calcium carbonate that sorb and co-precipitate P) (Jarvie et al., 2010). Particulate P can account for a significant fraction (up to 69%) of bioavailable P in runoff from clay soils (Uusitalo et al., 2000), as P is desorbed from the suspended soil material trying to maintain the new equilibrium concentration.

Thus, decreasing the load of suspended particles and preventing them from reaching the watercourses is critical from the eutrophication viewpoint. However, controlling soil erosion may not be sufficient in some areas with high sulphate concentration in receiving waters. Ekholm and Lehtoranta, 2012, suggested that since eroded soil contains Fe oxides, erosion control could result in decrease of Fe oxides which usually bind P, and in the presence of anoxic conditions, sulphate reduction is enhanced hence resulting in the release of bound P. Usually quick and episodic P transport events can substantially contribute to annual P transport within catchments. The majority of annual P losses can occur from a small portion of a land area (critical source area) and only during a few severe storm events (Sharpley et al., 1999; Gburek et al., 2000), or during winter rains and spring snowmelt (Turtola et al., 2007) (**Figure 1.11**). Since P loading is event-driven, mitigation measures to reduce P should be able to capture P that is lost during these types of events. A further challenge may be brought about by projected climate change, with increased rainfall in winter, but lower spring flow peaks because of higher winter temperatures (Ockenden et al., 2016; Arnell, 1999). Erosion rates are expected to increase due to increased winter rains, especially if soils are left without plant cover over winter. Phosphorus losses from agricultural soils can be controlled either at the sources or during transport.





**Figure 1.11:** Critical source areas for P loss from a watershed occur where areas of high soil P and transport potential coincide (adapted from Sharpley and Beegle, 2001)

Reducing nutrient input has been suggested as the most cost-effective way to cut down the load into downstream areas experiencing eutrophication (Sharpley et al., 2013; Granstedt, 2000). This means that fertilization should be reduced to equal the P levels removed by the following crop, and further adjusted according to the current soil P status. Liming or reduced tillage are suggested for improving soil structure and aggregate stability, as they can increase P uptake by plants and concurrently prevent soil loss by erosive water forces (Tebrügge and Düring, 1999). In order to prevent eroded soil and P from entering water courses, efforts have been made to establish buffer zones, sedimentation ponds and wetlands.

### **1.8 Bioavailability of different P fractions and the influence of particulate organic matter**

Historically eutrophication studies have focused on assessment of total phosphorus flux in fresh water bodies. Eutrophication in aquatic ecosystems has been attributed has been attributed to P and macro-nutrients such as carbon (C) and nitrogen (N). There is increased consensus that P is the main limiting nutrient for algae, phytoplankton and cyanobacteria in freshwater ecosystems (Schindler et al., 2016), though N possibly limits aquatic growth in estuaries and other coastal areas (Pearl, 2016).

Phosphorus flux through river transport is the ultimate link in the continental land and ocean interaction, and may constitute a sensitive indicator of global change. Therefore, studies on the transport of P to oceans by the rivers can provide useful information not only for global P budgets, but also for nutrient management in the coastal waters (Howarth et al., 1995).

Previous studies have shown that concentrations and forms of riverine P vary greatly and have been related to human activities such as land use, population density, and chemical fertilizer application (Correll, 1998). For example, McKee et al. (2000) found that particulate phosphorus (PP) was the dominant form, accounting for more than 40% of TP transport during storm discharge; while Russell et al. (1998) reported that PP loads accounted for 26 – 75% of the annual TP transport in various rivers in Britain. In Japan, (Inoue and Ebise, 1991), found that 88% of P in runoff from rivers during high flow events was in particulate form, and that this fraction of P was an important factor contributing to eutrophication in the enclosed coastal sea. Nevertheless, the influence of human activity on riverine particulate P fluxes is poorly known (Howarth et al., 1995). Since PP in suspended sediment, brought by a river into a receiving water body, begins to revisit with the receiving water's DP and becomes bioavailable, it is necessary to re-estimate PP transport and evaluate the potential effect on algal growth.

Despite the world-wide use of Total P (TP) as a standard for assessing eutrophication levels, only some forms of P are available to algae (Ellison and Brett, 2006). Hence, bioavailable phosphorus (BAP) transported in runoff can accelerate surface water eutrophication (Ekholm, 1994; Baker et al., 2014). BAP represents orthophosphate that is potentially available for algal uptake and comprises P in dissolved (DP) and particulate (PP) forms. Dissolved P is mostly available for algal uptake; PP which encompasses P associated with sediment and organic material eroded during runoff contributes a variable but long term source of bioavailable PP (Sharpley et al., 1992; Oladeji et al., 2008; Poirier et al., 2012). PP discharged from diffuse sources such as agricultural or urban runoff, is thought to be rapidly transported to lakes or bays through rivers. The discharged PP includes BAP (Uusitalo et al., 2000), some of which dissolved by the time it reached its outlet bay or lake.

While some studies on BAP have in the past been conducted on lake tributaries of some developed countries, such studies are non-existent in rivers flowing into coastal bays of Japan which experience eutrophication.

In Japan, development of hypoxia has been confirmed in the inner part of almost every major bay on the pacific coast from Tokyo southward and occurs to a greater extent in Mikawa bay (Suzuki, 2001). The increased loading of nutrients in the rivers is what has led to proliferation of algal blooms in Mikawa bay. Nutrient from land area is loaded through two major rivers of Toyogawa and Umedagawa (Angarra et al., 2004), and other rivers in the adjoining catchments. A greater proportion of P is carried in suspended sediments (SS) along the rivers especially during rain events, and it is important to assess whether this P is available for algal growth. Furthermore, rivers flowing through contrasting land uses such as urban and agricultural areas contribute to the organic matter load. Few studies have assessed the influence of particulate organic matter on the resultant P bioavailability. This presents a significant gap since previous studies suggest that organic matter previously protected in soil micro-aggregates can be released as a result of physical stresses caused by drying and re-wetting at varying flow conditions (Blackwell et al., 2010), and the discharged organic matter ultimately ends up into river runoff. The varying amounts and bioavailability of DP and PP transported in different runoff events warrant the need for the accurate measurement of BAP to evaluate the impact of runoff on the biological productivity of surface waters.

The BAP content of runoff can be determined by algal culture tests commonly referred to as algal assays or bioassays (Miller et al., 1978; Ekholm and Krogerus, 2003). A bioassay quantifies either growth (assuming constant P stoichiometry) or uptake of P by the test organism, usually a P- starved planktonic alga, to estimate bioavailability. The bioassay technique provides a direct measurement of P taken up by the test algal species (DePinto et al., 1981), and is considered superior to other methods, though some bioassays take several weeks for algae to reach maximum growth. Bioassays are tedious, relatively expensive and imprecise, and this severely limits their adoption for regular monitoring.

Besides, few studies have addressed the mechanisms that transform unavailable P forms into those that can be directly taken up by algae, which makes it difficult to develop suitable procedures for algal availability testing (Ekholm et al., 2009). Thus, more rapid chemical extraction procedures which simulate the removal of P by algae have been used to allow for the routine determination of BAP (Dorich et al., 1980; Hegemann et al., 1983; Jarvie et al., 2002). Chemical extraction is a methodology used to estimate the bioavailability of PP in runoff. This methodology was originally developed for agricultural crops and soils (Chang and Jackson, 1957; Williams et al., 1967), and has now gained wide applicability in evaluating P speciation in river sediments. Chemically defined bioavailability is a sequence of extraction of P from particulate matter in an increasing order of extractions rigor that yields P fractions in a sequence of decreasing bioavailability. Chemical extractions that have been used to measure the particulate BAP (PBAP) of runoff include; NaOH (Logan et al., 1979), ion exchange resins (Hanna, 1989; Huettl et al., 1979), iron oxide filter strips (Dils and Heathwaite, 1998) and citrate-dithionite-bicarbonate (Logan et al., 1979; Jensen and Thamdrup, 1993). Further, various sequential extraction schemes have been developed to recover P bound to different metal elements in sediments (Ruttenberg, 1992; Hupfer et al., 1995; Gu et al., 2016). This approach however has been limited given that P fractions are operationally defined, implying that comparison between fractionation studies are difficult to interpret (Pettersson et al., 1988). Nevertheless, sequential extraction schemes remain one of the only suitable means for unraveling discrete mineral phases of P associated with soils or sediments due to the inherently low concentrations of P in these materials (Wang et al., 2013).

In several studies, single extraction using 0.1M NaOH extraction has been preferred for use in PBAP measurement based on the fractionation of phosphorus (Dorich et al., 1985; Ellison and Brett, 2006). Phosphorus extracted by this method is thought to be iron or aluminum bound amorphous phosphate substances (Williams et al., 1967; Sharpley et al., 1991; Reddy et al., 1998), and also P associated with humic and fulvic acids (Reddy et al., 1998).

Phosphorus extracted by 0.1M NaOH was also found to be significantly correlated with 2- and 14-day available P for algae, thereby indicating that this PBAP fraction could be used to estimate both short- and long-term available P in sediments (Dorich et al., 1985). Despite the single extraction method being the most commonly used method to recover PBAP, the extraction process takes a minimum of 17 hours, and this limits its wide application. Ultrasonic treatment of SS using 0.1M NaOH allows for rapid extraction of PBAP, and yields PBAP amounts comparable to those estimated by conventional methods (Ngoc et al., 2017). Overall, P forms differ in bioavailability and therefore differentially contribute to the risk of eutrophication. Thus, failure to account for PBAP can create uncertainty regarding eutrophication (van der Grift et al., 2018).

The fraction of PBAP is influenced by chemical processes like adsorption-desorption, precipitation-dissolution and reduction-oxidation reactions, which regulate the amount of dissolved inorganic P that is released into the water body and / or sorbed to particles (Ellison and Brett, 2006; Withers and Jarvie, 2008; Weng et al., 2008). Adsorption/desorption reactions are dependent on environmental conditions, such as pH and redox, as well as competing organic matter complexes (Reddy et al., 1999). Precipitation and dissolution reactions are usually due to quick changes in pH (Aminot and Andrieux, 1996), precipitation of P with calcite ( $\text{CaCO}_3$ ) may be facilitated by biota during photosynthesis (Neal et al., 2001). However, the availability of metals, calcite and organic carbon is not only driven by catchment sources but by chemical gradients that can be created due to the presence of biofilms (Boano et al., 2014). Phosphate in the water column usually co-precipitates with iron (Fe), and these co-precipitated phosphates accumulate on sediment surfaces as Fe-bound P (Baken et al., 2015). Authigenic apatite referred to as calcium (Ca)-bound P also accumulates and acts as a sink for P in sediments (Ruttenberg, 2003).

Redox conditions change the binding of Al, Fe and manganese to mineral surfaces and humic substances (Mortimer, 1941; Borch et al., 2010). Anoxic conditions allow for the reduction of Fe oxy(hydr)oxides and the hydrolysis of organic P (Golterman, 1995; Jensen et al., 1992; Löfgren and Boström, 1989). The oxy(hydr)oxides of Fe and Al act as electron acceptors to the phosphate ion that has a high negative charge thus causing the phosphate ion to adsorb to the metal complex.

Additionally, metal transformations can modify the availability of P and significantly contribute to fluxes of P (Klotz, 1991). The change in the availability of metal (oxy)hydroxides will impact the labile P bound to metal coatings on sediments, with fewer available metal oxides likely resulting in less adsorption to sediments (Golterman, 2004). Hence, the deposition and accumulation of P in suspended sediments (SS) is closely linked to the presence of mineral elements. Despite this, few studies have examined the relationship between the mineral composition of SS and bioavailable P fractions in addition to particulate organic matter.

PP bioavailability may increase if P is bound to clays and degradable organic matter or if it is weakly sorbed to particles (Pacini and Gächter, 1999; Reynolds and Davies, 2001). Particulate organic carbon (POC) and particulate organic nitrogen (PON) which are important components of the particulate organic matter pool in rivers may influence the availability of PBAP. Compared to PBAP in rivers (Ellison and Brett, 2006), much is less known about the relationship between PBAP, and POC and PON stoichiometry despite the spike in SS during high flow events. The wide variability in PP bioavailability suggests that both river-flow characteristics and land use pattern in the river catchment may be important; in addition to POC and PON concentration in suspended sediments. Since PP is usually transported to rivers bound to SS, the quantity and mineral composition of sediment in runoff will influence the concentration of BAP by varying the relative amounts of DP and PP in the river. The amount of SS in runoff is affected by land use characteristics, and especially erosion, river-flows and soil saturation (Pacini and Gächter, 1999). Disturbed catchments like those in urban and agricultural areas are most likely to exhibit greater river bank erosion. Previous studies on PP bioavailability present highly variable results, and moreover, several studies do not compare the influence of land use types or estimate the amount of PBAP during low flow conditions.

Few studies have examined the relationship between PBAP and particulate organic matter constituents under different hydrological conditions in urban and agricultural rivers. In addition, several studies do not explicitly compare the relationships between P fractions and SS in different types of rivers.

This shows a significant deficiency because source apportionment studies have demonstrated that there can be a considerable change in the source of SS under differing flows, with subsurface inputs linked to low flow sediment supply and elevated surface source contributions associated with rain events (Cooper et al., 2015). Among rivers draining into Mikawa bay in Aichi prefecture, central Japan, the study of P transport has been very limited, especially PP transport under varying hydrologic conditions. Besides, no comparative studies have been conducted to assess the variability and contribution of different P fractions in rivers draining through different land uses such as agricultural and urban areas.

Knowledge of the potential bioavailability of the PP fraction in runoff would enhance the estimation of the fraction of TP potentially available to algae. It is posited that such estimates would be more realistic inputs to nutrient budgets than would total P values. Hence, here is the starting point of this thesis.

## 1.9 General objectives and organization of the thesis

The overall goal of this study was to evaluate the bioavailable phosphorus fractions in an urban and agricultural river at varying flow conditions and the influence of particulate organic matter and elemental composition of runoff suspended sediment. Specifically, the objectives were:

- (i) To estimate PBAP in runoff from agricultural and urban rivers in order to assess whether the PBAP content was markedly different at high and low flow.
- (ii) To determine the BAP proportion in river runoff, and to clarify the relationship between BAP and TP in the rivers.
- (iii) To examine the relationship between PBAP, POC and PON, and to relate this to the elemental composition of SS from the rivers.

PBAP, POC and PON exhibit complex interactions in suspended sediments. It was posited that the sediment size and elemental composition were distinct for both rivers. Consequently, it was hypothesized that a significant relationship exists between PBAP, PP, POC and SS in agricultural river in contrast to the urban river. Additionally, it was speculated that both PBAP and POC exhibit a positive relationship with the Fe content in SS from the agricultural river unlike the urban river due to the abundance of Fe oxyhydroxide depicted by the reddish brown color of SS from the agricultural river. Previous studies (Gerke, 1992; Antelo et al., 2007; Weng et al., 2008, Lehtoranta et al., 2015), suggest that the phosphate binding strength to Fe-rich particles increases with increasing Fe:POC ratio, due to reduced competition between phosphate and POC for sorption on a Fe oxyhydroxide phase. Hence, it was hypothesized that the Fe to POC ratio was much higher in agricultural river as compared to urban river implying high PBAP amounts associated with runoff SS in the agricultural river.

The above objectives and hypotheses were addressed by combining experimental work and sampling surveys conducted in the river catchments. The organization of this thesis is as described in the chapters mentioned below.

Chapter 1 highlights the general introduction to this thesis work. The prevailing literature was widely reviewed in order to put this work in the broader context of the previous studies.



The study objectives which feed the main objective and which are aimed at closing significant gaps in the past studies are included in this section of the thesis.

Chapter 2 presents the methodology developed for this study. The study area, sampling campaign, analytical methods, quality control and statistical analysis conducted in this study are all highlighted in this part of the thesis.

Chapter 3 explores in detail how different phosphorus fractions are impacted by the catchment land uses, which were classified as either urban or agricultural depending on the dominant land use pattern in the river catchments.

Chapter 4 addresses the differences in phosphorus bioavailability in an agricultural and urban river.

Chapter 5 highlights the influence of particulate organic matter and sediment elemental composition on particulate bioavailable phosphorus fractions in the rivers.

Lastly, chapter 6 presents a summary of conclusions of the main results of the thesis, highlighting the implications that could guide future research directions.

## References

- Alexander, R.B., Smith, R.A., Schwarz, G.E., Boyer, E.W., Nolan, J.V. and Brakebill, J.W., 2008. Differences in phosphorus and nitrogen delivery to the gulf of Mexico from the Mississippi river basin. *Environmental Science and Technology*, 42, pp. 822-830.
- Aminot, A. and Andrieux, F., 1996. Concept and determination of exchangeable phosphate in aquatic sediments. *Water Research*, 30(11), pp. 2805-2811.
- Anderson, D., 1988. The Effect of Parent Material and Soil Development on Nutrient Cycling in Temperate Ecosystems. *Biogeochemistry*, 5, pp. 71-97.
- Anggara Kasih G.A. and Kitada T., 2004. Numerical simulation of water quality response to nutrient loading and sediment resuspension in Mikawa Bay, central Japan: quantitative evaluation of the effects of nutrient-reduction measures on algal blooms. *Hydrological Processes*, 18(16), pp.3037-3059.
- Antelo, J., Arce, F., Avena, M., Fiol, S., López, R. and Macías, F., 2007. Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma*, 138(1-2), pp.12-19.
- Arnell, N. W., 1999. The effect of climate change on hydrological regimes in Europe: a continental perspective. *Global Environmental Change*, 9, 5-23.
- Baker, D. B.; Confesor, R. B.; Ewing, D. E.; Johnson, L. T.; Kramer, J. W. and Merryfield, B. J., 2014 Phosphorus loading to Lake Erie from the Maumee, Sandusky, and Cuyahoga Rivers: The importance of bioavailability. *Journal of Great Lakes Research*, 40, DOI: 50210.1016/j.jglr.2014.05.001.
- Baker, D.B., Johnson, L.T., Confesor, R.B. and Crumrine, J.P., 2017. Vertical stratification of soil phosphorus as a concern for dissolved phosphorus runoff in the Lake Erie basin. *Journal of Environmental Quality*, 46(6), pp.1287-1295.
- Baken, S., Verbeeck, M., Verheyen, D., Diels, J., Smolders, E., 2015. Phosphorus losses from agricultural land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches. *Water Research*, 71, pp. 160-170. <https://doi.org/10.1016/j.watres.2015.01.008>
- Baldwin, D. S., 2013. Organic phosphorus in the aquatic environment. *Environmental Chemistry*. 10, pp. 439–454. doi: 10.1071/EN13151
- Barrow, N. J., 1983. On the reversibility of phosphate sorption by soils. *European Journal of Soil Science* 34, pp. 751–758.
- Beeton, A.M., 1965. Eutrophication of the St. Lawrence Great Lakes 1. *Limnology and Oceanography*, 10(2), pp.240-254.
- Bennett, E.M., Schipanski, M.E., 2013. The Phosphorus Cycle. In: Weathers KC

- Bennett, E. M., Carpenter, S. R. and Caraco, N. F., 2001. Human impact on erodable phosphorus and eutrophication: A global perspective. *BioScience*, 51(3), 227–234.
- Blackwell, M.S.A., Brookes, R.C., de la Fuente-Martinez, N., Gordon, H., Murray, P.J., Snars, K.E., et al., 2010. Phosphorus solubilization and potential transfer to surface waters from the soil microbial biomass following drying-rewetting and freezingthawing. *Advances in Agronomy*, 106, pp. 1-35.
- Boardman, J., 1990. Soil erosion on the South Downs: A review. In: Soil Erosion on Agricultural Land, Boardman, J. (eds), John Wiley & Sons, London, pp. 87-105.
- Boano, F., Harvey, J. W., Marion, A., Packman, A. I., Revelli, R., Ridolfi, L. and Wörman, A., 2014. Hyporheic flow and transport processes: Mechanisms, models, and biogeochemical implications. *Reviews of Geophysics*, 52(4), pp.603-679.
- Borch, T., Kretzschmar, R., Kappler, A., Cappellen, P. V., Ginder-Vogel, M., Voegelin, A. and Campbell, K., 2010. Biogeochemical redox processes and their impact on contaminant dynamics. *Environmental Science and Technology*, 44(1), pp.15-23.
- Breeuwsma A. and Silva, S., 1992. Phosphorus fertilization and environmental effects in the Netherlands and the Po region (Italy). Rep. 57. *Agricultural Research Department*. The Winand Staring Center for Integrated Land, Soil and Water Research., Wageningen, Netherlands.
- Buffle J. and Leppard GG., 1995. Characterisation of aquatic colloids and macromolecules. 1. Structure and behavior of colloidal material. *Environmental Science and Technology*, 29(9), pp. 2169– 2175.
- Cade-Menun, B., Duhamel, S., Dodds, R., Lonborg, C., Parsons, C.T. and Taylor, W.D., 2019. Phosphorus along the soil-freshwater-ocean continuum. *Frontiers in Marine Science*, 6, pp.28.
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N. and Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological applications*, 8(3), pp.559-568.
- Chapra, S.C., Dove, A. and Warren, G.J., 2012. Long-term trends of Great Lakes major ion chemistry. *Journal of Great Lakes Research*, 38(3), pp.550-560.
- Chapra, S.C., 2008. *Surface water-quality modeling*. Waveland press. Long Grove, Illinois, USA
- Chardon, W.J. and Schoumans, O.F., 2007. Soil texture effects on the transport of phosphorus from agricultural land in river deltas of Northern Belgium, The Netherlands and North-West Germany. *Soil Use and Management*, 23, pp. 16–24.
- Chang, S.C. and Jackson, M.L., L. 1957. Fractionation of soil phosphorus. *Soil Science*, 84, pp.133-44.
- Chen YW and Buffle J. 1996. Physicochemical and microbial preservation of colloid characteristics of natural water samples. I: experimental conditions. *Water Research*, 30(9), pp.2178– 2184.
- Childers, D. L., Corman, J., Edwards, M. and Elser, J. J. 2011. Sustainability challenges of phosphorus and food: Solutions from closing the human phosphorus cycle. *Bioscience*, 61(2), pp.117–124.
- Collins, A.L., Stutter, M. and Kronvang, B., 2014. Mitigating diffuse pollution from agriculture: International approaches and experience. *Science of the Total Environment*, 468, pp.1173-1177.

- Cordell, D., Drangert, J-O. and White, S. 2009. The story of phosphorus: Global food security and food for thought. *Glob. Environ. Chang.* 19, pp.292–305.
- Cordell, D. and White, S., 2011. Peak Phosphorus: Clarifying the Key Issues of a Vigorous Debate about Long-Term Phosphorus Security. *Sustainability*, 3, pp. 2027-2049.
- Cordell, D. and White, S., 2014. Life's bottleneck: sustaining the world's phosphorus for a food secure future. *Annual Review of Environment and Resources*, 39, pp.161-188.
- Correll, D.L., 1998. The role of phosphorus in the eutrophication of receiving waters: A review. *Journal of Environmental Quality*, 27, pp.261-266.
- Cooper RJ, Krueger T, Hiscock KM, Rawlins BG, 2015. High-temporal resolution fluvial sediment source fingerprinting with uncertainty: a Bayesian approach. *Earth Surface Processes and Landforms*, 40(1):78-92. <https://doi.org/10.1002/esp.3621>
- Daniel, T. C., Sharpley, A. N. and Lemunyon, J. L. 1998. Agricultural phosphorus and eutrophication: A symposium overview. *Journal of Environmental Quality* 27, pp.251-257
- Darch T, Blackwell MSA, Hawkins JMB, Haygarth PM, Chadwick D., 2014. A Meta-Analysis of Organic and Inorganic Phosphorus in Organic Fertilizers, Soils, and Water: Implications for Water Quality. *Critical Reviews in Environmental Science and Technology*, 44, pp.2172-2202.
- Delmas, M., Saby, N., Arrouays, D., Dupas, R., Lemerrier, B., Pellerin, S., et al., 2015. Explaining and mapping total phosphorus content in French top soils. *Soil Use and Management*, 31, pp.259–269
- DePinto, J.V., Young, T.C and Martin. S.C., 1981. Algal-Availability of Phosphorus in Suspended Sediments from Lower Great Lakes Tributaries. *Journal of Great Lakes Research*. 7(3), pp.311-325.
- Diaz, R.J. and Rosenberg, R., 2008. Spreading dead zones and consequences for marine ecosystems. *Science*, 321(5891), pp.926-929.
- Dietz M and Strock J., 2016. Phosphorus Cycle. Southwest Research and Outreach Center, University of Minnesota.<http://swroc.cfans.umn.edu/agricultural-programs/soil-science/phosphorus-cycle>. accessed 19 July 2019
- Dillon, P.J. and Rigler, F. H., 1974. The phosphorus-chlorophyll relationship in lakes. *Limnology and Oceanography*, 19, pp.767-773.
- Dils, R. M. and Heathwaite, A. L. 1998. Development of an iron oxide-impregnated paper strip technique for the determination of bioavailable phosphorus in runoff. *Water Research*, 32(5), pp.1429-1436.
- Dodd, R. J. and Sharpley, A. N. 2015. Recognizing the role of soil organic phosphorus in soil fertility and water quality. *Resources, Conservation and Recycling*, 105, pp.282-293.
- Dorich R.A., Nelson D.W. and Sommers L.E. 1985. Estimating algal available phosphorus in suspended sediments by chemical extraction. *Journal of Environmental Quality*. 14, pp. 400-405
- Dorich R.A., Nelson D.W. and Sommers L.E. 1980. Algal availability of sediment phosphorus in drainage water of the Black Creek watershed. *Journal of Environmental Quality*, 9(4), pp.557-563.

- EC. 2014. The European critical raw materials review. Memo 14/377, 7 pp. [http://europa.eu/rapid/press-release\\_IP-14-599\\_en.htm](http://europa.eu/rapid/press-release_IP-14-599_en.htm). accessed on 20 June 2019
- Eckert, W., Nishri, A. and Parparova, R., 1997. Factors regulating the flux of phosphate at the sediment - water interface of a subtropical calcareous lake: a simulation study with intact sediment cores. *Water Air and Soil Pollution*. 99, pp.401–409.
- Edmondson, W. T. 1970. Phosphorus, nitrogen, and algae in Lake Washington after diversion of sewage. *Science*, 169, pp. 690–691.
- Egli M, Filip D, Mavris C, Fischer B, Götze J, Raimondi S and Seibert J., 2012. Rapid Transformation of Inorganic to Organic and Plant-Available Phosphorous in Soils of a Glacier Forefield. *Geoderma*, 189, pp. 215-226.
- Egli M, Alioth L, Mirabella A, Raimondi S, Nater M and Verel R., 2007. Effect of Climate and Vegetation on Soil Organic Carbon, Humus Fractions, Allophanes, Imogolite, Kaolinite, and Oxyhydroxides in Volcanic Soils of Etna (Sicily). *Soil Science*, 172, pp. 673-691
- Ekholm, P. and Lehtoranta, J. 2012. Does control of soil erosion inhibit aquatic eutrophication?. *Journal of Environmental Management*, 93(1), pp.140-146
- Ekholm, P., Rita, H., Pitkänen, H., Rantanen, P., Pekkarinen, J. and Münster, U. 2009. Algal-available Phosphorus Entering the Gulf of Finland as Estimated by Algal Assays and Chemical Analyses. *Journal of Environment Quality*, 38(6) .doi:10.2134/jeq2008.0356
- Ekholm, P. and Krogerus, K. 2003. Determining algal-available phosphorus of differing origin: routine phosphorus analyses versus algal assays. *Hydrobiologia*, 492(1-3), pp.29-42.
- Ekholm, P. 1994. Bioavailability of phosphorus in agriculturally loaded rivers in southern Finland. *Hydrobiologia*, 287, pp.179-194.
- Ellison M.E. and Brett M.T. 2006. Particulate phosphorus bioavailability as a function of stream flow and land cover. *Water Research*. 40, pp. 1258-1268.
- Elser, J.J. and Bennett, E.M., 2011. A broken biogeochemical cycle. *Nature*, 478, 29-31.
- Environment Canada Manitoba Water Stewardship. 2011. State of Lake Winnipeg: 1999 to 2007. *Manitoba Water Stewardship*.
- Falkowski, P., Scholes, R. J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., Hibbard, K, et al., 2000. The global carbon cycle: A test of our knowledge of Earth as a system. *Science* 290, 291–296.
- FAO, 2008. Efficiency of soil and fertilizer phosphorus use: reconciling changing concepts of soils phosphorus behaviour with agronomic information. In: *FAO Fertilizer and Plant Nutrition Bulletin* 18, Food and Agriculture Organization of the United Nations Rome.
- Fertil. Week. 2008. Industry ponders the impact of China's trade policy. *Thurs. Mark. Rep.*, April 24
- Filippelli, G.M., 2008. The global phosphorus cycle: Past, present, and future. *Elements*, 4, pp.89-95.
- Fink, J.R., A.V. Inda, T. Tiecher, and V. Barrón. 2016. Iron oxides and organic matter on soil phosphorus availability. *Cienc. Agrotecnol.* 40:369–379. doi:10.1590/1413-70542016404023016

- Förstner, U., 2004. Traceability of sediment analysis. *TrAC Trends in Analytical Chemistry*, 23(3), pp.217-236.
- Fraser, A.I., Harrod, T.R., Haygarth, P.M., 1999. The effect of rainfall intensity on soil erosion and particulate phosphorus transfer from arable soils. *Water Science and Technology*, 39, 41-45.
- Gburek, W. J., Sharpley, A. N., Heathwaite, L., & Folmar, G. J. 2000. Phosphorus management at the watershed scale: A modification of the phosphorus index. *Journal of Environmental Quality*, 29(1), 130-144.
- Gerke, J., 1992. Orthophosphate and organic phosphate in the soil solution of four sandy soils in relation to pH-evidence for humic-FE-(AL-) phosphate complexes. *Communications in Soil Science and Plant Analysis*, 23(5-6), pp.601-612.
- Gimbert, L.J., Worsfold, P.J. and Haygarth, P.M., 2007. Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: Colloid and sediment characterization methods. *Hydrological Processes: An International Journal*, 21(2), pp.275-279.
- Golterman, H.L. (2004). *The chemistry of phosphate and nitrogen compounds in sediments*. Springer Science and Business Media.
- Gottselig, N., Nischwitz, V., Meyn, T., Amelung, W., Bol, R., Halle, C., et al., 2017. Phosphorus binding to nanoparticles and colloids in forest stream waters. *Vadose Zone Journal*, 16, pp.1–14
- Gottselig, N. and Klumpp, E., 2016. The Role of Natural Nanoparticles and Colloids for Phosphorus Binding in Forested Headwater Catchments. Forschungszentrum Jülich GmbH, Zentralbibliothek.
- Gottselig, N., Bol, R., Nischwitz, V., Vereecken, H., Amelung, W., Klumpp, E., 2014. Distribution of phosphorus-containing fine colloids and nanoparticles in stream water of a forest catchment. *Vadose Zone Journal*, 13, pp.1–11.
- Granstedt, A. 2000. Increasing the efficiency of plant nutrient recycling within the agricultural system as a way of reducing the load to the environment—experience from Sweden and Finland. *Agriculture, Ecosystems and Environment*, 80, pp.169-185.
- Gu, S., Qian, Y., Jiao, Y., Li, Q., Pinay, G., & Gruau, G., 2016. An innovative approach for sequential extraction of phosphorus in sediments: Ferrous iron P as an independent P fraction. *Water Research*, 103, pp.352-361.
- Hanna, M., 1989. Biologically available phosphorus: Estimation and prediction using an anion-exchange resin. *Canadian Journal of Fisheries and Aquatic Sciences*, 46(4), pp.638-643.
- Haygarth, P.M., Jarvie, H.P., Powers, S.M., Sharpley, A.N., Elser, J.J., Shen, J.B., et al., 2014. Sustainable Phosphorus Management and the Need for a Long-Term Perspective: The Legacy Hypothesis. *Environmental Science and Technology*, 48, pp.8417-8419.
- Haygarth, P.M., Page, T.J.C., Beven, K.J., Freer, J., Joynes, A., Butler, P., et al., 2012. Scaling up the phosphorus signal from soil hillslopes to headwater catchments. *Freshwater Biology*, 57, pp.7-25.

- Haygarth, P.M., Condon, L.M., Heathwaite, A.L., Turner, B.L. and Harris, G.P., 2005. The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Science of the Total Environment*, 344, 5-14.
- Haygarth PM, Warwick MS and House WA. 1997. Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution. *Water Research*, 31(3): 439–448.
- Heathwaite, A.L., Quinn, P.F. and Hewett, C.J.M., 2005. Modelling and managing critical source areas of diffuse pollution from agricultural land using flow connectivity simulation. *Journal of Hydrology*, 304, 446-461.
- Hedley, M.J., Mortvedt, J.J., Bolan, N.S., and Syer, J.K. 1995. Chapter 5: Phosphorus Fertility Management in Agroecosystems. In SCOPE 54: Phosphorus in the Global Environment - Transfers, Cycles and Management. H. Tiessen ed., 1995, 480 pp, Wiley, U.K.
- Hegemann D.A., Johnson A.H. and Keenan J.D. 1983. Determination of algal-available phosphorus on soil and sediment: A review and analysis. *Journal of Environmental Quality*, 12(1), pp.12-16
- HELCOM, 2015. Updated fifth Baltic sea pollution load compilation (PLC-5.5). *Baltic Sea Environmental Proceedings*, No. 145.
- Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant and soil*, 237(2), pp.173-195.
- Hoffman, A. R., Armstrong, D. E., Lathrop, R. C. and Penn, M. R. 2009. Characteristics and influence of phosphorus accumulated in the bed sediments of a stream located in an agricultural watershed. *Aquatic Geochemistry*, 15, pp.371-389.
- Holtan, H., Kamp-Nielsen, L. and Stuanes, A. O. 1988. Phosphorus in soil, water and sediment: an overview. *Hydrobiologia*, 170, pp. 19-34.
- Howarth R.W., Jensen H.S., Marino R. and Postma H. 1995. Transport to and processing of P in nearshore and oceanic waters. In: Tissen H. (ed.), Phosphorus in the Global Environment: Transfers, Cycles and Management. John Wiley & Sons Ltd., Chichester, pp. 323–345.
- Huettl, P.J., Wendt, R.C. and Corey, R.B. 1979. Prediction of algal-available phosphorus in runoff suspensions. *Journal of Environmental Quality*, 8, pp.130-132.
- Hupfer, M. and Lewandowski, J., 2008. Oxygen controls the phosphorus release from lake sediments - a long-lasting paradigm in limnology. *International Review of Hydrobiology*, 93, pp. 415–432
- Hupfer, M., Gächter, R. and Giovanoli, R. 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. *Aquatic Sciences*, 57(4), 305-324.
- International Joint Commission. Pollution of Lake Erie, Lake Ontario and the International Section of the St. Lawrence River.; Ottawa, Canada, 1971.
- Inoue T. and Ebise S. (1991). Runoff characteristics of COD, BOD, C, N and P loadings from rivers to enclosed coastal seas. *Marine pollution bulletin*, 23, pp.11-14.

- Jarvie, H.P., Johnson, L.T., Sharpley, A.N., Smith, S.R., Baker, D.B., Bruulsema, T.W., et al., 2017. Increased soluble phosphorus load to Lake Erie: unintended consequences of conservation practices? *Journal of Environmental Quality*, 46, pp.123-132
- Jarvie, H.P., Sharpley, A.N., Spears, B., Buda, A.R., May, L., Kleinman, P.J.A., 2013. Water quality remediation faces unprecedented challenges from “Legacy phosphorus”. *Environmental Science and Technology*, 47, pp.8997-8998.
- Jarvie, H.P., Withers, P.J.A., Bowes, M.J., Palmer-Felgate, E.J., Harper, D.M., Wasiak, K., Wasiak et al., 2010. Streamwater phosphorus and nitrogen across a gradient in rural–agricultural land use intensity. *Agriculture, Ecosystems and Environment*, 135(4), pp.238-252.
- Jarvie, H. P., Withers, J. A. and Neal, C. 2002. Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity. *Hydrology and Earth System Sciences*, 6(1), pp.113-131.
- Jensen, H. S., Kristensen, P., Jeppesen, E. and Skytthe, A., 1992. Iron: phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. In *Sediment/Water Interactions* (pp. 731-743). Springer, Dordrecht.
- Jensen, H.S. and Thamdrup, B., 1993. Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. In *Proceedings of the Third International Workshop on Phosphorus in Sediments* (pp. 47-59). Springer, Dordrecht.
- Jordan-Meille, L., Rubaek, G.H., Ehlert, P.A.I., Genot, V., Hofman, G., Goulding, K., et al., 2012. An overview of fertilizer-P recommendations in Europe: soil testing, calibration and fertilizer recommendations. *Soil Use and Management*, 28, pp.419-435.
- Karl, D. M., 2014. Microbially mediated transformation of phosphorus in the sea: new views of an old cycle. *Annual Review of Marine Science*, 6, pp.279–335. doi: 10.1146/annurev-marine-010213-135046
- Keskinen, R., Ketoja, E., Heikkinen, J., Salo, T., Uusitalo, R. and Nuutinen, V., 2016. 35- year trends of acidity and soluble nutrients in cultivated soils of Finland. *Geoderma Regional* 7, pp.376-387.
- Kleinman, P. J., Sharpley, A. N., McDowell, R. W., Flaten, D. N., Buda, A. R., Tao, L., Bergström, L. and Zhu, Q., 2011. Managing agricultural phosphorus for water quality protection: principles for progress. *Plant and Soil*, 349, pp.169-182.
- Kleinman, P. J. 2017. The persistent environmental relevance of soil phosphorus sorption saturation. *Current Pollution Reports*, 3(2), pp.141-150.
- Klotz, R. L. 1991. Temporal relation between soluble reactive phosphorus and factors in stream water and sediments in Hoxie Gorge Creek, New York. *Canadian Journal of Fisheries and Aquatic Sciences*, 48(1), pp.84-90.



- Kröger, R., Dunne, E. J., Novak, J., King, K. W., McLellan, E., Smith, D. R., Strock, J., Boomer, K., Tomer, M. and Noe, G. B. 2013. Downstream approaches to phosphorus management in agricultural landscapes: Regional applicability and use. *Science of the Total Environment*, 442, pp.263-274.
- Kudela, R.M., Berdalet, E., Bernard, S., Burford, M., Fernand, L., Lu, S., Roy, S., Usup, G., Tester et al., 2015. Harmful algal blooms. *A Scientific Summary for Policy Makers* (IOC/UNESCO, 2015).
- Laakso, J., Uusitalo, R. and Yli-Halla, M., 2016. Phosphorus speciation in agricultural catchment soils and in fresh and dried sediments of five constructed wetlands. *Geoderma*, 271, pp.18-26.
- Lehtoranta, J., Ekholm, P., Wahlström, S., Tallberg, P. and Uusitalo, R., 2015. Labile organic carbon regulates phosphorus release from eroded soil transported into anaerobic coastal systems. *Ambio*, 44(2), pp.263-273.
- Lehtoranta, J., Ekholm, P. and Pitkänen, H. 2009. Coastal eutrophication thresholds: a matter of sediment microbial processes. *Ambio*, 38, 303-308.
- Lindsay, W. L.; Vlek, P. L. G.; Chien, S. H. Phosphate minerals. In: DIXON, J. B.; WEED, S. B. Minerals in soil environment, 2nd ed. Madison: Soil Science Society of America., 1989. pp.1089-1130.
- Logan, T.J., Oloya, T.O., and Yaksich, S.M. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. *Journal of Great Lakes Research*, 5, pp. 112-123.
- Löfgren, S. and Boström, B., 1989. Interstitial water concentrations of phosphorus, iron and manganese in a shallow, eutrophic Swedish lake - implications for phosphorus cycling. *Water research*, 23(9), pp. 1115-1125.
- Lund, J. W.G. 1970. Primary production. *Water Treatment and Examination*, 19, pp. 332-358.
- MacDonald, G.K., Bennett, E.M., Ramankutty, N. and Potter, P., 2011. Too much or not enough: Agronomic phosphorus balances across the world's croplands. *Proceedings of the National Academy of Sciences of the United States of America*, 108, pp.3086-3091.
- Mackey, K. R., Van Mooy, B., Cade-Menun, B. J. and Paytan, A. 2019 Phosphorus Dynamics in the Environment. *Encyclopedia of Microbiology*, 4e, doi:10.1016/B978-0-12-809633-8.20911-4
- Matsubae, K., Kajiyama, J., Hiraki, T. and Nagasaka, T., 2011. Virtual phosphorus ore requirement of Japanese economy. *Chemosphere*, 84(6), pp.767-772.
- McDowell, R.W., Biggs, B.J.F., Sharpley, A.N. and Nguyen, L., 2004. Connecting phosphorus loss from agricultural landscapes to surface water quality. *Journal of Chemical Ecology*, 20, pp.1– 40.
- McDowell, R., Sharpley, A., Withers, P., 2002. Indicator to predict the movement of phosphorus from soil to subsurface flow. *Environmental Science and Technology*, 36, pp.1505-1509.
- McDowell, R.W. and A.N. Sharpley. 2001a. Approximating phosphorus release from soils to surface runoff and subsurface drainage. *Journal of Environmental Quality*, 30, pp.508-520.

- McDowell, R., Sharpley, A., Brookes, P., Poulton, P., 2001. Relationship between soil test phosphorus and phosphorus release to solution. *Soil Science*, 166, pp. 137-149.
- McKee L., Eyre B. and Hossain S. 2000. Intra- and interannual export of nitrogen and phosphorus in the subtropical Richmond River catchment, Australia. *Hydrological Processes*, 14, pp.1787–1809.
- Mellander, P.-E., Jordan, P., Shore, M., McDonald, N.T., Wall, D.P., Shortle, G., et al., 2016. Identifying contrasting influences and surface water signals for specific groundwater phosphorus vulnerability. *Science of the Total Environment*, 541, pp.292–302.
- Michalak, A.M., 2016. Study role of climate change in extreme threats to water quality. *Nature News*, 535(7612), p.349.
- Michalak, A. M.; Anderson, E. J.; Beletsky, D.; Boland, S.; Bosch, N. S.; Bridgeman, T. B.; Chaffin, J., et al., 2013. Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proceedings of the National Academy of Sciences, USA*, 110, pp.6243–6244.
- Miller W.E. and Greene J.C. 1978. *The Selenastrum capricornutum Printz algal assay bottle test: Experimental design, application, and data interpretation protocol* (Vol. 78, No. 18). Environmental Protection Agency, Office of Research and Development, Corvallis Environmental Research Laboratory.
- Mortimer, C. H. 1941. The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology*, 29(2), pp.280-329.
- Neal, C. 2001. The potential for phosphorus pollution mediation by calcite precipitation in UK freshwaters. *Hydrology Earth Systems Sciences*, 5, pp.119–131.
- Neset, T.S.S. and Cordell, D., 2012. Global phosphorus scarcity: identifying synergies for a sustainable future. *Journal of the Science of Food and Agriculture*, 92, pp.2-6.
- Ngoc, N.M., Inoue, T. and Yokota, K., 2017. Ultrasonic extraction method for quantifying bioavailable phosphorus in particulate form. *Journal of Environmental Chemical Engineering*, 5(3), pp.2498-2507.
- NSF, 2015., Closing the human phosphorus cycle, *National Science Foundation (NSF) workshop report, June 8-9, Arlington, Virginia, USA*.
- Ockenden, M.C., Deasy, C.E., Benskin, C.M.H., Beven, K.J., Burke, S., Collins, A.L., Evans, R., Falloon, P.D., et al., 2016. Changing climate and nutrient transfers: Evidence from high temporal resolution concentration-flow dynamics in headwater catchments. *Science of the Total Environment*, 548, pp.325-339.
- Oelkers, E.H., Valsami-Jones, E., 2008. Phosphate mineral reactivity and global sustainability. *Elements*, 4, pp.83-88.

- Oladeji, O. O.; O'Connor, G. A. and Brinton, S. R. 2008. Surface applied water treatment residuals affect bioavailable phosphorus losses in Florida Sands. *Journal of Environmental Management*, 88, pp.1593–1600.
- Orihel, D. M., Baulch, H. M., Casson, N. J., North, R. L., Parsons, C. T., Seckar, D. C. M., et al., 2017. Internal phosphorus loading in Canadian freshwater lakes: a critical review and data analysis. *Canadian Journal of Fisheries and Aquatic Sciences*, 74, pp.2005–2029. doi: 10.1139/cjfas-2016-0500
- Pacini N and Gächter R.,1999. Speciation of riverine particulate phosphorus during rain events. *Biogeochemistry*, 47(1):87-109. <https://doi.org/10.1007/BF00993098>
- Paerl, H.W., Scott, J.T., McCarthy, M.J., Newell, S.E., Gardner, W.S., Havens, K.E., Hoffman, et al., 2016. It takes two to tango: when and where dual nutrient (N & P) reductions are needed to protect lakes and downstream ecosystems. *Environmental Science and Technology*, 50(20), pp.10805-10813.
- Paerl, H. W.; Gardner, W. S.; McCarthy, M. J.; Peierls, B. L.; Wilhelm, S. W. 2014. Algal blooms: Noteworthy nitrogen. *Science*, 346, 175.
- Pearsall, W. H. 1921. The development of vegetation in English lakes, considered in relation to the general evolution of glacial lakes and rock basins. *Proceedings of the Royal Society of London*, B, 92, pp.259-284.
- Peltovuori, T. 2007. Sorption of phosphorus in field-moist and air-dried samples from four weakly developed cultivated soil profiles. *European Journal of Soil Science* 58, pp.8-17.
- Pettersson, K., Boström, B. and Jacobsen, O.S., 1988. Phosphorus in sediments—speciation and analysis. In *Phosphorus in Freshwater Ecosystems*, pp.91-101. Springer, Dordrecht.
- Poirier, S. C., Whalen, J. K., & Michaud, A. R., 2012. Bioavailable phosphorus in fine-sized sediments transported from agricultural fields. *Soil Science Society of America Journal*, 76(1), pp.258-267.
- Reddy, K. R. & DeLaune, R. D. 2008. Biogeochemistry of wetlands: Science and applications. CRC press, Boca Raton, Florida.
- Reddy, K.R., Kadlec, R.H., Flaig, E., Gale, P.M. 1999. Phosphorus retention in streams and wetlands: a review. *Critical Reviews in Environmental Science and Technology*, 29(1), pp.83-146.
- Reddy, K. R., Wang, Y., DeBusk, W. F., Fisher, M. M. and Newman, S. 1998. Forms of soil phosphorus in selected hydrologic units of the Florida Everglades. *Soil Science Society of America Journal*, 62(4), pp.1134-1147.
- Renneson, M., Vandenberghe, C., Dufey, J., Marcoen, J.M., Bock, L. and Colinet, G., 2015. Degree of phosphorus saturation in agricultural loamy soils with a near-neutral pH. *European Journal of Soil Science*, 66, pp.33–41

- Reynolds C.S. and Davies P.S. 2001. Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. *Biological Reviews*, 76(1), pp.27-64.
- Richardson, A.E., Lynch, J.P., Ryan, P.R., Delhaize, E., Smith, F.A., Smith, S.E., Harvey, P.R., Ryan et al., 2011. Plant and microbial strategies to improve the phosphorus efficiency of agriculture. *Plant and soil*, 349(1-2), pp.121-156.
- Roden, E.E. and Edmonds, J.W., 1997. Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe (III) oxide reduction versus iron-sulfide formation. *Archiv für Hydrobiologie*, 139(3), pp.347-378.
- Russell M.A., Walling D.E., Webb B.W. and Bearne R. 1998. The composition of nutrient fluxes from contrasting UK river basins. *Hydrological Processes*, 12, pp.1461–1482
- Ruttenberg K.C., 2003. The global phosphorus cycle. In: Holland HD, Turekian KK (eds) *Treatise on geochemistry*, 2nd edn. Elsevier, Amsterdam, pp.499-558
- Ruttenberg, K. C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and oceanography*, 37(7), pp.1460-1482.
- Sakamoto, M. 1966. Primary production by phytoplankton community in some Japanese lakes and its dependence upon lava depth. *Archiv fur Hydrobiologie*, 62, pp.1-28.
- Scavia, D., Allan, J.D., Arend, K.K., Bartell, S., Beletsky, D., Bosch, N.S., Brandt, S.B., Briland et al., 2014. Assessing and addressing the re-eutrophication of Lake Erie: Central basin hypoxia. *Journal of Great Lakes Research*, 40(2), pp.226-246.
- Schindler, David W., Stephen R. Carpenter, Steven C. Chapra, Robert E. Hecky, and Diane M. Orihel., 2016. Reducing phosphorus to curb lake eutrophication is a success. *Environmental Science and Technology*, 50(17), pp.8923-8929.
- Schindler, D.W. and Vallentyne, J. R., 2008. The Algal Bowl: Overfertilization of the World's Freshwaters and Estuaries; *University of Alberta Press*: Edmonton, Canada.
- Schindler, D. W. 2001. The cumulative effects of climate warming and other human stresses on Canadian freshwaters in the new millennium. *Canadian Journal of Fisheries and Aquatic Sciences*, 58, pp.18–29
- Schindler, D. W. 1974. Eutrophication and recovery in experimental lakes: implications for lake management. *Science*, 184, pp.897–899.
- Schoumans, O.F. and Chardon, W.J., 2015. Phosphate saturation degree and accumulation of phosphate in various soil types in The Netherlands. *Geoderma*, 237, pp.325-335.
- Schoumans, O.F., Chardon, W.J., Bechmann, M.E., Gascuel-Oudou, C., Hofman, G., Kronvang et al., 2014. Mitigation options to reduce phosphorus losses from the agricultural sector and improve surface water quality: A review. *Science of the Total Environment*, 468-469, pp.1255-1266.

- Sharpley, A., Jarvie, H., Flaten, D. and Kleinman, P., 2018. Celebrating the 350th anniversary of phosphorus discovery: a conundrum of deficiency and excess. *Journal of Environmental Quality*, 47(4), pp.774-777.
- Sharpley, A., Jarvie, H.P., Buda, A., May, L., Spears, B. and Kleinman, P., 2013. Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. *Journal of Environmental Quality*, 42(5), pp.1308-1326.
- Sharpley and Beegle, 2001. Managing phosphorus for agriculture and the environment <https://extension.psu.edu/programs/nutrient-management/educational/soil-fertility/managing-phosphorus-for-agriculture-and-the-environment>, accessed on 18 July 2019
- Sharpley, A. N., Gburek, W. J., Folmar, G. and Pionke, H. B. 1999. Sources of phosphorus exported from an agricultural watershed in Pennsylvania. *Agricultural Water Management*, 41(2), pp.77-89.
- Sharpley, A.N., Beegle, D.G., Gburek., W.J., Weld, J. and Folmar, G. 1998. Modification and application of the phosphorus index screening tool to identify critical sources of phosphorus in the Upper Chesapeake Bay Watershed. Final Rep. To the Scientific and Technical Advisory Committee to the Chesapeake Bay Program. Chesapeake Bay Program. Annapolis, MD.
- Sharpley A.N., Smith S.J., Jones O.R., Berg W.A. and Coleman G.A. 1992. The transport of bioavailable phosphorus in agricultural runoff. *Journal of Environmental Quality*, 21(1), pp.30-35
- Sharpley, A. N., Troeger, W. W. and Smith, S. J. 1991. The measurement of bioavailable phosphorus in agricultural runoff. *Journal of Environmental Quality*, 20(1), pp.235-238.
- Shen, J., Yuan, L., Zhang, J., Li, H., Bai, Z., Chen et al., 2011. Phosphorus dynamics: from soil to plant. *Plant physiology*, 156(3), pp.997-1005.
- Smekc, N. E. 1985. Phosphorus dynamics in soils and landscapes. *Geoderma*, 36, pp.185-189.
- Smith V. H. and Schindler, D.W. 2009. Eutrophication science: Where do we go from here? *Trends in Ecology and Evolution*, 24, pp.201–207.
- Strayer DL, Likens GE, eds. 2012. *Fundamentals of Ecosystem Science*, Academic Press, Waltham, MA: Elsevier. pp 159–178.
- Bundy, L.G., Tunney, H. and Halvorson, A.D., 2005. Agronomic aspects of phosphorus management. *Phosphorus: Agriculture and the environment*, (phosphorusagric), pp.685-727.
- Suzuki T. 2001. Oxygen-deficient waters along the Japanese coast and their effects upon the estuarine ecosystem. *Journal of Environmental Quality*, 30(2), pp.291-302.
- Sutton MA, Bleeker A, Howard CM, Bekunda M., Grizzetti et al. 2012. *Our Nutrient World: The Challenge to Produce More Food and Energy with Less Pollution*. Edinburgh: Center for Ecology and Hydrology.
- Syers, K., Bekunda, M., Cordell, D., Corman, J., Johnston, J., Rosemarin, A. and Salcedo, I. 2011. Phosphorus and food production. In UNEP (Ed.), *UNEP Year Book 2011. Emerging issues in our environment*, pp.34-45. New York: UNEP

- Tebrügge, F. and Düring, R. A. 1999. Reducing tillage intensity – a review of results from a long-term study in Germany. *Soil and Tillage Research*, 53, 15-28.
- Tiessen, H. J. W. B., Stewart, J. W. B. and Cole, C. V. 1984. Pathways of phosphorus transformations in soils of differing pedogenesis 1. *Soil Science Society of America Journal*, 48(4), pp. 853-858.
- Turtola, E., Alakukku, L., Uusitalo, R. and Kaseva, A. 2007. Surface runoff, subsurface drainflow and soil erosion as affected by tillage in a clayey Finnish soil. *Agricultural and Food Science*, 16, pp.332-351.
- Uusitalo, R., Yli-Halla, M. and Turtola, E. 2000. Suspended soil as a source of potentially bioavailable phosphorus in surface runoff waters from clay soils. *Water Research*, 34, pp.2477-2482.
- Vaccari, D.A., 2009. Phosphorus: a looming crisis. *Scientific American*, 300(6), pp.54-59.
- van der Grift, B., Osté, L., Schot, P., Kratz, A., van Popta, E., Wassen, M., & Griffioen, J., 2018. Forms of phosphorus in suspended particulate matter in agriculture-dominated lowland catchments: Iron as phosphorus carrier. *Science of the Total Environment*, 631, pp.115-129.
- van der Salm, C., Dupas, R., Grant, R., Heckrath, G., Iversen, B.V., Kronvang, B., et al., 2011. Predicting Phosphorus Losses with the PLEASE Model on a Local Scale in Denmark and the Netherlands. *Journal of Environmental Quality*, 40, pp.1617-1626.
- Villalba, G., Liu, Y., Schroder, H., Ayres, R. U. 2008. Global phosphorus flows in the industrial economy from a production perspective. *Journal of Industrial Ecology*, 12, pp.557-569.
- Vitousek PM, Porder S, Houlton BZ, Chadwick OA., 2010. Terrestrial Phosphorus Limitation: Mechanisms, Implications, and Nitrogen-Phosphorus Interactions. *Ecological Applications*, 20, pp.5-15.
- Vollenweider, R. A., 1968. Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters, With Particular Reference to Nitrogen and Phosphorus As Factors in Eutrophication; OECD Technical Report, DAS/CS/68.27, Paris, France
- Walker, T. W. and Syers, J. K. 1976. The fate of phosphorus during pedogenesis. *Geoderma*, 15, pp.1-19.
- Wall, D.P., Jordan, P., Melland, A.R., Mellander, P.E., Mechan, S. and Shortle, G., 2013. Forecasting the decline of excess soil phosphorus in agricultural catchments. *Soil Use and Management*, 29, pp.147-154.
- Wang, C., Zhang, Y., Li, H. and Morrison, R.J., 2013. Sequential extraction procedures for the determination of phosphorus forms in sediment. *Limnology*, 14(2), pp.147-157.
- Weng, L.; van Riemsdijk, W. H. and Hiemstra, T. 2008. Humic nanoparticles at the oxide-water interface: Interactions with phosphate ion adsorption. *Environmental Science and Technology*, 42, pp. 8747-8752.
- Withers, P.J.A. and Jarvie, H.P. 2008. Delivery and cycling of phosphorus in rivers: a review. *Science of the Total Environment*, 400, pp.379-395.

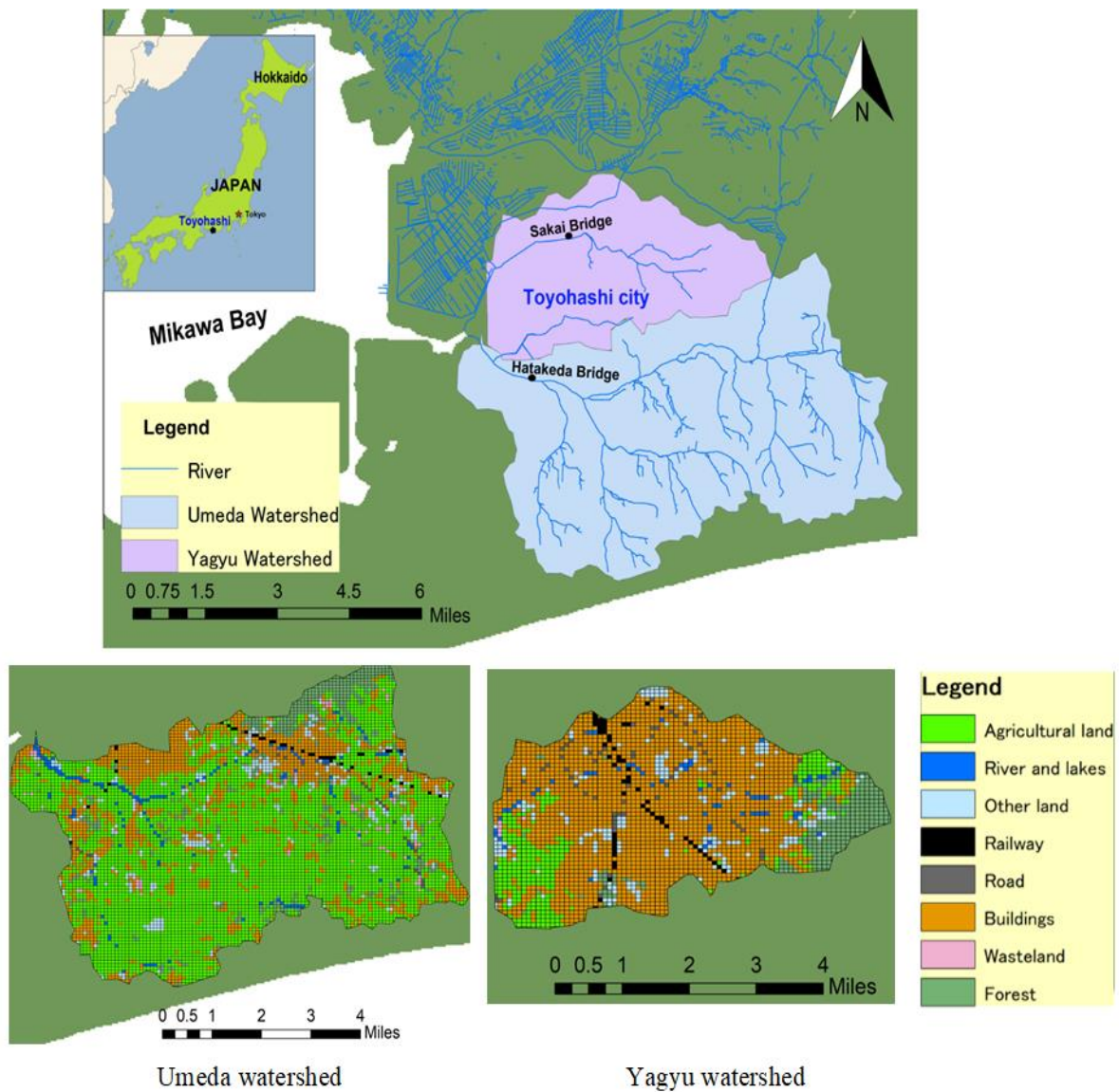
- Williams J, Walker T., 1969. Fractionation of Phosphate in a Maturity Sequence of New Zealand Basaltic Soil Profiles: 2. *Soil Science*, 107, pp.213-219.
- Williams J.D.H., Syers J.K. and Walker T.W., 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. *Soil Science Society of America Journal*, 31(6), pp.736-739.
- Wilson, E.K., 2014. Danger from microcystins in Toledo water unclear. *Chem. Eng. News*, 92(32), p.9.
- World Resources Institute (WRI). (2008). *World Hypoxic and Eutrophic Coastal Areas* [Online]. Available: <http://www.wri.org/resource/world-hypoxic-and-eutrophic-coastal-areas>. accessed on 14 August 2019
- Yan, J., Jiang, T., Yao, Y., Lu, S., Wang, Q., Wei, S., 2016. Preliminary investigation of phosphorus adsorption onto two types of iron oxide-organic matter complexes. *Journal of Environmental Sciences*, 42, pp.152–162.

## Chapter 2 Methodology

### 2.1 Description of the study environmental area

This study was conducted on two rivers named Umeda and Yagyu, which flow into Mikawa bay through Toyohashi city in the Aichi Prefecture of Central Japan (**Figure 2.1**). The bay is enclosed by the two peninsulas of Chita and Atsumi and has a 604 km<sup>2</sup> surface area with a mean depth of 9.2 m (Sakamoto and Tanaka, 1989). The eastern half of Mikawa Bay is called Atsumi Bay. One large river (Toyo) and several small rivers including Umeda and Yagyu flow into the bay (**Figure 2.1**). The water depth varies from about 7.5 m downstream of Toyokawa River to 24 m at the mouth of the bay near the Pacific Ocean (Anggara and Kitada, 2004). The two big cities in the watershed are Toyohashi with a population of around 380,000, and Toyokawa, with around 116,000. This bay is a commercial and recreational resource for about 700,000 people living in the watershed and the Atsumi Peninsula. The bay is also the habitat of a wide variety of fish and animal species. In the past years, increased human activities in the watershed and the bay area together with the change in the land use pattern have resulted in damage to the ecosystem of Mikawa Bay. Several activities have contributed to a decline in water quality and the loss of aquatic habitats in the bay (Suzuki, 2001). The rapid increase of nutrient inputs due to human activity is usually known to escalate algal blooms, which deplete dissolved oxygen, block sunlight rays, and finally force fish and other aquatic organism to perish (Marie Anne et al., 1997). This phenomenon has been attributed to the combination of high nutrient loading and long residence time of sea water in the closed region due to a weak flushing rate (Anggara and Kitada, 2004). The weak flushing rate comes from the topography of the bay, which is enclosed by two peninsulas and leaves a small gate to the open sea (Marie Anne et al., 1997). The nutrient from the land area is loaded through Toyo and Umeda rivers, and the municipal waste-water treatment plants at Noda and Nakashima. Yagyu river which flows through largely an urban area in Toyohashi city also contributes to nutrient loading in the bay as elevated TP amounts have been estimated in the river. River water was obtained by dipping a bucket into the river while standing on the bridge.





**Figure 2.1:** Location of the study area

**Table 2.1:** Land use pattern in the watershed of the rivers

River	Land type classification	Land use (%)							
		Rice paddy	Other crops	Forest	Buildings	Rivers	Roads	Railway	Wasteland
U	Agricultural	17.5	49.1	7.5	21.8	2.1	0.5	0.6	0.9
Y	Urban	9.3	8.9	8.5	67.2	2	2	1.8	0.2

U is Umeda river and Y is Yagyū river. Other crops denote tea and leafy vegetables such as cabbage

Sample sites were categorized as agricultural, urban or forested according to the type of land use within the river catchments (**Table 2.1**). The Yagyu river was classified as an urban river as its catchment consists of largely paved areas and forested area upstream. The Umeda river was classified as an agricultural river as it flows through an area with a high percentage of cultivated fields and poultry farms. The main crops grown in the Umeda river watershed include rice, cabbage and tea. Phosphate and Nitrogen fertilizers including composted poultry manure have been intensively applied to fields that are cultivated during spring and autumn to replace P depletion (Rasul et al., 2013). Consequently, a greater proportion of phosphorus is transported in Umeda river runoff especially during rain events and it is important to assess whether this P could potentially be available for aquatic plant growth since in the summer, algae blooms have been persistent in the adjacent Mikawa bay. Hence, it is suspected that elevated proportions of P and organic matter are entrained in runoff along the rivers especially during rain events. It is critical to assess whether this P is available for aquatic plant growth since in the summer, algae blooms have been prevalent in the adjacent Mikawa bay with devastating consequences for marine life.

Previous studies have focused on improvement of the water quality in the semi-enclosed bay area including: efforts to increase the tidal exchange between an inner bay and an outer sea area by arrangement of artificial bottom roughness (Komatsu et al., 1999); to enhance the purification ability by generating an artificial sandy beach. Attempts were also made to suppress loading from the bottom sediment either by covering it with sand or by dredging the pollutant site of sediment (Murakami, 1998). Marie Anne et al. (1997), studied the influence of tide on the eutrophication in Mikawa bay and concluded that the effect of tidal currents was evident in the deepest part of the bay, and that tide did not seem to be the main factor that controls the dinoflagellates (ostracods) population in the inner part of the bay. As described above, it is evident that past studies majorly focused on water quality restoration by means of hydrodynamic and physical methods. In this study, we also focus on potential bioavailability of PP associated with SS in the agricultural and urban river.

Additionally, by comparing the estimates of SS, PP, DP, PBAP, BAP, POC, PON and sediment elemental composition in the rivers, the influence of land use pattern on nutrient inputs to downstream Mikawa bay can be inferred for subsequent water quality improvement efforts.

## **2.2 Sampling survey**

### ***2.2.1 River water***

Water samples from which suspended sediments were recovered were collected from an agricultural and urban river at varying flow conditions between May 2016 and May 2019 (**Table 2.2 and 2.3**). River water was obtained by dipping a bucket into the river while standing on the bridge across the river. The samples were collected in 20 L containers that had been rinsed with analytical grade de-ionized water. High flow samples were always collected during storm events averaging 5 mm/h of rain or more. Low flow samples were collected at the time of no rain or prior to rain events. We attempted to reduce the effects of sample storage on DP concentrations by filtering the subsamples of water samples upon returning to the laboratory and measuring DP concentration within 48 h after sampling.

### ***2.2.2 River-bed sediments***

River-bed sediments were collected between January 2019 and May 2019; hereinafter referred to as sampling moments (**Table 2.2**). The bed sediments were collected in polyethylene bottles fitted with lids, which had been rinsed with 1M HCl and deionized water, and immediately transported to the laboratory within 2 hours. The bed sediments were then dried at 40 °C for 72 h and later crushed in a mortar with a pestle, and sieved (0.149 mesh size) to remove plant residues and larger debris. The samples were then stored at 4 °C until further analysis.

### ***2.2.3 Soil samples***

Soil samples were collected in September 2016 from cultivated fields within the agricultural river watershed (**Table 2.4**). Soil sampling using a trowel was carried out from the upper soil surface (0 – 50 mm).

**Table 2.2:** Sampling campaign for SS and river bed sediments

<b>Sampling date (day-month-year)</b>	<b>Sample ID</b>	<b>Flow</b>
11-May-16	U1	High
20-Jun-16	U2	High
8-Sep-16	U3	High (typhoon)
20-Sep-16	U4, Y1	High (typhoon)
20-Jun-17	U5, Y2	High
7-Aug-17	U6, Y3	High
6-Oct-17	U7	High
6-Jun-18	U8, Y4	High
18-Jun-18	Y5	High
10-Sep-18	U9, Y6	High
9-Nov-18	U10, Y7	High
17-Oct-16	Y8	Low
1-Nov-16	Y9	Low
7-Aug-17	U11, Y10	Low
6-Oct-17	U12	Low
23-Feb-18	U13, Y11	Low
5-Mar-18	U14, Y12	Low
8-Nov-18	U15, Y13	Low
8-Jan-19	U16, Y14	Low
29-Jan-19	U17, Y15, U17_bsed, Y15_bsed	Low
4-Mar-19	U18, Y16, U18_bsed, Y16_bsed	Low
22-Apr-19	U19, Y17, U19_bsed, Y17_bsed	Low
20-May-19	U20, Y18, U20_bsed, Y18_bsed	Low

\*River bed sediment samples were collected only between January 2019 and May 2019. The abbreviation "U1, U2.." depicts SS samples collected from Umeda (agricultural) river whereas "U17\_bsed,..." denotes bed sediments from agricultural river; "Y1,..." represents SS samples from urban river and "Y16\_bsed,..." denotes bed sediments from urban river

This top layer represents the soil horizon that is most likely to be eroded and entrained in surface runoff during a storm event. The collected soil samples were dried at 40 °C for 72 h and later crushed in a mortar and sieved (0.149 mm mesh size) to remove plant fibers and large particles.

**Table 2.3:** Continuous sampling episodes during a storm event of 24/25<sup>th</sup> April 2018

	<b>Time</b>	<b>Sample ID</b>	<b>Flow depth (m)</b>
	15:00	UT1	0.80
	22:00	UT2	1.11
Rising flow-depth	2:00	UT3	1.05
	4:00	UT4	1.47
	6:00	UT5	1.61
	7:00	UT6	1.84
	8:00	UT7	2.00
	9:00	UT8	1.98
Falling flow-depth	10:00	UT9	1.51
	12:00	UT10	1.22
	15:00	UT11	1.10
	18:00	UT12	0.75

\*UT1 denotes sample collected from the agricultural river at time T1. In total, 12 samples were collected at different intervals during a storm event.

**Table 2.4:** Soil samples from different cultivated fields in agricultural river watershed

<b>Sampling date (day-month-year)</b>	<b>Crops grown at site</b>	<b>Sample ID</b>	<b>Coordinate N</b>	<b>Coordinate E</b>
26-Sep-16	Chinese cabbage	C1	37.718074	137.418093
26-Sep-16	Cabbage; grown with fertilizer	C2	34.671825	137.378231
26-Sep-16	Cabbage; grown with no fertilizer	C3	34.671825	137.378231
26-Sep-16	Cabbage; Tobacco in summer	C4	34.673007	137.375147
26-Sep-16	Rice	R1	34.714261	137.401658
27-Sep-16	Rice	R2	34.733463	137.473234
26-Sep-16	Tea	T1	34.714247	137.401592
26-Sep-16	Tea	T2	34.715001	137.415362
27-Sep-16	Forested	F1	34.745011	137.473116
	Forested	F2	34.738546	137.456235

The sieved samples were placed in an air-tight polyethylene sheet or aluminum foil and kept at 4 °C prior to further analysis.

## **2.3 Laboratory analyses**

### ***2.3.1 Suspended sediment concentration***

Suspended sediment concentrations were determined by filtering a measured volume (50 – 250 mL) of water sample through a pre-weighed and dry filter (GF/F glass microfiber filters, 47 mm diameter, Whatman, GE Healthcare, Tokyo, Japan). The wet filter with SS was dried in an oven at 105 °C for 2 h (Gray et al., 2000). The ratio of the difference in filter weights, measured using an ultra-microbalance (Mettler-Toledo, Columbus, Ohio, U.S.A) and the volume of river water filtered was taken as SS concentration. The filtrate from this process was collected and stored at 4 °C before subsequent measurement of DP concentration typically within 48 hours.

### ***2.3.2 Continuous flow centrifugation***

The suspended sediment, from which PBAP was later extracted, was separated from river water by means of continuous-flow centrifugation (Himac CR22G high-speed refrigerated centrifuge; R18C continuous rotor; Hitachi Koki, Tokyo, Japan). An average centrifugal force of  $196,000 \text{ ms}^{-2}$  was applied allowing for a discharge of 150 mL / min at 15,000 rpm. This centrifugal force was meant to concentrate the sediment at the bottom of the rotor body assy. The concentrated sediment obtained was then dried in an oven at 40 °C for 72 h and later stored at 4 °C prior to further analysis within 48 h.

### ***2.3.3 PBAP extraction***

PBAP was extracted from SS, river-bed sediments and soils using the ultrasonic extraction method (Ngoc et al., 2016). The method uses an ultrasonic horn (Branson, Connecticut, USA; Ultrasonic Disrupter Sonifier II, W-450) which generates different intensities at a fixed operating frequency of 20 kHz. During treatment, 25 mg of sediment or soil was placed in a centrifuge vial and 25 mL of 0.1M NaOH added as the extractant. The horn was placed at about 1 cm from the bottom of the vial which was fully immersed in an ice-water bath to prevent temperature increase and the intensity was set at 30 W for 1 min.

The clear supernatants from the extracts were collected by centrifugation at an average centrifugal force of  $7,350 \text{ ms}^{-2}$  maintained at 2,300 rpm (Kubota, Tokyo, Japan; model 5100 table-top centrifuge) for 30 min. The residue remaining in the centrifuge vial was washed twice with 25 mL of distilled water for 10 min each using an orbital mechanical shaker to remove P that could have adsorbed onto the sediment. The supernatants (water extracts) were obtained after centrifugation at 2,300 rpm. In preparation for P analysis, both NaOH and water extracts were neutralized with either 1M NaOH or 1M HCl, and kept at 4 °C until analysis within 24 h. The P concentration in each extract was analyzed colorimetrically using the standard molybdenum blue method (Murphy and Riley, 1962) with ascorbic acid as the reducing agent.

#### ***2.3.4 DP, TP, PBAP and BAP fractions***

DP and TP were measured in filterate and raw water respectively, after digestion with 4 % w/w potassium persulphate in an autoclave at 120 °C for 30 min so as to convert all forms of P including refractory organic P into soluble reactive phosphorus detectable using the standard molybdenum blue technique (Murphy and Riley, 1962), with ascorbic acid as the reducing agent. Total PP in soil and river-bed sediments was measured after adding 25 mL of de-ionised water to 25 mg of soil followed by digestion with 4 % w/w potassium persulphate in an autoclave at 120 °C for 30 min. All P measurements were done in triplicate using an Autoanalyzer (Bran + Luebbe, TRAACS 800 Autoanalyzer, Norderstedt, Germany) for the samples collected between May 2016 and November 2017. Other samples collected post November 2017 were analyzed using a flow injection analyzer (OGAWA, OG-AS-300, Tokyo, Japan). The sum of P measured in raw extracts was taken to be particulate BAP (PBAP). PP in river runoff refers to P bound to SS and was determined as the difference between TP and DP. BAP was estimated as the sum of DP and PBAP. Non BAP was estimated as the difference between TP and BAP.

#### ***2.3.5 POC and PON analysis***

POC and PON concentrations were measured for SS, river-bed sediments and soil samples.

SS samples recovered from the continuous flow centrifugation process described earlier, were first oven-dried at 40 °C for 72 hours. The ashed SS samples were then crushed to a fine proportion using a mortar and pestle, and kept at 4 °C before further analysis. Sieving of the crushed SS was not done prior to POC and PON analysis but any visible plant fibers and large particles were physically removed by hand so as to retain only fine SS for measurement. Soil and river-bed sediment samples were also oven dried at 40 °C for 72 h, and later sieved through a 0.149 mm mesh which allowed isolation of very coarse particles. The fine soil and bed sediment samples recovered were later analyzed for particulate organic matter forms.

Firstly, POC and PON concentrations were measured after combusting a measured amount of the standard contained on a dry-clean analyzer cup, at a temperature of 600 °C using an NC analyzer (Sumigraph NC-22A, Sumika Chemical Analysis Service, Ltd., Tokyo, Japan). Acetanilide (71.09 % C by weight and 10.36 % N by weight) was used as a standard compound to establish a calibration curve between the mass of C, N and the response of the thermal conductivity detector in the NC analyzer. Three proportions of the same standard were used in succession, with the measured standard contained on a dry-clean analyzer cup ranging between (1 to 3 mg), (3 to 5 mg ) and (8 to 10 mg) respectively, so as to generate a calibration curve from the obtained absorbance values. Next, the measured soil and sediment samples also contained on a clean, pre-dried analyzer cup were combusted at a temperature of 600 °C and the plotted absorbance values corresponding to the areal extent of the generated graph were recorded simultaneously in the NC-22A software; an extension of the NC analyzer system. POC and PON concentration of samples were then estimated from the generated standard calibration curve.

### ***2.3.6 Sediment elemental composition analysis***

The elemental composition of sediments were analyzed using an Atomic absorption spectrophotometer (Shimadzu AA-7000, Kyoto, Japan) after sediment digestion with concentrated hydrochloric acid (95 °C, 15 min). The digestion of sediment was done according to the standard method 3050B EPA (EPA, 1996).



The mineral elements measured in digested sediments were iron (Fe), Calcium (Ca), Magnesium (Mg) and Sodium (Na). The relative standard deviations of three repeat analyses of the sediment were less than 1.9% for all the elements. The detection limit of Atomic absorption spectrophotometer was equal to three times the standard deviation of the blank (ultrapure water). In all cases three replicate samples were prepared for analysis.

#### **2.4 Quality control and statistical analysis**

The chemical analyses were performed in the laboratory of Water Environment and Water Conservation Engineering at the Department of Architecture and Civil Engineering, Toyohashi University of Technology. The calibration of all devices was performed according to manufacturers' instructions. All measurements were made on three independent replicates. For colorimetric analyses of P fractions, we attempted to analyse the standard solutions before and after 5 sample runs so as to ascertain the change in concentration. For elemental composition analysis, all standard solutions were analysed before and after every six sample runs to detect possible concentration drifts. Every sample was analysed twice and a 5 % maximum difference in concentration tolerated. For elemental composition analysis, the detection limit of Atomic Absorption Spectrophotometer was equal to the sum of the blank mean and three times the standard deviation of the blank. The blank used was 1% HCl solution, and in all cases three replicate samples were prepared for analysis. Precision expressed as relative standard error of triplicate analysis was between 0.2 to 12.1% for DP and TP concentrations. The relative standard error for PBAP and BAP concentrations ranged from 0.3 to 12.6% similar to other studies (Nurnberg et al., 2018). Pearson regression analysis was used to identify the relationship between SS and PP, PBAP, and between BAP and TP. In addition, Pearson product-moment correlation was used to clarify the relationship between POC, PON; and, POC, SS and elemental composition. A probability (p-value) of  $< 0.01$  was regarded as statistically significant in all cases unless otherwise specified. Statistical analysis were conducted Microsoft Excel Windows 10.

## References

- Anggara Kasih, G. A. and Kitada, T. 2004. Numerical simulation of water quality response to nutrient loading and sediment resuspension in Mikawa Bay, central Japan: Quantitative evaluation of the effects of nutrient-reduction measures on algal blooms, *Hydrological Processes*, 18(16), pp. 3037–3059. doi: 10.1002/hyp.5748.
- Gray, J.R., Glysson, G.D., Turcios, L.M. and Schwarz, G.E., 2000. Comparability of suspended-sediment concentration and total suspended solids data. *US Geological Survey Water-Resources Investigations Report 00-4191*, 20.
- <https://www.city.toyokawa.lg.jp/shisei/tokei/index.html>. accessed on 24 June 2019
- <http://www.city.toyohashi.lg.jp/1758.htm?turef=http%3A%2F%2Fwww.city.toyohashi.lg.jp%2F#itemid3255>. accessed on 24 June 2019)
- Komatsu K., Yano S., Gug S. and Kohashi N. 1999. A feasibility study on the water-purification method in a semi-enclosed bay by bottom roughness. In *Proceedings of the 12th Congress of ADP-IAHR*, Bangkok, Thailand; pp.385–394.
- Nürnberg, G.K., Fischer, R. and Paterson, A.M., 2018. Reduced phosphorus retention by anoxic bottom sediments after the remediation of an industrial acidified lake area: Indications from P, Al, and Fe sediment fractions. *Science of the Total Environment*, 626, pp.412-422.
- Marie Anne, B., Rio, M. and Noriyuki, K., 1997. ‘Tide versus eutrophication. Impact on ostracods populations structure of Mikawa Bay (Japan)’, *Revue de Micropaleontologie*, 40(1), pp. 3–13. doi: 10.1016/S0035-1598(97)90080-5.
- Murakami K., 1998. *Study on hydraulics and water quality environmental and enclosed coastal and its improvement techniques*. Technical Report No. 900, The Port and Harbor Research Institute Nagase, Yokosuka, Japan Seas (in Japanese).
- Murphy JA, Riley JP., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, 27, pp. 31-36.
- Ngoc NM., Inoue T. and Yokota K. 2016 Ultrasonic treatment for quantification of bioavailable phosphorus in soils and suspended sediments. *Water Science and Technology: Water Supply*, 16(6) pp.1745-1752. <https://doi.org/10.2166/ws.2016.100>
- Rasul, E., Inoue, T., Aoki, S., Yokota, K., Matsumoto, Y., Okubo Y., 2013. Nutrient enrichment and physical environmental effects caused by typhoons in a semi-enclosed bay, *Journal of Ecotechnology Research*, 17 (3–4) (2013) 107–114. <https://doi.org/10.11190/jer.17.107>
- Sakamoto, M. and Tanaka, T. 1989. ‘Phosphorus dynamics associated with phytoplankton blooms in eutrophic Mikawa Bay, Japan’, *Marine Biology*, 101(2), pp. 265–271. doi: 10.1007/BF00391466.
- Suzuki T. 2001. Oxygen-deficient waters along the Japanese coast and their effects upon the estuarine ecosystem. *Journal of Environmental Quality*, 30(2), pp.291-302.



## **Chapter 3      Phosphorus fractions in rivers impacted by catchment land use**

### **Summary**

Eutrophication of surface waters resulting from excessive phosphorus (P) inputs is one of the current challenging environmental issues. Riverine total phosphorus (TP) concentrations have high temporal patterns influenced by changing flow conditions with both DP and PP exhibiting significant variability. In this part of the thesis, DP, PP and suspended sediment (SS) concentration in rivers draining through contrasting land uses was evaluated. PP was the dominant fraction at high flow in the agricultural river whereas DP dominated at low flow. In the urban river, DP was almost always the main P fraction during high and low flow conditions. A significant statistical relationship was observed between PP, TP, and SS in the river classed as agricultural in contrast to the urban one where no correlation was observed, implying that the particle size and composition of SS in both rivers was markedly different. Continuous monitoring of P fractions and SS in the agricultural river during a storm event, revealed significant correlation between PP, TP and SS for both the rising and falling river-flow depth, indicating a near-river or within river channel mobilization of P and SS.

### 3.1 Introduction

Eutrophication has emerged as a global problem that produces a myriad of negative effects including nuisance algae blooms, hypoxia and fish kills, taste and odor problems, toxins and trihalomethanes in drinking water supplies (Smith and Schindler et al., 2009; Anderson et al., 2002). Eutrophication of water bodies is attributed to excessive input of nutrients such as, nitrogen (N) and phosphorus (P), commonly derived from anthropogenic activities in the watershed. There is increased consensus that, in most freshwaters, algal growth is limited by P input (Schindler et al., 2016; Carpenter, 2008). Consequently, emphasis has been placed on the quantification of P in water owing to its fundamental value as a plant nutrient and major cellular constituent (Sylvan et al., 2006).

The speciation of P in natural waters is quite complex (Lukkari et al., 2007; McKelvie et al., 1995), and total P (TP) has been widely used as a standard for assessing the eutrophication potential, yet only some forms of P are available to algae (Ekholm and Krogerus, 2003; Bostrom et al., 1988). Total P in aquatic ecosystems is comprised of dissolved P (DP) and particulate P (PP) forms. DP is considered mostly available for algal uptake (Reynolds and Davies, 2001), while PP, which encompasses P associated with suspended sediment (SS) and organic material eroded during runoff, contributes a variable but long-term source of bioavailable PP (Baker et al., 2014; Ellison and Brett, 2006; Sharpley and Menzel, 1987). PP normally accounts for the major part of TP in riverine and lacustrine environments (Bridgeman et al., 2012), and PP can consist of a several different fractions that range in bioavailability from loosely sorbed orthophosphate that may be considered readily bioavailable, to P that is refractory as it is tightly bound in the lattice of apatite minerals (Kerr et al., 2011; Pacini and Gachter, 1999; Bostrom et al., 1988). PP discharged from point and diffuse sources such as agricultural or urban runoff, is thought to be rapidly transported downstream to lakes (Colborne et al., 2019; Bridgeman et al., 2012) or bays through rivers. This may be the most important case in Japan because of meteorological conditions like periodic storm events and the short length of rivers (Yamada et al., 2005).

The discharged PP includes particulate bioavailable P (PBAP), some of which dissolves in the water column by the time it reaches the downstream bay or lake (Uusitalo et al., 2000; Jensen et al., 2006). In some cases, particulate BAP (PBAP) often exceeded DP concentration in tilled watersheds (Sharpley and Smith, 1993). Consequently, the varying amounts and bioavailability of DP and PP transported in different runoff events emphasize the need for their continuous assessment so as to evaluate the impact of runoff on the primary productivity of surface waters (Bowes et al., 2005; Ruzzycki et al., 2014; Shinohara et al., 2018), which is associated with proliferation of algae blooms. Even under conditions where total P loading does not change, variation in the stoichiometry of DP and PP can have detrimental impacts on receiving waters (Colborne et al., 2019; Lin et al., 2015). For example, recent record algae blooms in Lake Erie are attributed in part to an increase in the concentration of DP supplied from tributary rivers (Baker et al., 2014; Scavia et al., 2014). In rivers, P concentrations are highly variable over time, with storm events potentially contributing significantly to overall fluxes (Jordan et al., 2007; Cassidy and Jordan, 2011). Hence adequate monitoring of different riverine P forms and other highly variable parameters such as SS in rivers impacted by different land use patterns is paramount for water quality management.

The literature on P presents highly variable results as several studies do not explicitly evaluate the relationships between P fractions and SS in different types of rivers concurrently during high and low flow conditions. This part of the study investigated the variation in SS, DP, PP and TP in rivers draining through contrasting land uses. The main aim was to compare the variation in SS and PP concentration in order to assess whether SS can be used as a proxy for PP in the urban and agricultural river. Further, the relationship between SS and TP for both rivers was assessed, especially taking into account the change in the measured parameters during a continuous monitoring event in the agricultural river when there was rising and falling flow-depth.

### **3.2 Sampling protocol and analysis**

Grab water samples were taken from the rivers at varying flow conditions during the period May 2016 to May 2019.

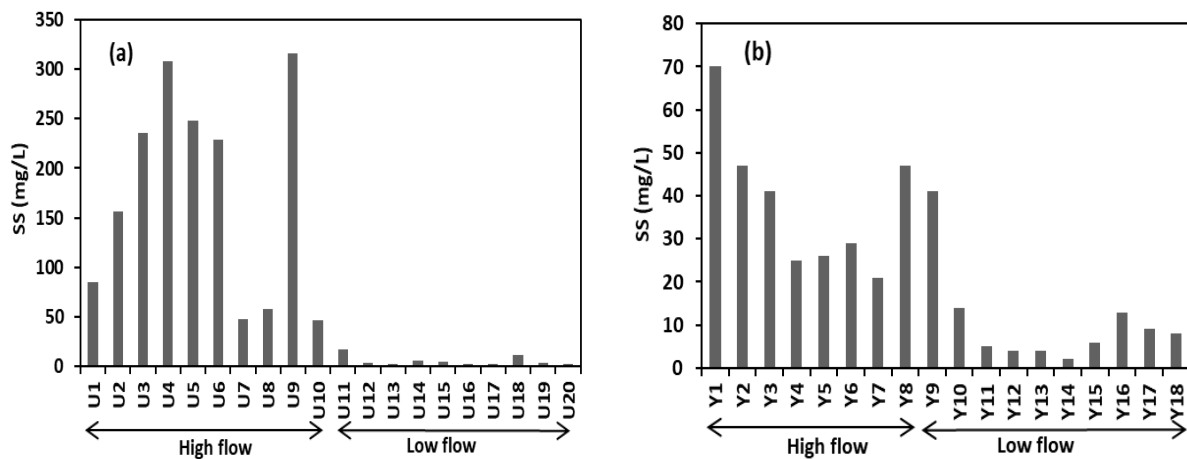
Both rivers were sampled during low flow conditions, and again during high flow. The high flow samples were collected during or immediately after rain events, when there was elevated runoff in both rivers. Low flow samples were collected at the time of no rain or prior to rain events. The samples were collected in 20 L containers that had been rinsed with analytical grade deionized water. Additionally, more water samples were collected continuously at different time intervals during a storm event of 24/25<sup>th</sup> April 2018. This was meant to gain a deeper understanding of the fluctuation in SS, DP, PP and TP in the agricultural river during the rising and falling flow-depth. Immediately after collection, all samples were transported to the laboratory and stored at 4 °C prior to analysis of DP, TP and SS concentration typically within 24 hours. In order to reduce the effects of sample storage on DP concentrations, the samples were filtered upon returning to the laboratory. The SS and P concentrations were measured following the procedures described in Chapter 2.

### 3.3 Results and discussion

#### 3.3.1 Variability of Suspended Sediment and Phosphorus fractions

##### Suspended sediment concentration

For the agricultural river, elevated SS concentration was associated with high flow during or after storm events when sampling was conducted. SS concentration varied from 48 to 316 mg/L for high flow samples collected from the agricultural river. SS declined at low flow periods ranging between 2 to 17 mg/L (**Figure 3.1a**).



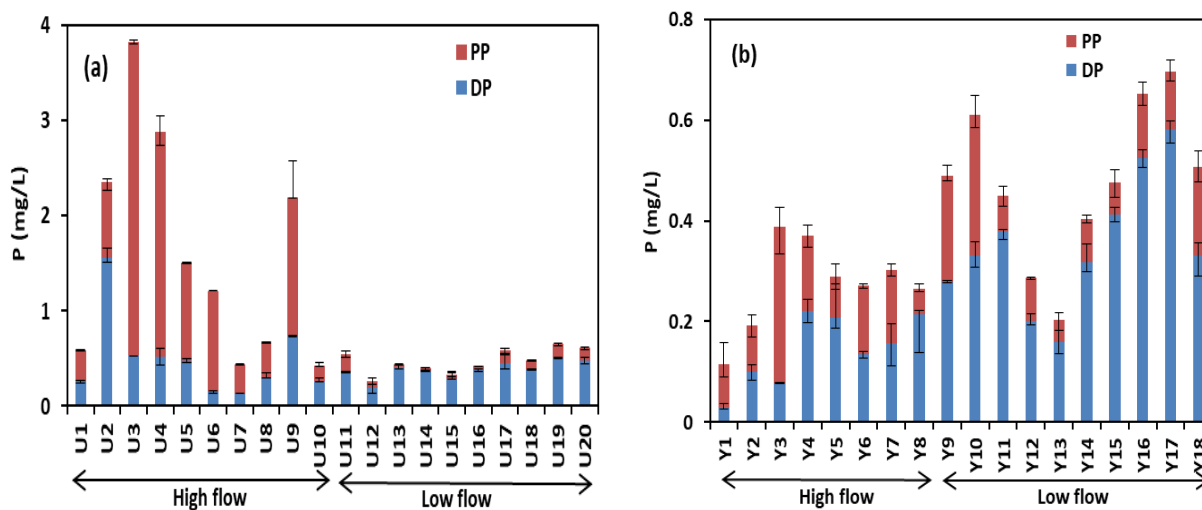
**Figure 3.1:** SS concentration in river runoff; (a) agricultural river, (b) urban river

SS concentrations were most influenced by flow state, and SS was substantially higher at high flow as compared to low flow. SS was also significantly related to land use type with higher concentrations in the agricultural river as compared to the urban river. High SS concentration in Umeda river was possibly due to eroded soil since the river flows through intensively cultivated areas. On the other hand, SS was considerably lower in Yagyu river as it flows through an urban area with a large percentage of paved areas which are largely impervious. The SS concentration ranged from 21 to 70 mg/L at high flow in the urban river, with a significant variability between SS at different sampling periods during low flow (**Figure 3.1b**). The low flow samples (Y9) collected from the urban river had elevated SS concentration almost similar to that of the high flow samples. This could be due to sediment resuspension from the river bed as the sampling was conducted prior to the start of rain. It has been suggested that during base-flow, low flows continually erode river banks which suspend new sediments within the water column (Ellison and Brett, 2006). This is of particular significance as resuspension can release P from river bed sediments hence contributing to internal loading and the resultant deterioration in water quality. Samples U3, U4, U9, Y1 and Y6 in both rivers were collected after typhoon events hence the elevated SS concentration. The extreme high flows resulting from typhoon events mobilise SS from different areas within the catchment which is subsequently entrained in river runoff.

### **Phosphorus fractions in the rivers**

At high flow in the agricultural river, DP concentration ranged from 0.13 to 1.56 mg/L whereas PP concentration varied from 0.15 to 3.29 mg/L (**Figure 3.2a**). For the urban river, P concentrations were considerably low at high flow with DP varying from 0.03 to 0.22 mg/L, and PP ranging between 0.05 to 0.31 mg/L (**Figure 3.2b**). Clearly, PP was the dominant fraction during high flow in the agricultural river whereas DP was the dominant fraction during low flow. In the urban river, DP was almost always the main form of P for both flow conditions. The high DP concentration in the rivers at low flow potentially contributes to algae growth in the downstream bay especially during ecological sensitive periods such as summer.





**Figure 3.2:** P concentration in the rivers; (a) agricultural river, (b) urban river. Error bars represent the standard error (n = 3)

In some cases, DP can be transformed into PP depending on the local pH at the sediment-water interface, redox potential and ambient temperature. Moreover, the PP concentration in both rivers at high flow was above the eutrophication limit of 0.02 mg/L in Japan (MoE, 2018). Since previous studies such as that by Baker et al. (2014) found that the bioavailability of PP exported from agricultural areas varies markedly (20-28%), further understanding of PP bioavailability would be of considerable importance for the correct evaluation of the eutrophication risks associated with PP delivery from different source areas.

PP is apparently associated with the fine solid fraction of particulate matter in runoff, and it was found that PP increased in parallel with the increase in SS concentration. Particulate P may be low during low flow but becomes the predominant form of transported P during storm events reaching elevated concentrations (Pacini and Gachter, 1999; Jensen et al., 2006). Therefore, low flow DP concentrations and high flow PP concentrations contributed to the fluctuations in TP over time. DP relates to land use type, and both DP and TP concentrations were highest in the agricultural river at high flow. This could be attributed to leaching of dissolved P from the catchment's soil which may have a build-up of phosphate resulting from fertilizers and manure applied in the cultivated fields.

Despite the relatively high SS concentration in sample U5 and U6, PP concentration was low as compared to other high flow samples. At the time of sampling, the volume of runoff was unusually high resulting in the mobilization of a larger amount of SS. With the higher volume at the time of rain, we could intuitively assume that high flows transport a higher proportion of coarse particles with less P than do low flows. Additionally, sediments deposited after a period of high water levels originate partly from the watershed and do not depend only on soil characteristics, but also on the physical and chemical processes governing P mobility during sediment transport and deposition (Sharpley and Menzel, 1987). This scenario could account for the high PP concentration observed in sample U3, U4 and U9 which correlated with SS concentration at the same period (**Figure 3.1a and Figure 3.2b**). These samples were collected at high flow after typhoon events that marked the end of the dry season and the onset of planting in the agricultural fields. Further, it has been reported that rapid decrease of DP concentration following increased SS concentration reflects adsorption processes that can occur in the space of a few hours in response to alteration of ambient equilibrium DP concentration (Pacini and Gachter, 1999).

### ***3.3.2 Effect of increasing flow on P fractions and SS in the agricultural river***

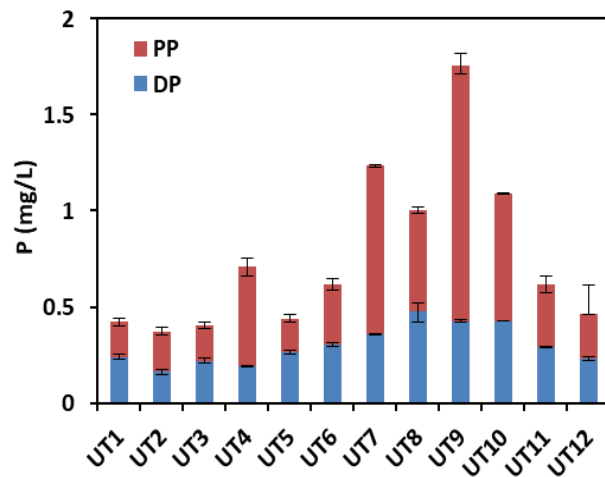
#### **Insights from a continuous sampling event**

Due to the observed spikes in SS concentration in the agricultural river at high flow, it became critical to assess how the P forms and SS fluctuate during an entire storm event. In order to understand this, a continuous sampling survey was conducted during and after a rain event of 24/25 April 2018. The results obtained (**Table 3.1**) reveal several aspects of P and SS behavior on the rising and falling limb of event hydrograph as discussed below. Generally SS, DP, PP and TP all increased with the rising limb of the hydrograph as the flow depth in the river increased (**Table 3.1; Figure 3.3**). With the increasing flow depth, DP slightly declined from 0.24 mg/L at the start of the sampling (UT1) to 0.17 mg/L after a few hours possibly due to dilution with incoming river water. Thereafter, DP concentration showed a steady increase with rising flow in the river channel in concert with PP concentration (**Figure 3.3**).

**Table 3.1:** SS and P fractions in the agricultural river during a storm event

	Time	Sample ID	Flow depth (m)	SS	mg/L		
					DP	PP	TP
Rising flow depth	15:00	UT1	0.80	2	0.24	0.18	0.42
	22:00	UT2	1.11	23	0.17	0.21	0.37
	2:00	UT3	1.05	11	0.22	0.19	0.41
	4:00	UT4	1.47	71	0.19	0.51	0.71
	6:00	UT5	1.61	116	0.27	0.18	0.44
	7:00	UT6	1.84	64	0.30	0.31	0.62
	8:00	UT7	2.00	145	0.36	0.88	1.23
Falling flow depth	9:00	UT8	1.98	70	0.48	0.53	1.00
	10:00	UT9	1.51	76	0.42	1.33	1.75
	12:00	UT10	1.22	61	0.43	0.66	1.09
	15:00	UT11	1.10	31	0.29	0.32	0.62
	18:00	UT12	0.75	22	0.23	0.24	0.47

\*UT1 denotes sample collected from the agricultural river at time T1. 12 samples were collected in total at different intervals



**Figure 3.3:** P fractions in the agricultural river during a continuously monitored storm

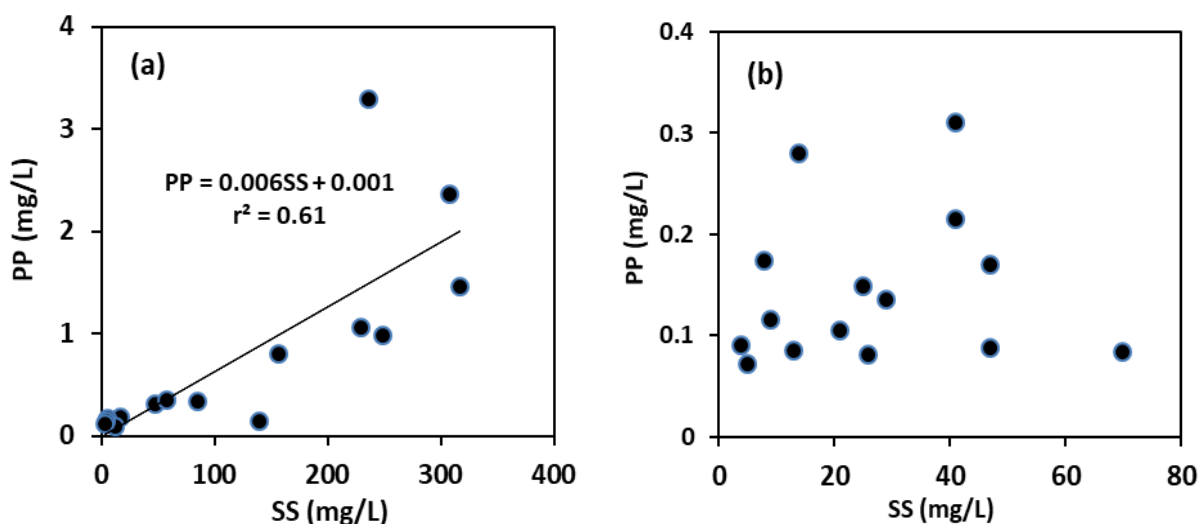
The hysteresis pattern of P fractions with SS showed a positive trajectory for the entire duration of the sampling event, indicating the mobilization of within-channel and riverbank phosphorus, and rapid inputs of runoff P from agricultural field drains.

Phosphorus fractions declined to pre-storm levels on the falling limb of the flow event - hydrograph at the end of the continuous sampling campaign potentially due to reduced SS amounts and the bound P.

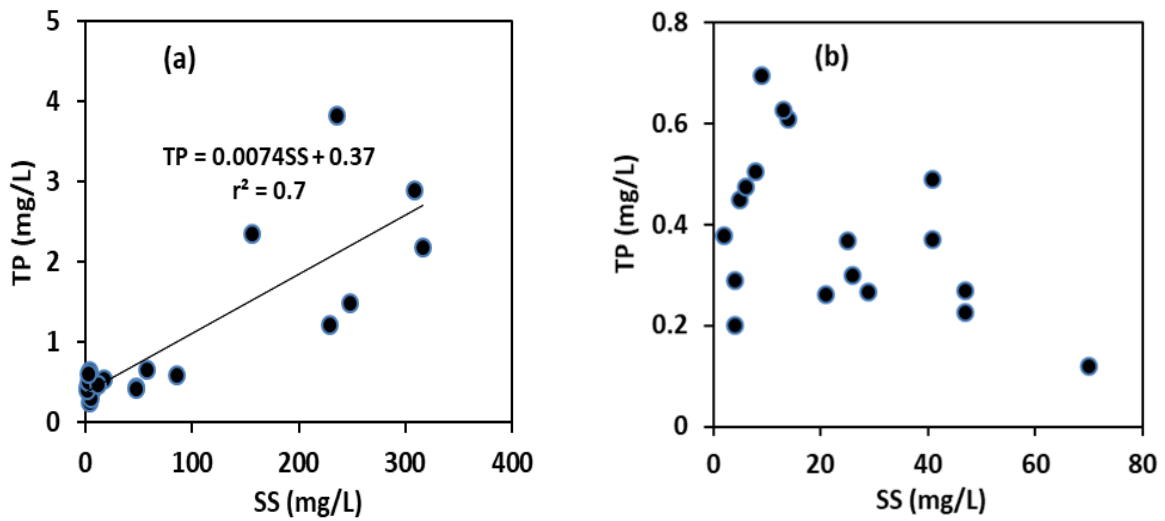
### 3.3.3 SS as a proxy for PP and TP in the rivers

The concentration of PP in the agricultural river plotted against SS concentration gave a moderate statistical relationship ( $r^2 = 0.61$ ,  $p < 0.01$ ) (**Figure 3.4a**), indicating that PP increased with SS concentration in river runoff. This was consistent with the findings of other studies (Uusitalo et al., 2000). Since PP is normally associated with fine sediments, it is presumable that SS in the agricultural river consists of mainly clay and silt particles resulting from erosion in cultivated fields. On the otherhand, no correlation was observed between PP and SS in the urban river (**Figure 3.4b**). PP didn't match SS dynamics in the urban river, an indication that the SS composition in the urban river could be different from that in the agricultural river. As most of the urban river catchment is paved with a large percentage of impervious surfaces, erosion is minimal and SS in runoff largely consists of coarse sand particles which are considered to carry less PP.

TP was significantly correlated with SS in the agricultural river ( $r^2 = 0.7$ ,  $p < 0.01$ ) unlike the urban river where no correlation was observed (**Figure 3.5**).



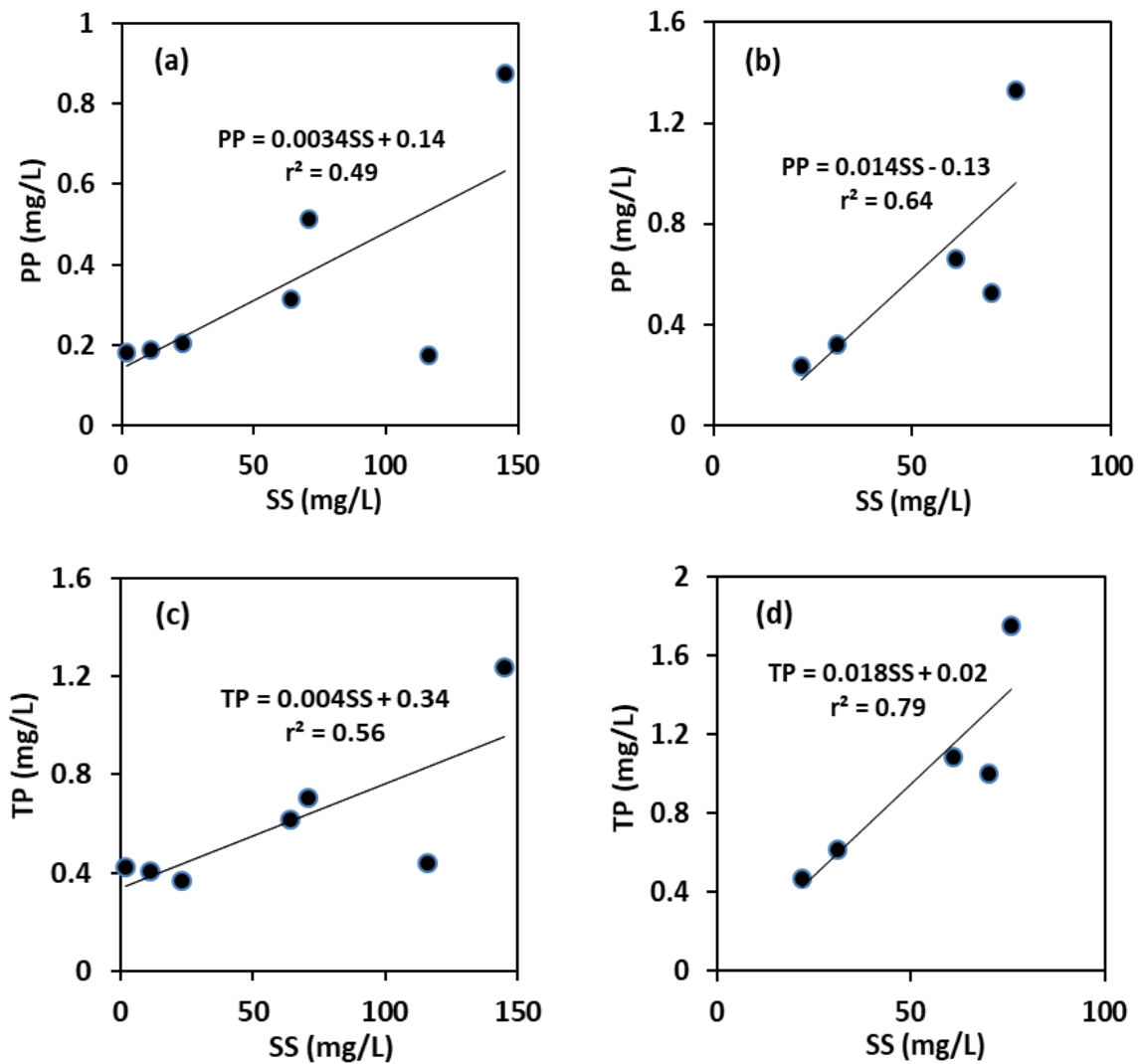
**Figure 3.4:** Correlation between PP and SS; (a) agricultural river; (b) urban river



**Figure 3.5:** Correlation between TP and SS; (a) agricultural river; (b) urban river

The positive relationship between SS and TP in the agricultural river was consistent with previous studies (Jones et al., 2011; Ruzycki et al., 2014). It was however important to analyse the factors affecting these correlations to better evaluate the usefulness of SS as a proxy for PP and TP under varying flow conditions. Processes controlling TP concentrations in rivers may explain why the correlation between TP and SS varies significantly between rivers. Lannergård et al. (2019) noted that streams with low correlations between the parameters but high TP concentrations could be affected by point sources. On the otherhand, streams with high correlations and high TP concentrations were likely to drain agricultural areas with significant amounts of P transport connected to SS and particulate organic matter. This was the case for the agricultural river in our study as the river drains through intensive farmlands which contribute sediment bound P in surface runoff that ultimately ends up in the river channel. However, TP concentrations in the urban river were almost always less than those in the agricultural river largely due to the elevated PP concentrations in concert with high SS content in the agricultural river runoff.

In order to unravel the behavior between PP, TP and SS in the agricultural river, assessment of the fluctuation in P fractions and SS during a storm event is always necessary.



**Figure 3.6:** Relationship between PP, TP, and SS during the rising and falling flow depth in the agricultural river; **(a)** Relationship between PP and SS during rising flow depth; **(b)** PP and SS during falling flow depth; **(c)** TP and SS during rising flow; **(d)** TP and SS during falling flow depth.

To this end, a sustained sampling campaign was carried out during a storm event so as to determine whether a positive correlation exists between PP, TP and SS, during increasing and declining flow-depth in the agricultural river. The relationship between PP, TP, and SS was significant on both the rising and falling river flow-depth (**Figure 3.6**). This points to a clockwise hysteresis pattern possibly indicating a continuous near river or within-river channel mobilisation of P and SS in the agricultural river.

Most previous studies (Williams, 1989; Bowes et al., 2005) have also observed similar relationships during storm events pointing to the increase in external phosphorus being mobilised from the marginal zone, as a consequence of rising river levels.

### 3.4 Conclusions

The fluctuation of P fractions and SS in rivers draining through different land uses was assessed in this study. Often, PP was the dominant fraction during high flow in the agricultural river in contrast to low flow periods when DP dominated. The DP fraction was consistently higher than PP in urban river at either low or high flow conditions. Positive correlations were observed between PP, TP, and SS in the agricultural river in contrast to the urban river where no correlation was exhibited between the parameters. This potentially was due to the differing particle size and composition in the rivers, with fine sediment having high bound P, most likely abundant in the agricultural river unlike the urban river where coarse sediment particles dominate. Continuous monitoring of P fractions and SS in the agricultural river during a storm event, revealed significant correlation between PP, TP and SS for both the rising and falling river-flow depth, indicating a near-river or within river channel mobilization of P and SS.

### References

- Baker, D.B., Confesor, R., Ewing, D.E., Johnson, L.T., Kramer, J.W. and Merryfield, B.J., 2014. Phosphorus loading to Lake Erie from the Maumee, Sandusky and Cuyahoga rivers: The importance of bioavailability. *Journal of Great Lakes Research*, 40(3), pp.502-517, <https://doi.org/10.1016/j.jglr.2014.05.001>
- Boström, B., Persson, G. and Broberg, B., 1988. Bioavailability of different phosphorus forms in freshwater systems. *Hydrobiologia*, 170(1), pp.133-155, <https://doi.org/10.1007/BF00024902>
- Bowes, M.J., House, W.A., Hodgkinson, R.A. and Leach, D.V., 2005. Phosphorus–discharge hysteresis during storm events along a river catchment: the River Swale, UK. *Water Research*, 39(5), pp.751-762.
- Bridgeman, T.B., Chaffin, J.D., Kane, D.D., Conroy, J.D., Panek, S.E. and Armenio, P.M., 2012. From River to Lake: Phosphorus partitioning and algal community compositional changes in Western Lake Erie. *Journal of Great Lakes Research*, 38(1), pp.90-97.

- Carpenter, S.R., 2008. Phosphorus control is critical to mitigating eutrophication. *Proceedings of the National Academy of Sciences, USA*, 105(32), pp.11039-11040.
- Cassidy, R. and Jordan, P., 2011. Limitations of instantaneous water quality sampling in surface-water catchments: comparison with near-continuous phosphorus time series data. *Journal of Hydrology*, 405(1–2), pp.182–193
- Colborne, S.F., Maguire, T.J., Mayer, B., Nightingale, M., Enns, G.E., Fisk, A.T. and Drouillard et al., 2019. Water and sediment as sources of phosphate in aquatic ecosystems: The Detroit River and its role in the Laurentian Great Lakes. *Science of The Total Environment*, 647, pp.1594-1603.
- Ekholm, P. and Krogerus, K., 2003. Determining algal-available phosphorus of differing origin: routine phosphorus analyses versus algal assays, *Hydrobiologia*, 492(1-3), 29-42.
- Ellison Brett, M.E. 2006. Particulate phosphorus bioavailability as a function of stream flow and land cover. *Water Research*, 40, pp.1258-1268, <https://doi.org/10.1016/j.watres.2006.01.016>
- Jensen, H.S., Bendixen, T., Andersen, F.O., 2006. Transformation of particle-bound phosphorus at the land–Sea interface in a Danish Estuary. *Water, Air and Soil Pollution: Focus*, 6(5-6), pp.547-555. <https://doi.org/10.1007/s11267-006-9038-1>
- Jones, A.S., Stevens, D.K., Horsburgh, J.S. and Mesner, N.O., 2011. Surrogate Measures for Providing High Frequency Estimates of Total Suspended Solids and Total Phosphorus Concentrations 1. *JAWRA Journal of the American Water Resources Association*, 47(2), pp.239-253.
- Jordan, P., Arnscheidt, A., McGrogan, H. and McCormick, S., 2007. Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser. *Hydrology Earth System Science Discussion*, 11(1), pp.372–381
- Kerr, J.G., Burford, M.A., Olley, J.M., Bunn, S.E. and Udy, J., 2011. Examining the link between terrestrial and aquatic phosphorus speciation in a subtropical catchment: the role of selective erosion and transport of fine sediments during storm events. *Water Research*, 45(11), pp.3331-3340.
- Lannergård, E.E., Ledesma, J.L., Fölster, J. and Futter, M.N., 2019. An evaluation of high frequency turbidity as a proxy for riverine total phosphorus concentrations. *Science of the Total Environment*, 651, pp.103-113.
- Lin, J., Klump, J.V., Guo, L., 2015. Dynamics of dissolved and particulate phosphorus influenced by seasonal hypoxia in Green Bay, Lake Michigan, *Science of the Total Environment*, 541, pp.1070-1082. <https://doi.org/10.1016/j.scitotenv.2015.09.118>
- Lukkari, K., Hartikainen, H. and Leivuori, M., 2007. Fractionation of sediment phosphorus revisited. I: Fractionation steps and their biogeochemical basis. *Limnology and Oceanography: Methods*, 5(12), pp.433-444. <https://doi.org/10.4319/lom.2007.5.433>
- McKelvie, I.D., Peat, D.M., Worsfold, P.J., 1995. Analytical perspective. Techniques for the quantification and speciation of phosphorus in natural waters, in: *Analytical Proceeding Including Analytical Communication, Royal Society of Chemistry*, 32(10), pp. 437-445.



- MoE., 2018 Ministry of the Environment - Government of Japan. Environmental Quality Standards for Water pollution, Nitrogen and Phosphorus for Rivers, Lakes and Coastal waters. Available online: <http://www.env.go.jp/kijun/index.html>, accessed 26 September 2018.
- Pacini, N. and Gächter, R., 1999. Speciation of riverine particulate phosphorus during rain events. *Biogeochemistry*, 47(1), pp.87-109, <https://doi.org/10.1007/BF00993098>
- Reynolds, C.S. and Davies, P.S., 2001. Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. *Biological Reviews*, 76(1), pp.27-64.
- Ruzycski, E.M., Axler, R.P., Host, G.E., Henneck, J.R. and Will, N.R. 2014. Estimating sediment and nutrient loads in four western lake superior streams. *Journal of American Water Resource Association*, 50 (5), pp.1138–1154.
- Scavia, D., Allan, J.D., Arend, K.K., Bartell, S., Beletsky, D., Bosch, N.S., Brandt, S.B., Briland et al., 2014. Assessing and addressing the re-eutrophication of Lake Erie: Central basin hypoxia. *Journal of Great Lakes Research*, 40(2), 226-246. <https://doi.org/10.1016/j.jglr.2014.02.004>
- Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E. and Orihel, D.M., 2016. Reducing phosphorus to curb lake eutrophication is a success. *Environmental Science and Technology*, 50(17), pp.8923–8929. <https://pubs.acs.org/doi/abs/10.1021/acs.est.6b02204>
- Sharpley, A.N. and Smith, S.J., 1993. Prediction of bioavailable phosphorus loss in agricultural runoff. *Journal of Environmental Quality*, 22(1), pp.32-37.
- Sharpley, A.N. and Menzel, R.G., 1987. The impact of soil and fertilizer phosphorus on the environment, *Advances in Agronomy*, 41, pp.297-324. [https://doi.org/10.1016/S0065-2113\(08\)60807-X](https://doi.org/10.1016/S0065-2113(08)60807-X)
- Shinohara, R., Ouellette, L., Nowell, P., Parsons, C.T., Shin-ichiro, S.M. and Voroney, R.P., 2018. The composition of particulate phosphorus: A case study of the Grand River, Canada. *Journal of Great Lakes Research*, 44(3), pp.527-534.
- Smith, V.H. and Schindler, D.W., 2009. Eutrophication science: where do we go from here?, *Trends in Ecology and Evolution*, 24(4), pp.201-207. <https://doi.org/10.1016/j.tree.2008.11.009>
- Sylvan, J.B., Dortch, Q., Nelson, D.M., Maier Brown, A.F., Morrison, W., Ammerman, J.W., 2006. Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation, *Environmental Science and Technology*, 40(24), pp.7548-7553.
- Uusitalo, R., Yli-halla, M., Turtola, E., 2000. Suspended soil as a source of potentially bioavailable phosphorus in surface runoff water from clay soil. *Water Research*, 34(9), pp.2477-2482. [https://doi.org/10.1016/S0043-1354\(99\)00419-4](https://doi.org/10.1016/S0043-1354(99)00419-4)
- Williams, G.P., 1989. Sediment concentration versus water discharge during single hydrologic events in rivers. *Journal of Hydrology*, 111, pp. 89–106
- Yamada, Y. and Inoue, T., 2005. Influence of phosphorus runoff from agricultural areas on enclosed sea downstream, *Journal of Water and Environmental Technology*, 3(2), pp.157-164.

## **Chapter 4      Phosphorus bioavailability in an agricultural and urban river**

### **Summary**

Bioavailable phosphorus (BAP) is a constituent of total phosphorus (TP) that accelerates algae growth in aquatic ecosystems. BAP is comprised of dissolved phosphorus (DP) and a portion of particulate phosphorus (PP). Algal assays and chemical extractions have been applied to determine BAP, despite several constraints such as long extraction time and high costs hindering their frequent use. Here, a new rapid procedure which involves ultrasonic treatment was used to extract BAP from suspended sediment (SS) samples. This part of the study aimed to assess particulate bioavailable phosphorus (PBAP) and BAP in runoff from rivers flowing through different land uses, and the relationship with SS and TP respectively. PP was the dominant fraction of TP at high flow and between 6 to 79% of PP was estimated to be bioavailable. A strong statistical relationship was observed between PBAP and SS in the river classed as agricultural ( $r^2 = 0.69$ ), in contrast to the urban one where no correlation was observed, pointing to the difference in the particle size and composition of SS in the rivers. A strong correlation was observed between BAP and TP in the urban river ( $r^2 = 0.84$ ), indicating TP could be a reliable substitute for BAP in assessment of the eutrophication potential. However, the BAP and TP relationship in the agricultural river revealed that elevated PP concentration at high flow may not translate into higher BAP in runoff, implying that quantification of BAP in SS is critical for the effective implementation of watershed management programs.

## 4.1 Introduction

Regardless of the large efforts to regulate nutrient inputs to surface waters, eutrophication is a recurring problem in several parts of the world (Sharpley et al., 2013), and is considered to be one of today's most challenging water quality issues in developed countries (Cassidy and Jordan, 2011). There is now increased consensus that, freshwater productivity is limited by P inputs (Schindler et al., 2016; Carpenter, 2008). Total P (TP) has been widely used as a standard for assessing the eutrophication potential in aquatic environments, yet only some forms of P are biologically available to algae (Anderson et al., 2002; Ekholm and Krogerus, 2003; Bostrom et al., 1988). Hence, bioavailable phosphorus (BAP) transported in runoff can exacerbate eutrophication of aquatic ecosystems (Baker et al., 2014; Abell et al., 2013; Ekholm, 1994). BAP represents primarily soluble orthophosphate that is immediately available for algal uptake (Reynolds and Davies, 2001), -and comprises P in dissolved (DP) and particulate (PP) forms (Van Moorlehem et al., 2013; Uusitalo et al., 2000). Further, P species other than orthophosphate, such as polyphosphate, orthophosphate monoesters, and diesters, are also potentially bioavailable since they are degraded in the sediment and water column (Shinohara et al., 2012), by enzymatic or surface catalyzed hydrolysis reactions. Hence, DP is considered mostly available for algal uptake (Reynolds and Davies, 2001), while PP, which encompasses P associated with suspended sediment (SS) and organic material eroded during runoff, contributes a variable but long-term source of bioavailable PP (Ellison and Brett, 2006). PP normally accounts for the major part of TP in riverine and lacustrine environments (Bridgeman et al., 2012), and PP can consist of a several different fractions that range in bioavailability from loosely sorbed orthophosphate that may be considered readily bioavailable, to P that is refractory as it is tightly bound in the lattice of apatite minerals (Bostrom et al., 1988).

The BAP concentration of runoff or SS can be derived from algal assay tests (Ekholm and Krogerus, 2003; Miller and Greene, 1978). This method has been considered superior as it depicts the growth response of P-limited algae, though it is labor-intensive and time consuming taking a minimum of 14 days for algae to reach maximum growth.

Therefore, chemical extraction procedures which mimic the removal of P by algae have been used for the routine determination of BAP (Ekholm and Krogerus, 2003; Baker et al., 2014). In most cases, chemical sequential extraction schemes based on the fractionation of P have been widely adopted for the measurement of BAP (Lukkari et al., 2007; Pacini and Gachter, 1999; Hupfer et al., 1995). However, the extraction process takes at least 17 hours per sequence (Gu et al., 2016), and the use of strong acidic or alkaline solvents for a long duration may interfere with the physico-chemical structure of extracted phosphorus, hence affecting the accuracy of BAP measurement. Single extraction with 0.1M NaOH has been used, and P concentrations measured by this extraction technique have been found to be similar to BAP concentrations estimated from algal assay experiments (Baker et al., 2014; Sharpley et al., 1991; Dorich et al., 1985). Despite the single extraction method being the most commonly used to measure particulate BAP, the extraction process takes around 17 hours.

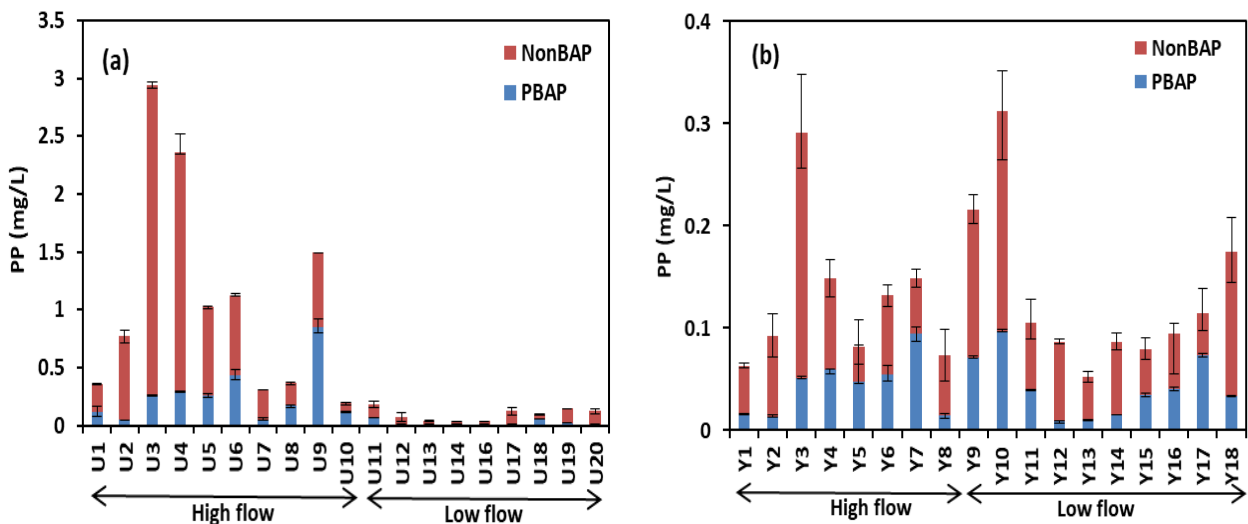
Here, a new rapid procedure was adopted which involves ultrasonic extraction of BAP from SS samples using 0.1M NaOH solution (Ngoc et al., 2017). Measurement of bioavailability of the particulate P fraction of runoff allows estimation of the percentage of total P that could ultimately be available to algae. Such estimates would be more realistic inputs in consideration of nutrient management efforts than would total P values since not all P is bioavailable. Previous studies on P bioavailability depict significant gaps as several studies do not explicitly compare the relationships between the PBAP fraction and SS in different types of rivers concurrently during high and low flow. In this thesis chapter, the variation in PBAP and BAP fractions in rivers draining through contrasting land uses was investigated. The objectives of the study were: (i) to estimate PBAP in runoff from agricultural and urban rivers in order to assess whether the PBAP content was markedly different in the rivers, (ii) to determine the BAP proportion in river runoff, and to clarify its relationship with TP in the rivers.

## **4.2 Results and discussion**

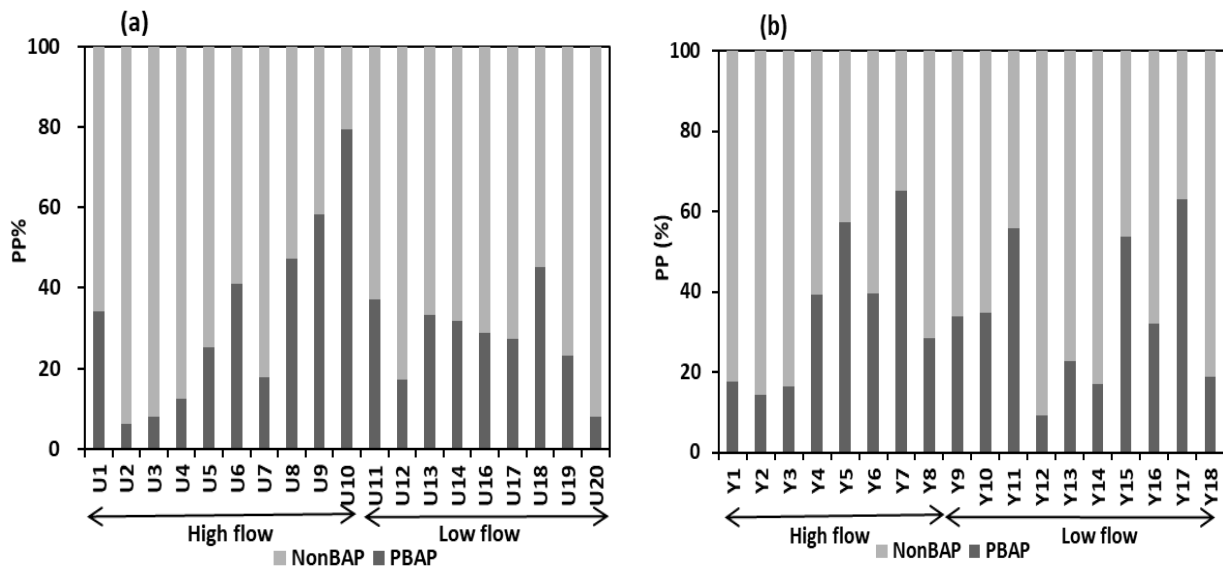
### ***4.2.1 Particulate bioavailable phosphorus in suspended sediments***

PBAP concentrations in urban and agricultural rivers at varying flow conditions are presented in **Figure 4.1**.

PBAP in the agricultural river was significantly affected by the change in river-flow with elevated concentration at high flow and reduced PBAP concentration at low flow (**Figure 4.1a**). On the contrary, PBAP in the urban river exhibited significant variability during high and low flow conditions (**Figure 4.1b**). The PBAP concentrations in the agricultural river were between 0.01 and 0.85 mg/L whereas for the urban river, PBAP concentrations ranged from 0.01 to 0.1 mg/L. During high flow, PBAP concentration was high in runoff from the agricultural river compared to the urban river. However at low flow, PBAP concentration increased in the urban river relative to agricultural river possibly due to release of bioavailable P by resuspended river-bed sediments. The bioavailability of PP in the agricultural river varied from 6 to 79% for samples collected at both high and low flows (**Figure 4.2a**). For the urban river, percentage PBAP varied from 9 to 65% at varying flow conditions (**Figure 4.2b**). This amount of PBAP derived from suspended sediment in the present study is similar (though slightly higher in some cases) to PBAP as reported by several investigations (**Table 4.1**). Young and DePinto (1982) observed a bioavailability between 6.1 and 35.8% of tributary particulate phosphorus. Baker et al. (2014) found that PBAP averaged 20 and 28% of PP for Maumee river which delivers the highest P load to Lake Erie. Poirier et al. (2012) also found that PBAP represented 23 to 47% of PP concentration in agricultural runoff.



**Figure 4.1:** PBAP concentration in runoff; (a) agricultural river, (b) urban river. Values are means of three replicate analyses; error bars indicate the positive and negative error

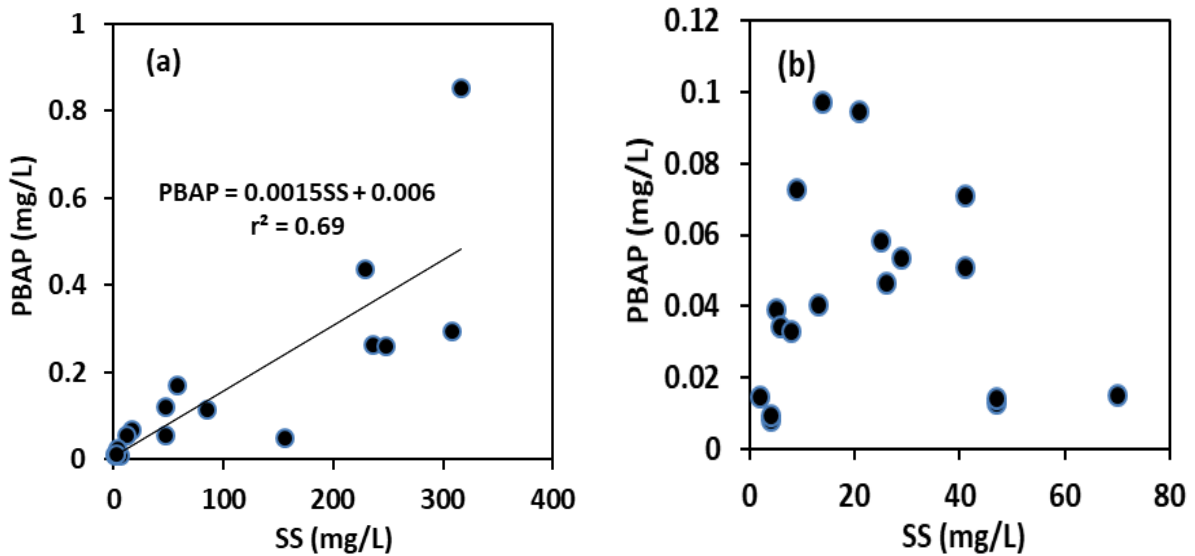


**Figure 4.2:** Bioavailability of PP. PBAP and NonBAP are expressed as a percentage of PP; **(a)** agricultural river, **(b)** urban river

**Table 4.1:** Comparison of the PBAP estimated from this study and estimates from previous studies

Reference	Location	Study description	PBAP (%)
Dorich et al. (1985)	Indiana, USA	Particulate bioavailable phosphorus estimated by chemical extraction	33 to 45
DePinto et al. (1985)	Great Lakes, USA	Bioavailability of phosphorus in suspended sediments from lower Great Lakes Tributaries	4 to 38
Logan et al. (1979)	Great Lakes, USA	Bioavailability of PP in streams draining into Lake Erie	14 to 42
Engle and Sarnelle (1990)	Amazon river, Brazil	Algal use of sedimentary phosphorus from an Amazon floodplain lake	21 to 38
Maynard et al. (2009)	San Joaquin river, USA	Bioavailability and fate of agricultural runoff	36 to 52
Tu et al. (2019)	Ponte Tresa basin, Switzerland	Phosphorus fractions in sediments and their relevance for historical lake eutrophication	20 to 39
Pacini and Gachter, 1999	Kleine Aa stream, Switzerland	Speciation of riverine particulate phosphorus during rain events	11 to 40
Ballantine et al. (2008)	Shropshire, UK	Phosphorus content of fluvial suspended sediment in groundwater-dominated agricultural catchments	3 to 77
Walling et al. (2001)	UK	Nutrient content of suspended sediment transported by British rivers	48 to 59
Su et al. (2014)	Quebec, Canada	Phosphorus algal availability and release potential in suspended and streambed sediments	19
Poulenard et al. (2008)	French Alps, France	Fractionation of fine and colloidal particulate-phosphorus in riverbed and suspended sediments	40 to 50
Ye et al. (2017)	Changjiang, China	Phosphorus fraction distribution and influencing factors of suspended and surface sediments in the Tiaoxi watershed	45 to 51
This study	Toyohashi, Japan	Particulate bioavailable phosphorus in suspended sediments from agricultural and urban rivers	(6 to 79) <sup>a</sup> , (9 to 65) <sup>b</sup>

\*a – denotes agricultural river; b – denotes urban river



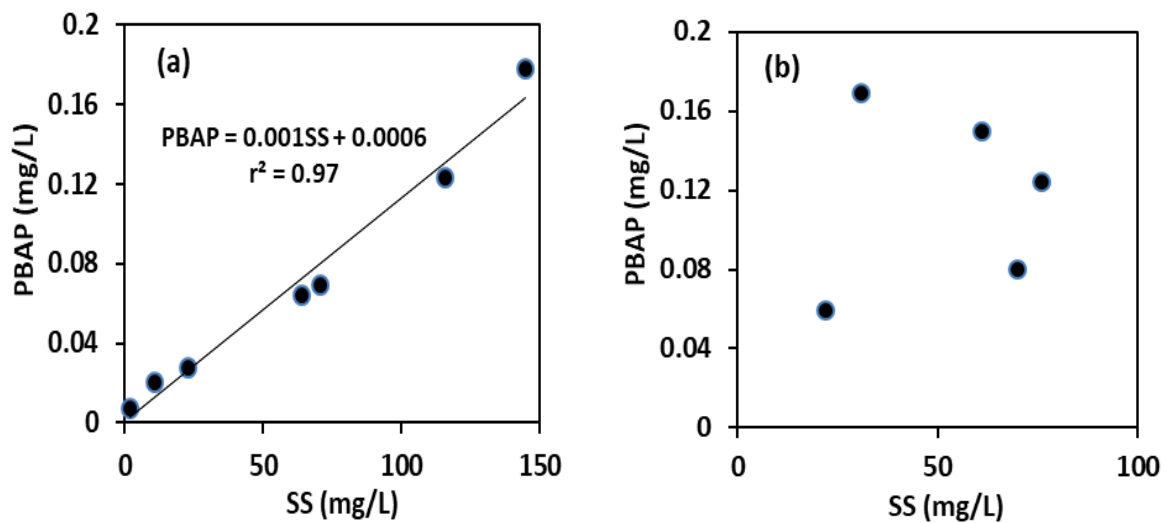
**Figure 4.3:** Relationship between PBAP and SS; (a) agricultural river, (b) urban river

Consequently, elevated PBAP in both rivers merits further investigation due to its potential bioavailability to algae in the downstream Mikawa bay especially during the low flow period in summer when eutrophication is likely to be extreme.

PBAP was strongly correlated with SS in the agricultural river ( $r^2 = 0.69$ ,  $p < 0.01$ ) (**Figure 4.3a**). This implies that since PP is associated with SS, increased surface runoff contributed to elevated PBAP concentrations. This was found to be the case as PBAP was positively correlated with SS ( $r^2 = 0.97$ ,  $p < 0.01$ ) for samples collected during the rising flow-depth in the agricultural river when continuous sampling of a storm event was conducted (**Figure 4.4a**). This potentially indicates that there is a continuous supply of fine sediment in agricultural river runoff during a storm event. The source of this fine sediment could be from a near river agricultural field drain or within river channel mobilization of SS and bound P. In a study examining the link between terrestrial and aquatic P speciation, Kerr et al. (2011) found that as finer particles are eroded from the soil surface during storm events, there is a preferential export of non-apatite P (PBAP) forms. Due to the preferential erosion and transport of fine SS during the rising flow periods, the associated labile P most likely accumulates in the receiving downstream bay area.

However, PBAP and SS exhibited an anticlockwise hysteresis pattern (**Figure 4.4b**) with no obvious correlation during the decline of the flow depth.





**Figure 4.4:** Relationship between PBAP and SS in the agricultural river; (a) during rising flow depth, (b) during declining flow depth

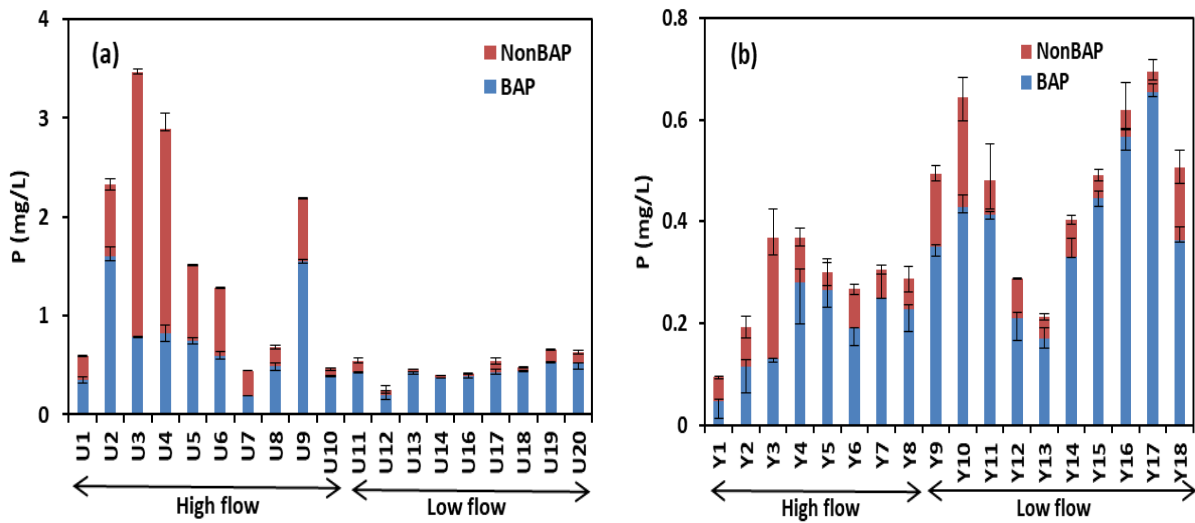
This potentially indicates the depletion of fine sediment source contribution, and possibly due to mixing of water originating from outside the agricultural river catchment. Suspended sediment in runoff from river U was yellowish brown in color unlike SS in river Y which was dark grey, and this could be an indication that eroded soil from cultivated areas was clayey in nature. Particulate BAP could be sorbed to SS entrained with orthophosphate resulting from manure and phosphate fertilizers from cultivated fields. Previous studies have shown that phosphorus is closely associated with clay particles which comprise fine sediments, and due to their high specific area, fine sediments carry a greater P load per unit mass than coarse sediment (Naden et al., 2010). In addition, (Ngoc et al., 2017) also noted that sediments which are yellowish brown in color may be so due to the presence of iron compounds. Since 0.1M NaOH extracts P bound to iron compounds (Lukkari et al., 2007; Hupfer et al., 1995), PBAP concentrations obtained by extracting SS from an agricultural river with NaOH would be higher than those obtained in SS from an urban river, where SS probably contains less iron. The difference in the color of SS in both rivers could also point to the difference in SS composition with the dark grey urban river SS potentially containing higher fractions of organic matter originating from the forested area upstream of the river.

It has been reported that PBAP is influenced by sediment composition (e.g., metal oxides or hydroxides, clay minerals, organic matter) which determine the magnitude of P retention and the pattern of P fractionation (Evans et al., 2004).

For the urban river, there was no obvious correlation between PBAP and SS concentration (**Figure 4.3b**). The contrasting relationship between PBAP and SS in both rivers points to the differing particle sizes in river runoff though assessment of the particle size range of the SS was not conducted in this study. Sediment particle size has been identified as one of the factors affecting sediment composition (Kerr et al., 2011; Palmer-Felgate et al., 2009), which ultimately influences the PBAP fraction of SS.

#### ***4.2.2 Bioavailable phosphorus in runoff***

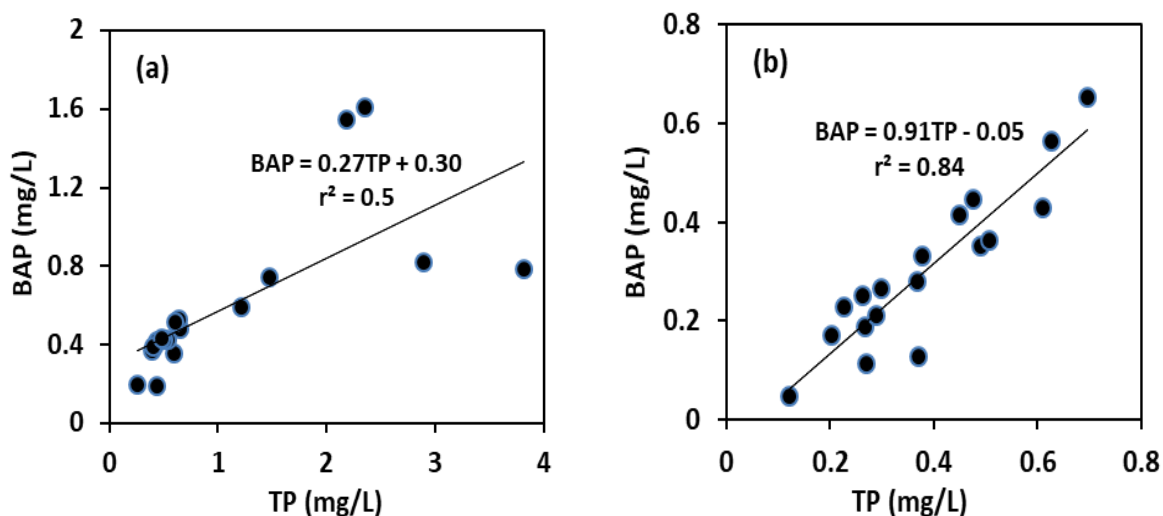
BAP concentration in the agricultural river ranged from 0.19 to 1.6 mg/L during high flow and from 0.2 to 0.53 mg/L during low flow (**Figure 4.5a**). In the urban river, BAP concentration ranged from 0.05 to 0.28 mg/L during high flow and from 0.17 to 0.65 mg/L during low flow (**Figure 4.5b**). Generally, elevated BAP concentrations were associated with low flow in the urban river. During high flow, BAP as a proportion of TP on average ranged from 60 to 68% for sample U1 and U2 whereas it was from 21 to 28% for sample U3 and U4 obtained from the agricultural river. High BAP amounts for sample U1 and U2 could be due to the influx of orthophosphate in runoff from cultivated fields when soils are loose after harvesting. Erosion and surface runoff control practices such as the use of buffer strips have been implemented in agricultural watersheds, but their use could be affecting the DP load. Michalak et al. (2013) also found that though agricultural erosion control programs such as no-till, reduced till and buffer strips, have reduced SS and PP loading in Lake Erie tributaries over the years, more bioavailable DP forms have increased. BAP was high for samples collected from the urban river at low flow largely due to the dominance of dissolved P forms. This may be due to release of bioavailable P pool after resuspension of river bed sediments into the water column. As mixing and dilution with incoming fresh water is minimal at low flow, anoxic conditions tend to develop at the interface of the river bed sediment and the water column (Reynolds and Davies, 2001).



**Figure 4.5:** BAP concentration in river runoff; (a) agricultural river, (b) urban river. Values are means of three replicate measurements, error bars represent the positive and negative error

Continued anoxia at low flow has the potential to allow iron oxyhydroxide-bound phosphorus to be released to the water column (Zhou et al., 2013), hence contributing to the BAP pool. Moreover, interaction of P with sediments has been found to be an important factor in controlling concentrations of dissolved P in the water column during both low and high river-flows.

Antecedent weather conditions have been identified as important in controlling the pool of fine sediment and associated P available for remobilization during rain events (House, 2003). In the absence of bed-scouring which is typical in rivers such as Yagyu (Y), sediments may act as a sink for DP, and hence a potential source of BAP if they are remobilized or when concentrations of DP in the overlying water are reduced. In addition, Nakajima et al. (2006) suggested that SS in rivers flowing through agricultural areas mainly consists of clay or silt, while SS in urban rivers consists of a large percentage of organic particles as well. Consequently, phosphorus in SS recovered from runoff in urban rivers was found to be more bioavailable than that in SS from rivers flowing through intensively cultivated areas. In accordance with (Young and DePinto, 1982), it was noticed that a high content of particulate P causes a low bioavailability. Sonzogni et al. (1982) suggested that about 25-50% of TP is available, and the differences are based largely on the different content of dissolved phosphorus.



**Figure 4.6:** Relationship between BAP and TP; (a) agricultural river, (b) urban river

In addition, the average BAP concentration in runoff was high enough at all sites to contribute to algal growth (**Figure 4.5**), when compared with the threshold value of 0.02 mg/L TP in receiving water that has been adopted in the water quality standards of Japan for conservation of natural environment (MoE, Japan 2018).

A medium correlation existed between BAP and TP in the agricultural river ( $r^2 = 0.5$ ,  $p < 0.05$ ) (**Figure 4.6a**). Due to the medium correlation, it was conceivable that a significant amount of TP in the agricultural river was not readily bioavailable. In most cases, high TP concentration in the agricultural river at high flow was driven by dramatic increase in PP concentration most of which was potentially non-bioavailable. Runoff SS at the intermediate of the peak and falling limb of the storm event hydrograph originates partly from the watershed. This runoff has unique characteristics which do not depend entirely on soil and watershed characteristics, but also on the physico-chemical processes influencing P composition and lability during the course of sediment transport and subsequent deposition (Sharpley and Menzel, 1987; Cooper et al., 2015).

BAP was strongly correlated with TP in the urban river ( $r^2 = 0.84$ ,  $p < 0.01$ ) (**Figure 4.6b**); implying that BAP could be used in place of TP as a conservative measure of the eutrophication potential of runoff. Hence, these results demonstrate that TP may not be a reliable estimate of BAP especially in the agricultural river at high flow.

However, this may not be the case when considering longer-term bioavailability as adsorbed orthophosphate associated with SS may be readily released back into the water column if anoxic conditions exist or under altered ambient equilibrium DP concentration. Such a scenario could occur for example following resuspension of sediments into the overlying water column at low flow. Thus, merely using TP as a surrogate for BAP is questionable from a management perspective as this overestimates the eutrophication potential. Hence, it is important to quantify BAP in runoff with respect to the implementation process of watershed management programs since TP includes complex P forms that may not be available to algae.

### **4.3 Conclusions**

Phosphorus bioavailability in samples collected from two rivers flowing through contrasting land use was investigated. A considerable fraction of PP (6 to 79%) was found to be potentially bioavailable. PBAP was strongly correlated with SS in the agricultural river unlike in the urban river where no obvious correlation existed between PBAP and SS, possibly an indication of differing particle size and SS composition in both rivers. A strong correlation was observed between BAP and TP in the urban river, implying that BAP could be used in place of TP as a conservative measure of the eutrophication potential of runoff. In contrast, a significant but not strong relationship observed between BAP and TP in the agricultural river points to the decreased bioavailability of PP at high flow when elevated TP concentration is impacted by PP associated with runoff SS. Hence, understanding of the availability of phosphorus associated with suspended sediments is critical for the effective implementation of best management practices to combat the eutrophication phenomenon in the aquatic ecosystem.

## References

- Abell, J.M. and Hamilton, D.P., 2013. Bioavailability of phosphorus transported during storm flow to a eutrophic, polymictic lake. New Zealand. *Journal of Marine and Freshwater Research*, 47(4), pp.481-489. <https://doi.org/10.1080/00288330.2013.792851>
- Anderson, D.M., Glibert, P.M. and Burkholder, J.M., 2002. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences, *Estuaries*, 25(4), pp.704-726. <https://doi.org/10.1007/BF02804901>
- Baker, D.B., Confesor, R., Ewing, D.E., Johnson, L.T., Kramer, J.W., Merryfield, B.J., 2014. Phosphorus loading to Lake Erie from the Maumee, Sandusky and Cuyahoga rivers: The importance of bioavailability. *Journal of Great Lakes Research*, 40(3), pp.502-517,
- Ballantine, D.J., Walling, D.E., Collins, A.L. and Leeks, G.J., 2008. The phosphorus content of fluvial suspended sediment in three lowland groundwater-dominated catchments. *Journal of Hydrology*, 357(1-2), pp.140-151.
- Boström, B., Persson and G., Broberg, B., 1988. Bioavailability of different phosphorus forms in freshwater systems. *Hydrobiologia*, 170(1), pp.133-155, <https://doi.org/10.1007/BF00024902>
- Carpenter, S.R., 2008. Phosphorus control is critical to mitigating eutrophication. *Proceedings of the National Academy of Sciences, USA*, 105(32), pp.11039-11040.
- Cassidy, R. and Jordan, P., 2011. Limitations of instantaneous water quality sampling in surface-water catchments: comparison with near-continuous phosphorus timeseries data. *Journal of Hydrology*. 405(1–2), pp.182–193
- Cooper, R.J., Rawlins, B.G., Krueger, T., Lézé, B., Hiscock, K.M. and Pedentchouk, N., 2015. Contrasting controls on the phosphorus concentration of suspended particulate matter under baseflow and storm event conditions in agricultural headwater streams. *Science of the Total Environment*, 533, pp.49-59. <https://doi.org/10.1016/j.scitotenv.2015.06.113>
- DePinto, J.V., Young, T.C. and Martin, S.C. 1981. Algal-Availability of Phosphorus in Suspended Sediments from Lower Great Lakes Tributaries. *Journal of Great Lakes Research*, 7(3), pp.311-325.
- Dorich, R.A., Nelson, D.W., Sommers, L.E., 1985. Estimating algal available phosphorus in suspended sediments by chemical extraction. *Journal of Environmental Quality*, 14, pp.400-405.
- Engie, D.L. and Sarnelle, O., 1990. Algal use of sedimentary phosphorus from an Amazon floodplain lake: Implications for total phosphorus analysis in turbid waters. *Limnology and Oceanography*, 35(2), pp.483-490.
- Ekholm, P., Krogerus, K., 2003. Determining algal-available phosphorus of differing origin: routine phosphorus analyses versus algal assays, *Hydrobiologia*, 492(1-3), pp.29-42. <https://doi.org/10.1023/A:1024857626784>

- Ekholm, P., 1994. Bioavailability of phosphorus in agriculturally loaded rivers in southern Finland. *Hydrobiologia*, 287(2), pp.179-194. <https://doi.org/10.1007/BF00010733>
- Ellison Brett, M.E., 2006. Particulate phosphorus bioavailability as a function of stream flow and land cover. *Water Research*, 40, pp.1258-1268, <https://doi.org/10.1016/j.watres.2006.01.016>
- Evans, D.J., Johnes, P.J. and Lawrence, D.S., 2004. Physico-chemical controls on phosphorus cycling in two lowland streams. Part 2 - the sediment phase. *Science of the Total Environment*, 329(1-3) pp.165-182. <https://doi.org/10.1016/j.scitotenv.2004.02.023>
- Gu, S., Qian, Y., Jiao, Y., Li, Q., Pinay, G. and Gruau, G., 2016. An innovative approach for sequential extraction of phosphorus in sediments: Ferrous iron P as an independent P fraction, *Water Research* 103, pp.352-361. <https://doi.org/10.1016/j.watres.2016.07.058>
- House, W.A., 2003. Geochemical cycling of phosphorus in rivers. *Applied Geochemistry*, 18(5), pp.739-748, [https://doi.org/10.1016/S0883-2927\(02\)00158-0](https://doi.org/10.1016/S0883-2927(02)00158-0)
- Hupfer, M., Gächter, R. and Giovanoli, R., 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. *Aquatic Sciences*, 57(4), pp.305-324.
- Kerr, J.G., Burford, M.A., Olley, J.M., Bunn, S.E. and Udy, J., 2011. Examining the link between terrestrial and aquatic phosphorus speciation in a subtropical catchment: the role of selective erosion and transport of fine sediments during storm events. *Water Research*, 45(11), pp.3331-3340. <https://doi.org/10.1016/j.watres.2011.03.048>
- Logan, T.J., Oloya, T.O., and Yaksich, S.M. 1979. Phosphate characteristics and bioavailability of suspended sediments from streams draining into Lake Erie. *Journal of Great Lakes Research*, (5), pp.112-123.
- Lukkari, K., Hartikainen, H. and Leivuori, M., 2007. Fractionation of sediment phosphorus revisited. I: Fractionation steps and their biogeochemical basis. *Limnology and Oceanography: Methods*, 5(12), pp.433-444. <https://doi.org/10.4319/lom.2007.5.433>
- Maynard, J.J., O'Geen, A.T. and Dahlgren, R.A., 2009. Bioavailability and fate of phosphorus in constructed wetlands receiving agricultural runoff in the San Joaquin Valley, California. *Journal of Environmental Quality*, 38(1), pp.360-372.
- McKelvie, I.D., Peat, D.M., Worsfold, P.J., 1995. Analytical perspective. Techniques for the quantification and speciation of phosphorus in natural waters, in: Analytical Proceedings. Including Analytical Communication, *Royal Society of Chemistry*, 32(10), pp.437-445.
- Michalak, A.M., Anderson, E.J., Beletsky, D., Boland, S., Bosch, N.S., Bridgeman, T.B., Chaffin et al., 2013. Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proceedings of the National Academy of Sciences, USA*, 110(16), pp.6448-6452. <https://doi.org/10.1073/pnas.1216006110>

- Miller, W.E. and Greene, J.C., 1978 The Selenastrum capricornutum Printz algal assay bottle test: Experimental design, application, and data interpretation protocol, *Environmental Protection Agency, Office of Research and Development*, Corvallis Environ Research Laboratory: Oregon, USA, 78 (18).
- MoE., 2018 Ministry of the Environment - Government of Japan. Environmental Quality Standards for Water pollution, Nitrogen and Phosphorus for Rivers, Lakes and Coastal waters. Available online: <http://www.env.go.jp/kijun/index.html>, accessed 26 September 2018.
- Naden, P.S., 2010. The Fine-Sediment Cascade, in: Sediment cascades: an integrated approach, Burt, T., Allison, R (Eds.), John Wiley & Sons: Oxford, UK, pp. 271–306, ISBN: 978-0-470-84962-0
- Nakajima, J., Murata, Y. and Sakamoto, M., 2006. Comparison of several methods for BAP measurement. *Water Science and Technology*, 53(2), pp.329-336, DOI: 10.2166/wst.2006.067
- Ngoc, N.M., Inoue, T. and Yokota, K., 2017. Ultrasonic extraction method for quantifying bioavailable phosphorus in particulate form. *Journal of Environmental Chemical Engineering*, 5(3), pp.2498-2507. <https://doi.org/10.1016/j.jece.2017.04.047>
- Pacini, N. and Gächter, R., 1999. Speciation of riverine particulate phosphorus during rain events. *Biogeochemistry*, 47(1), pp.87-109, <https://doi.org/10.1007/BF00993098>
- Palmer-Felgate, E.J., Jarvie, H.P., Withers, P.J., Mortimer, R.J. and Krom, M.D., 2009. Stream-bed phosphorus in paired catchments with different agricultural land use intensity. *Agriculture, Ecosystems and Environment*, 134(1-2), pp.53-66. <https://doi.org/10.1016/j.agee.2009.05.014>
- Poulenard, J., Dorioz, J.M. and Elsass, F., 2008. Analytical electron-microscopy fractionation of fine and colloidal particulate-phosphorus in riverbed and suspended sediments. *Aquatic Geochemistry*, 14(3), pp.193-210.
- Reynolds, C.S. and Davies, P.S., 2001. Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. *Biological Reviews*, 76(1), pp.27-64.
- Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E., Orihel, D.M., 2016. Reducing phosphorus to curb lake eutrophication is a success. *Environmental Science and Technology*, 50(17), pp.8923–8929. <https://pubs.acs.org/doi/abs/10.1021/acs.est.6b02204>
- Sharpley, A., Jarvie, H.P., Buda, A., May, L., Spears, B. and Kleinman, P., 2013. Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. *Journal of Environmental Quality*, 42(5), pp.1308–1326.
- Sharpley, A.N., Troeger, W.W. and Smith, S.J., 1991. The measurement of bioavailable phosphorus in agricultural runoff. *Journal of Environmental Quality*, 20(1), pp.235-238.
- Sharpley, A.N. and Menzel, R.G., 1987. The impact of soil and fertilizer phosphorus on the environment, *Advances in Agronomy*, 41, pp.297-324. [https://doi.org/10.1016/S0065-2113\(08\)60807-X](https://doi.org/10.1016/S0065-2113(08)60807-X)



- Shinohara, R., Imai, A., Kawasaki, N., Komatsu, K., Kohzu, A., Miura, S., Sano, T., Satou et al., 2012. Biogenic phosphorus compounds in sediment and suspended particles in a shallow eutrophic lake: a <sup>31</sup>P-nuclear magnetic resonance (<sup>31</sup>P NMR) study. *Environmental Science and Technology*, 46(19), 10572-10578. DOI: 10.1021/es301887z
- Smith, V.H. and Schindler, D.W., 2009. Eutrophication science: where do we go from here?, *Trends in Ecology and Evolution*, 24(4), pp.201-207. <https://doi.org/10.1016/j.tree.2008.11.009>
- Sonzogni, W.C., Chapra, S.C., Armstrong, D.E. and Logan, T.J., 1982. Bioavailability of phosphorus inputs to lakes. *Journal of Environmental Quality*, 11(4), pp.555-563.
- Su, J., Van Bochove, E., Auclair, J.C., Thériault, G., Denault, J.T., Bossé, C., Li, X. and Hu, C., 2014. Phosphorus algal availability and release potential in suspended and streambed sediments in relation to sediment and catchment characteristics. *Agriculture, Ecosystems and Environment*, 188, pp.169-179
- Tu, L., Jarosch, K.A., Schneider, T. and Grosjean, M., 2019. Phosphorus fractions in sediments and their relevance for historical lake eutrophication in the Ponte Tresa basin (Lake Lugano, Switzerland) since 1959. *Science of The Total Environment*, 685, pp.806-817.
- Uusitalo, R., Yli-halla, M. and Turtola, E., 2000. Suspended soil as a source of potentially bioavailable phosphorus in surface runoff water from clay soil. *Water Research*. 34(9), pp.2477-2482. [https://doi.org/10.1016/S0043-1354\(99\)00419-4](https://doi.org/10.1016/S0043-1354(99)00419-4)
- Van Moorleghe, C., De Schutter, N., Smolders, E. and Merckx, R., 2013. The bioavailability of colloidal and dissolved organic phosphorus to the alga *Pseudokirchneriella subcapitata* in relation to analytical phosphorus measurements, *Hydrobiologia*, 709(1), pp.41-53.
- Walling, D.E., Russell, M.A. and Webb, B.W., 2001. Controls on the nutrient content of suspended sediment transported by British rivers. *Science of the Total Environment*, 266(1-3), pp.113-123.
- Ye, H., Yuan, X., Han, L., Yin, H. and Jin, J., 2017. Comparison of phosphorus fraction distribution and influencing factors of suspended and surface sediments in the Tiaoxi watershed, China. *Water Science and Technology*, 75(9), pp.2108-2118.
- Zhou, Y., Obenour, D.R., Scavia, D., Johengen, T.H. and Michalak, A.M., 2013. Spatial and temporal trends in Lake Erie hypoxia, 1987–2007. *Environmental Science and Technology*, 47(2), pp.899-905. DOI: 10.1021/es303401b

## **Chapter 5      Particulate bioavailable phosphorus influenced by particulate organic matter and sediment elemental composition**

### **Summary**

Suspended sediments (SS) play a key role as carriers of particulate nutrients which support primary productivity in aquatic systems. In this study, we assessed the relationship between particulate bioavailable phosphorus (PBAP), particulate organic carbon (POC) and particulate organic nitrogen (PON) in rivers flowing through contrasting land use at high and low flow. In most cases, elevated POC and PON concentrations in both rivers were associated with low flow. POC and PON concentrations in both rivers declined at high flow presumably due to the mixing effects of water from different sources in the watershed which could have altered the particulate organic matter composition. A significant correlation existed between POC and SS in both rivers, and POC to PON ratios of SS from the rivers point to the change in the nature of particulate organic matter at varying flow conditions. PBAP exhibited a positive relationship with POC and PON concentration in both rivers possibly an indication that particulate organic matter contributes to bioavailable phosphorus in the rivers. Increasing Fe to POC ratio resulted in a positive trend in PBAP concentration in the agricultural river, revealing that POC and PBAP compete for binding with Fe in sediments.

## 5.1 Introduction

Nutrient loading into aquatic ecosystems results in eutrophication and serious degradation of ecosystem health in rivers, lakes, and estuaries (Smith and Schindler, 2009; Jarvie et al., 2018). The increase in the concentrations of the major macronutrients: nitrogen (N), phosphorus (P), and carbon (C) fuels primary productivity (Rabalais et al., 2001; Jarvie et al., 2015); though P has been identified as the main limiting nutrient especially in freshwaters (Schindler et al., 2016). Land use is an important factor controlling the export of N, P and C from catchments (Howarth et al., 1996; Carpenter et al., 1998), and extensive usage of nitrate and phosphate fertilizers to support agricultural production contributes legacy nutrient reserves in soil which are prone to release especially during episodic weather events. Phosphorus exists in several chemical forms (Dodds, 2003), which differ substantially with respect to their availability to support primary production. Whilst considerable information in recent years has pointed to the importance of considering bioavailability in the implementation of point and nonpoint P control programs, target load reduction plans are still based on total phosphorus (TP) (Baker et al., 2014). River water P is usually separated into particulate P (PP) and dissolved P (DP), and the forms of P that support algal production are termed bioavailable (DePinto and Young, 1981; Young and Depinto, 1982; Auer et al., 1998). Therefore, none of the commonly measured P fractions are accurate measures of bioavailable phosphorus (BAP). In general, PP is much more variable than dissolved P (Inoue and Ebise, 1991; Pacini and Gachter, 1999), and storm events are extremely important for PP dynamics because large portions of annual river PP loads can be transported attached to sediment and organic matter during only a few major events (Baker et al., 2014).

The particulate BAP (PBAP) content in runoff is affected by chemical processes like adsorption-desorption, precipitation-dissolution and reduction-oxidation reactions, which regulate the amount of dissolved inorganic P that is released into the water body and / or sorbed to particles (Ellison and Brett, 2006). Phosphate in the water column usually co-precipitates with sediment elemental components such as iron (Fe), and these co-precipitated phosphates accumulate on sediment surfaces as Fe-bound P (Baken et al., 2015).

Authigenic apatite referred to as calcium (Ca)-bound P also accumulates and acts as a sink for P in sediments (Ruttenberg, 2003). Hence, the deposition and accumulation of P in suspended sediments (SS) is intimately influenced by the presence of mineral elements. Particulate P bioavailability may increase if P is bound to clays and degradable organic matter (Reynolds and Davies, 2001; Pacini and Gachter, 1999) or if it is weakly sorbed to particles such as those composed of Fe-oxides (Gottselig et al., 2017) and other reactive compounds. Particulate organic carbon (POC) and particulate organic nitrogen (PON) which are important components of the particulate organic matter pool in rivers may influence the availability of PBAP.

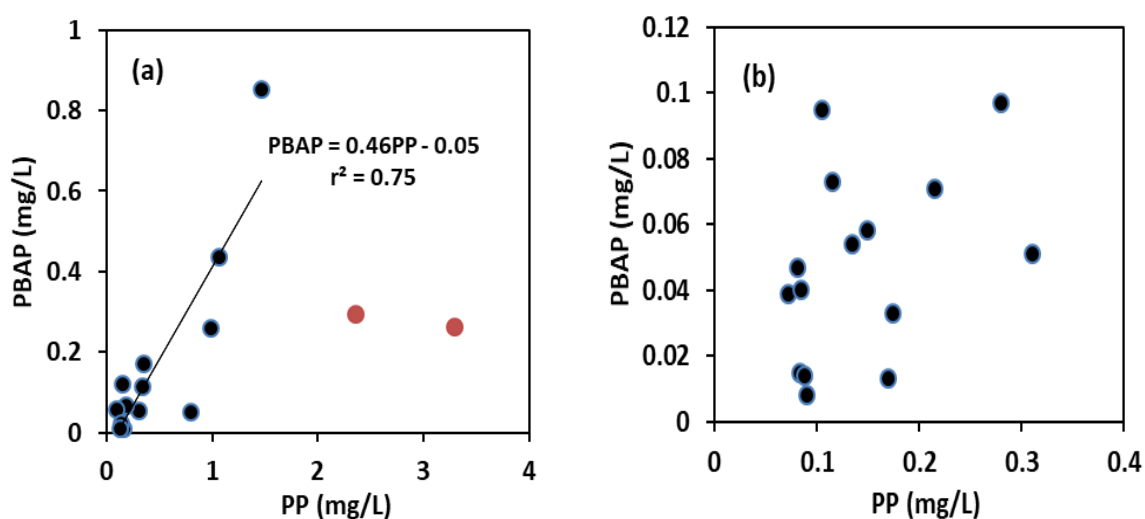
Compared to PBAP in rivers (Ellison and Brett, 2006; Mbabazi et al., 2019), much is less known about the relationship between PBAP, and POC and PON stoichiometry despite the dramatic increase in SS during high flow events. The wide variability in PP bioavailability suggests that both river-flow characteristics and land use pattern in the river catchment may be important; in addition to POC and PON concentration in suspended sediments. Since PP is usually transported to rivers bound to SS, the quantity and type of sediment in runoff will influence the concentration of BAP by varying the relative amounts of DP and PP entering the river. The amount of SS in runoff is affected by land use characteristics, and especially erosion, river-flows and soil saturation (Pacini and Gachter, 2009). Disturbed catchments like those in urban and agricultural areas are likely to exhibit greater river bank erosion.

Some few studies have examined the relationship between PBAP, SS elemental composition and particulate organic matter constituents under different hydrological conditions in urban and agricultural rivers. This shows a significant deficiency because source apportionment studies have demonstrated that there can be a considerable change in the source of SS under differing flows. Therefore, the primary aim of this part of the study was to compare the PBAP, POC and PON in an urban and agricultural river during high and low flow conditions. Relating the sediment elemental composition to PBAP could also reveal the hidden influence of the metal elements on the PBAP content in runoff SS. The proportion of PBAP varies between urban and agricultural rivers, and it is important to clarify the relationship between PBAP, POC, PON and sediment elemental content in river runoff.

## 5.2 Results and discussion

### 5.2.1 Relationship between PBAP and PP in the rivers

The concentration of PBAP plotted against PP concentration in each river gave significant linear relationships, indicating that PBAP concentration increased with an increasing PP concentration in runoff (**Figure 5.1**). PBAP and PP were strongly correlated in the agricultural river when samples U3 and U4 with exceptionally high PP concentrations are excluded; the points in red color in the graph shown in **Figure 5.1a**. These samples were collected at high flow after a strong typhoon event which most likely contributed SS with different biogeochemical properties originating from different areas of the drainage basin. SS associated with large storm events originate partly from the watershed and do not depend exclusively on the watershed soil characteristics, but also on physical and chemical processes influencing P mobility during sediment transport and deposition (Sharpley and Menzel, 1987). The strong correlation between PBAP and PP concentration in the agricultural river ( $r^2 = 0.75$ ,  $p < 0.01$ ); suggests that PP contributes to a significant amount of PBAP in the river. This pattern was similar to observations of PP transport in surface runoff from various cropland soils (Uusitalo et al., 2000). As PP is mostly associated with SS, it implies that agricultural fields in the watershed have a great influence on the PBAP forms as a result of soil erosion.



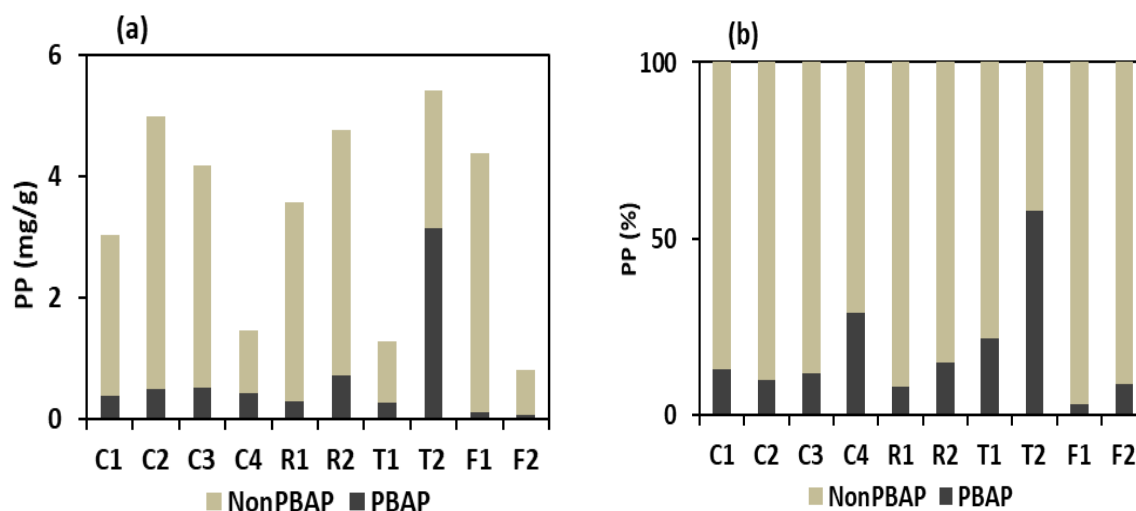
**Figure 5.1:** Relationship between PBAP and PP; (a) agricultural river, (b) urban river

Elevated PBAP concentrations in the agricultural river were associated with SS recovered at high flow while low flow PBAP concentrations in the agricultural river were approximate to those in the urban river.

The PBAP fraction in the agricultural river SS obtained at high flow was influenced by soil erosion since a large quantity of particulate matter was transported from the agricultural catchment during rain events. PBAP in sediments depends on the soil characteristics of the drainage basin, on sediment composition as well as the physico-chemical conditions prevailing at the sediment-water interface (Reynolds and Davies, 2001). The PBAP and PP in the urban river showed no obvious correlation (**Figure 5.1b**). Particulate P is normally bound to SS and clay particles in runoff (Ellison and Brett, 2006), and the relationship between PP and PBAP in the urban river could be attributed to the PP and SS dynamics which were markedly different in both rivers. PP was strongly correlated with SS in the agricultural river contrary to the urban river where no obvious correlation was observed (Mbabazi et al., 2019), implying that the SS composition in the urban river was different from that in the agricultural river. The urban river catchment is mainly paved with a large percentage of impervious surfaces. Hence, contribution of SS in river runoff as a result of erosion was minimal, and runoff most likely consisted of coarse sand particles which are considered to carry less PP including less PBAP forms.

### ***5.2.2 Potential contribution of PBAP from watershed soils***

PBAP concentration in soils collected from cultivated fields in the agricultural river watershed varied considerably as shown in (**Figure 5.2a**). The PBAP concentration range was between 0.07 to 3.16 mg/g for the different soil samples with soil from tea fields having the highest average concentration. PBAP averaged 40% in soils from tea fields, 17% in soil from cabbage fields and, 6% in soil from forested areas upstream of the urban river (**Figure 5.2b**). High percentage PBAP in soils from cultivated fields implies potential bioavailability of runoff soil from tillage operations, and this could account for the elevated PBAP in the agricultural river during high flow.



**Figure 5.2:** PBAP proportion in soils from agricultural river watershed; (a) PBAP concentration in mg/g-SS, and (b) PBAP expressed as a percentage of PP in soil, \*C- Cabbage field soil, R-soil from rice paddy field, T- Tea field soil, F-soil from forested area

Suspended sediment in runoff from agricultural river was yellowish brown in color unlike SS in urban river which was dark grey and smelly; which could be an indication that eroded soil from cultivated fields was composed of clay particles. Other studies have shown that phosphorus is found to be closely associated with clay particles which comprise fine sediments, and due to their high specific area, fine sediments carry a greater P load per unit mass than coarse sediment (Naden et al., 2010). In addition, Ngoc et al. (2016) also noted that sediments which are yellowish brown in color may be so owing to the presence of iron compounds. Since 0.1M NaOH extracts P bound to Fe compounds (Lukkari et al., 2007), the proportions of PBAP obtained by extracting bioavailable P from the agricultural river SS with NaOH would be higher than those obtained in SS from the urban river, where SS contained less iron.

### 5.2.3 Geochemistry of the river sediments

#### Suspended sediments

Fe was the most abundant of the sediment mineral elements studied and showed significant variation in both rivers at different flow conditions (**Table 5.1** and **Table 5.2**). The Fe content was relatively high in the agricultural river and varied from 24.8 to 61.2 mg/g in the agricultural river, and from 18.03 to 40.04 mg/g.

**Table 5.1:** Elemental composition of SS from the agricultural river

Sample ID	Flow condition	SS (mg/L)	Fe	Ca	Mg	Na	Fe:PP	Fe:POC	C:N
			mg/g						
U1	High	85	61.2	0.26	7.66	0.03	15.35	1.17	7.51
U2	High	156	32.57	1.38	2.87	0.12	6.36	0.34	6.45
U3	High	236	50.23	1.67	4.35	0.31	3.63	1.84	8.79
U4	High	308	32.68	1.31	2.74	0.2	4.27	0.75	14.98
U5	High	248	30.56	1.29	3.21	0.08	7.66	0.97	8.62
U6	High	229	34.3	0.92	6.55	0.52	7.41	0.51	8.94
U7	High	48	33.63	1.9	5.35	0.32	5.21	0.59	8.27
U8	High	58	29.4	0.61	4.89	0.31	4.83	0.38	8.39
U9	High	316	39.8	1.03	3.05	0.18	8.61	1.51	8.18
U10	High	140	32.3	0.7	5.96	0.23	29.75	0.34	7.95
U11	Low	17	36.49	5.47	5.17	0.56	3.45	0.25	6.99
U14	Low	6	31.89	5.68	7.73	0.8	1.15	0.22	7.11
U18	Low	12	33.7	1.2	8.57	-	4.17	0.22	6.87
U19	Low	4	24.8	3.72	4.41	-	0.70	0.17	6.68
U20	Low	3	29.7	2.11	3.79	-	0.72	0.20	6.31

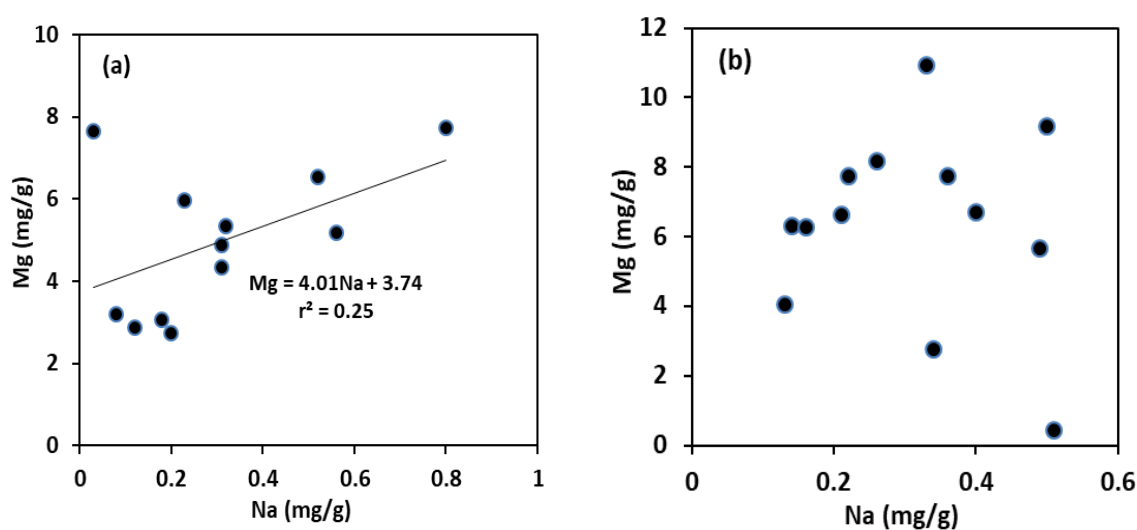
In both rivers, Fe content slightly declined at low flow in contrast to the Ca content which showed a marked increase at low flow. At high flow, the elevated Fe content in the agricultural river SS is capable of binding dissolved P in the water column, depending on water temperature, pH and the oxygen level at the sediment-water interface; thereby contributing to PBAP. The Mg content of SS showed significant variability ranging from 2.74 to 8.57 mg/g in the agricultural river and from 0.43 to 10.93 mg/g in the urban river. Shimotori et al. (2019) suggested that the Mg content in sediments can be used as a proxy to trace P originating from phytoplankton cells in sediments. Hence, the relatively high Mg content of sediment could point to increased productivity in the rivers especially during low flow.



**Table 5.2:** Elemental composition of SS from the urban river

Sample ID	Flow condition	SS (mg/L)	Fe	Ca	Mg	Na	Fe:PP	Fe:POC	C:N
			mg/g						
Y1	High	70	35.48	1.28	6.32	0.14	29.57	0.81	8.74
Y2	High	47	24.35	1.58	4.07	0.13	6.73	0.51	9.09
Y3	High	41	33.06	4.94	7.74	0.22	4.37	0.50	9.27
Y4	High	25	35.9	0.54	8.18	0.26	6.02	0.43	9.20
Y5	High	26	39.6	0.79	10.93	0.33	12.71	0.55	8.63
Y6	High	29	40.4	0.74	7.76	0.36	8.68	0.62	8.46
Y7	High	21	30.7	0.59	9.18	0.5	6.14	0.19	5.80
Y8	Low	47	31.32	1.81	6.26	0.16	16.73	0.32	6.96
Y9	Low	41	27.42	2.07	6.62	0.21	5.23	0.17	7.25
Y10	Low	14	24.71	4.94	2.77	0.34	1.24	0.10	6.09
Y11	Low	5	23.82	6.35	0.43	0.51	1.65	0.12	7.00
Y12	Low	4	18.03	5.47	5.65	0.49	0.80	0.08	7.22
Y16	Low	13	21.9	1.02	6.71	0.4	3.35	0.09	7.35
Y17	Low	9	27.5	3.97	4.96	-	2.15	0.14	6.92
Y18	Low	8	31.9	1.84	4.63	-	1.47	0.21	6.31

Previous studies indicated that metal elements such as Mg, Na and potassium are associated with clay minerals (Cooper et al., 2015b). **Figure 5.3** represents correlation plots for Mg and Na in the rivers.



**Figure 5.3:** Figure: Correlation between Mg and Na. (a) agricultural river; (b) urban river

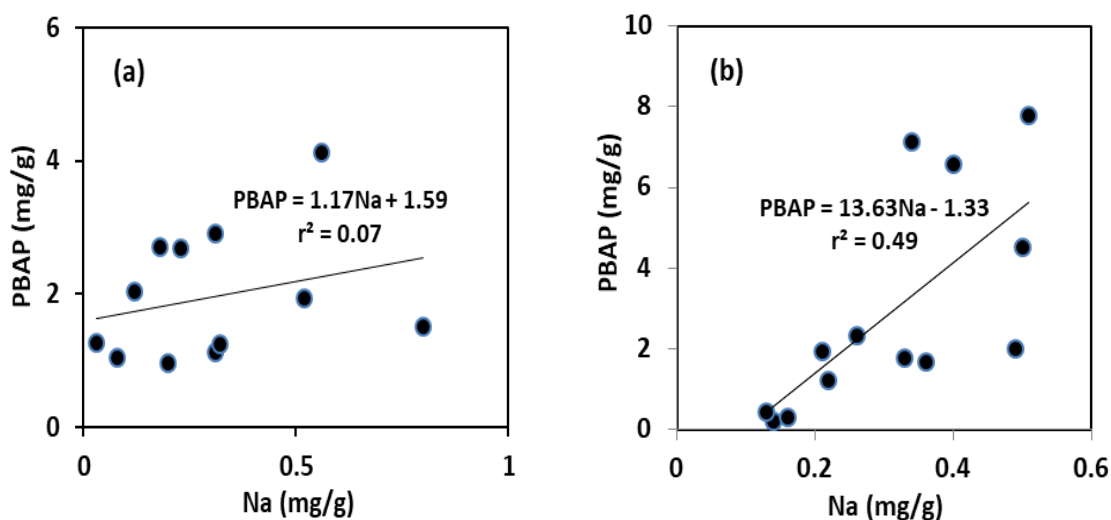
There was a significant and positive correlation between Mg and Na in the agricultural river. In contrast, no obvious associations are apparent between Mg and Na in the urban river (**Figure 5.3**). This result likely points to the dominance of clay mineral particles in SS from the agricultural river.

### Riverbed sediments

**Table 5.3** presents the geochemistry of the agricultural and urban river bed sediment. The concentration of Na in agricultural river-bed sediments was relatively stable and ranged from 0.33 to 0.6 mg/g whereas the range was from 0.42 to 10.33 mg/g in urban river-bed sediments. The elevated Na content in bed sediments from the urban river at low flow possibly indicates the impact of point source inputs. Further PBAP was moderately correlated with Na concentration in the urban river runoff, whereas a weak correlation was observed between PBAP and Na concentration in the agricultural river (**Figure 5.4**). Neal et al. (2010) considered Na concentration combined with discharge behaviours (concentration - flow relationship) in river waters as a good indicator to evaluate point source impacts of P associated with effluent sources. However, further extensive sampling is critical so as to trace the contribution of effluent sources in the urban river catchment.

**Table 5.3:** P fractions and geochemical composition of river bed sediments

Sample ID	Flow state	PP	Fe	Ca	Na	Mg	POC	PON	PBAP	Fe:POC	Fe:PP
mg/g											
Agricultural river											
U17_bsed	Low	0.39	8.82	0.21	0.60	1.35	8.17	1.07	0.37	1.08	22.35
U18_bsed	Low	0.51	-	0.34	0.33	-	6.83	0.57	0.38	-	-
U19_bsed	Low	1.23	10.63	0.65	0.45	2.08	12.90	1.62	0.51	0.82	8.66
U20_bsed	Low	0.73	8.10	0.79	0.49	1.75	4.48	0.46	1.14	1.81	11.08
Urban river											
Y15_bsed	Low	0.66	17.37	0.54	0.68	4.69	33.62	3.07	0.53	0.52	26.46
Y16_bsed	Low	1.12	-	1.10	0.42	-	53.04	4.78	0.78	-	-
Y17_bsed	Low	0.88	17.48	0.40	4.68	5.49	37.77	3.71	0.66	0.46	19.80
Y 18_bsed	Low	0.58	16.90	0.91	10.33	3.99	25.63	2.68	0.26	0.66	29.31



**Figure 5.4:** Relationship between PBAP and Na. (a) agricultural river; (b) urban river

The Fe contents in the bed sediments from the urban river were higher by a factor of 2 compared to those in the agricultural river. This potentially could be due to the abundance of iron sulphide (FeS) in the urban river bed sediments. Previous studies have indicated that FeS usually forms beneath the surface of the stream bed due to the prevailing redox conditions (Large et al., 2001). FeS is known to inhibit P immobilisation in sediment which results into the release of phosphate previously adsorbed onto the sediment surface. Further, POC and PON concentrations in urban river-bed sediments were remarkably higher than those in agricultural river-bed sediments which could be indicative of increased primary productivity in the urban river. This assertion was supported by the elevated Mg content (3.99 – 5.49 mg/g) in the urban river bed-sediments as compared to the bed sediments for the agricultural river. Previous research suggests that the Mg content in sediments can be used as a proxy to identify P originating from phytoplankton cells in sediments (Shimotori et al., 2019). Accordingly, the relatively high Mg content of the urban river bed-sediments could point to increased autochthonous production during low flow. The higher POC and PON concentration in the urban river bed sediment may also relate to organic matter being a source of P through mineralisation reactions and soluble reactive phosphorus sorbing onto the surfaces of organic matter in the sediments.

However, organic molecules also liberate phosphate ions into solution by replacing them on clay minerals and metal oxyhydroxide surface binding sites, whilst also blocking the pore spaces of mineral aggregates and acting as a protective barrier around mineral surfaces (Kaiser and Guggenberger, 2003; Wagai et al., 2013).

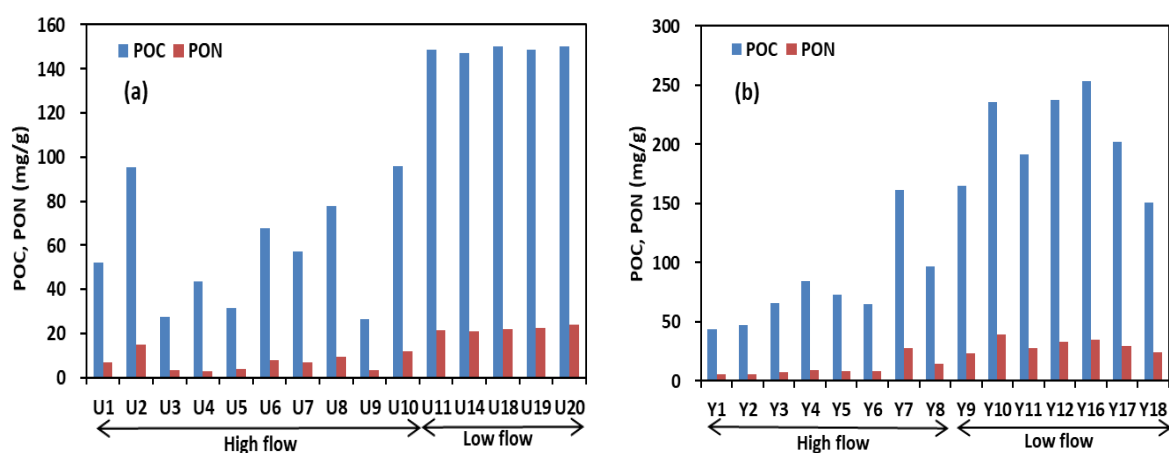
The Fe to POC ratios in the agricultural river-bed sediments ranged from 0.82 to 1.81. On the otherhand, Fe to POC ratios in the urban river bed sediment ranged from 0.46 to 0.66 (**Table 5.3**). Clearly, the bed sediments from the agricultural river have higher Fe to POC ratios than those from the urban river. This creates geochemical conditions in the agricultural river-bed sediments which are conducive to the sorption of phosphate ions onto the surfaces of Fe containing complexes. This Fe-P association may arise in the river-bed sediments as a consequence of changing redox conditions initiating the precipitation of Fe-bound P (Jarvie et al., 2008). Thus, the relatively higher PBAP content in the agricultural river-bed sediments likely results from the sorption of soluble reactive phosphorus onto Fe oxy(hydr)oxides phases prevalent in sediments. Conversely, the low Fe to POC ratios in the urban river-bed sediment points to the increased primary productivity as indicated by the elevated POC and PON concentration in the bed sediments. Previous research illustrates that P and POC compete for binding sites on the Fe oxy(hydr)oxide phases in sediments (Antelo et al., 2007; Weng et al., 2008), and low Fe to POC ratios indicate incorporation of POC within Fe oxy(hydr)oxides. This phenomenon could account for the slightly lower PBAP associated with bed sediments from the urban river despite their corresponding elevated total Fe content. This may also in part be explained by the occurrence of range of poorly crystalline Fe (ii) or mixed Fe(ii) / Fe(iii) minerals (coupled with Fe oxyhydroxides) that have vastly different P binding properties, as observed by Bortleson (1974) based on analyses of lake sediments

The Fe to PP ratios in the bed sediments were much higher in the urban river compared to the agricultural river (**Table 5.3**). Previous research has demonstrated that Fe to PP ratios can be useful indicators of the P buffering capacity of aquatic sediments (Jensen et al., 1992). Specifically, the higher the Fe to PP ratio, the greater the potential for the adsorption of phosphate onto the surfaces of Fe containing compounds within sediments.

Thus, higher Fe to PP ratios allow sediment to isolate phosphate from uptake by biota and thereby minimise the risk of eutrophication. The Fe to PP ratios in the bed sediments from the urban river were generally greater than 15, the value above which it has been shown sediments can moderate temporal soluble reactive phosphorus variability in lacustrine environments (Jensen et al., 1992).

#### 5.2.4 Particulate organic carbon and nitrogen in river suspended sediments

In both rivers, POC and PON exhibited similar trends with higher concentrations at low flow and reduced concentration during high flow. At low flow, POC concentration in the agricultural river varied from 147 to 150 mg/g whereas PON concentration changed from 21 to 24 mg/g (**Figure 5.5a**). In contrast at the same flow condition, POC concentration in the urban river varied from 97 to 254 mg/g while the change in PON concentration was from 14 to 39 mg/g as shown in **Figure 5.5b**. It is important to note that the samples were collected during different seasons of the year, with some of the low flow samples collected at the end of the winter season and others during summer, when SS concentration was low, remaining almost constant in the urban river and with a subtle increase in the agricultural river. The elevated POC concentrations in both rivers at low flow points to increased primary productivity, and less dilution of the particulate organic matter accumulated in the river channel. It has been suggested that mixing and dilution among other factors including; retention time, adsorption and aggregation, influence the riverine carbon concentration (Day et al., 2013).



**Figure 5.5:** POC and PON concentration in river samples; (a) agricultural river, (b) urban river

At high flow, POC concentration in the agricultural river varied from 26 to 95 mg/g whilst PON concentration changed from 3 to 15 mg/g. POC concentration in the urban river varied from 44 to 162 mg/g while PON concentration ranged from 5 to 28 mg/g at high flow. It can be noted that variation in discharge plays an important role in influencing particulate organic carbon and nitrogen dynamics. It has been found that drastic increases in the concentrations of SS and POC at the outlet of the agricultural stream and the levelling off along the downstream rivers is due to deposition of coarse particles and to the mixing of river water with runoff from the less erodible land surface downstream (Jung et al., 2015). Further, the presence of organic debris in the river channel along with high inorganic SS associated with high flows dictates the overall POC content in suspended sediments. It has been suggested that organic and inorganic particles have vastly different hydrodynamic properties, particularly in shape and density (Bin Omar and Bin MatJafri, 2009), which likely influences the POC amount in the rivers at high flow. In order to evaluate the impact of rising river-flows on particulate organic matter constituents in the agricultural river, a storm event during the spring of April 2018 was examined in closer detail. Continuous sampling of a storm event at hourly intervals yielded valuable information regarding the variation of POC and PON in the agricultural river.

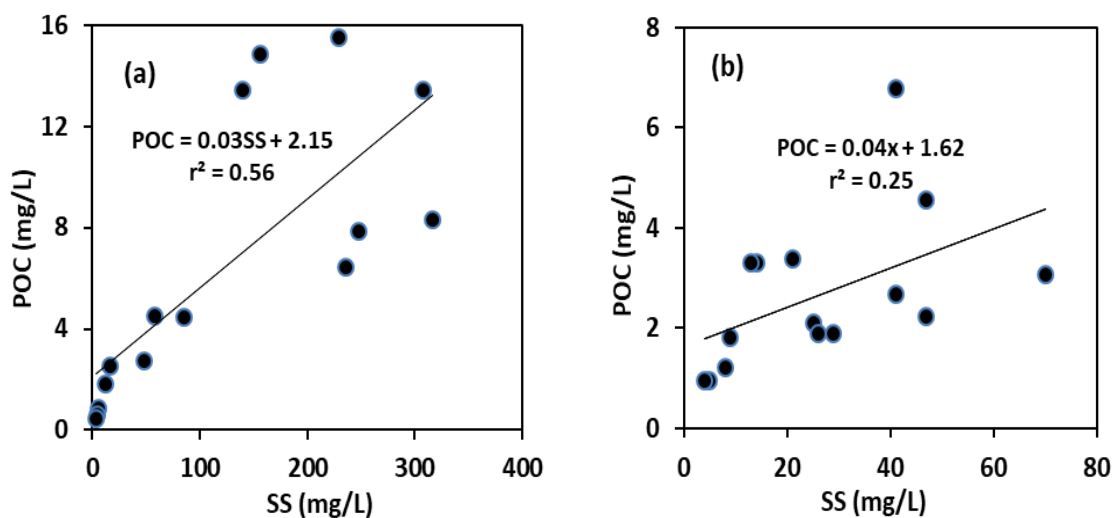
POC and PON concentrations in the agricultural river showed remarkable fluctuations throughout a continuously monitored storm event as depicted in **Table 5.4**. Prior to the onset of the storm, POC was high (236.99 mg/g) but significantly declined to 89.77 mg/g with increasing flow depth in the river. PON also depicted the same behavior as POC throughout the progression of the storm event. This indicated that dilution exerts a strong effect on riverine POC and PON due to mixing processes at elevated flows. It is likely that inorganic matter from eroded surface soil layers combines with organic matter already in the river channel, hence the resulting fluctuations in POC and PON. POC and PON dynamics differ from PP as PP concentration increased significantly in both rivers at high flow. This behavior is similar to that reported in previous studies and can be explained from a hydrologic perspective.

**Table 5.4:** Fluctuation in the agricultural river-POC and PON concentration during a storm event

	Time	Sample ID	Flow depth	SS	POC	PON
			m	mg/L	mg/g	
Rising limb	15:00	UT1	0.8	2	236.99	33.74
	22:00	UT2	1.11	23	89.77	10.83
	2:00	UT3	1.05	11	105.67	13.57
	4:00	UT4	1.47	71	63.11	7.16
	6:00	UT5	1.61	116	50.46	6.24
	7:00	UT6	1.84	64	42.98	4.99
	8:00	UT7	2	145	36.63	4.39
Falling limb	9:00	UT8	1.98	70	43.80	4.95
	10:00	UT9	1.51	76	33.95	3.95
	12:00	UT10	1.22	61	46.25	6.43
	15:00	UT11	1.1	31	51.85	7.14
	18:00	UT12	0.75	22	61.86	9.30

During rain, there is increase in river flow which erodes river channels producing a sharp rise in the quantity of particulates, including particulate C and N associated with organic matter. Particulate P is also affected by increasing flow, but high concentrations prevail as the water level rises, whereas POC and PON concentrations fall (Sauders and Lewis, 1998). It has been suggested that PP is associated primarily with SS and secondarily with organic matter, but POC and PON are associated almost exclusively with organic matter (Sauders and Lewis, 1998; Onstad et al., 2000). The rapid response of POC and PON concentration to changes in flow suggests a near river or in-river source of particulate organic matter especially during low flow. Hence, more likely particulate organic matter accumulated in both river channels at low flow, and was continually replaced with inorganic matter from the watershed at storm flow as a result of mixing processes in the rivers.

There was a positive relationship between POC and SS in both rivers as shown in (Figure 5.6). POC was moderately correlated with SS in the agricultural river ( $r^2 = 0.56$ ,  $p < 0.01$ ), while the correlation was weak in the urban river ( $r^2 = 0.25$ ,  $p < 0.01$ ).



**Figure 5.6:** Correlation between POC and SS; (a) agricultural river, (b) urban river

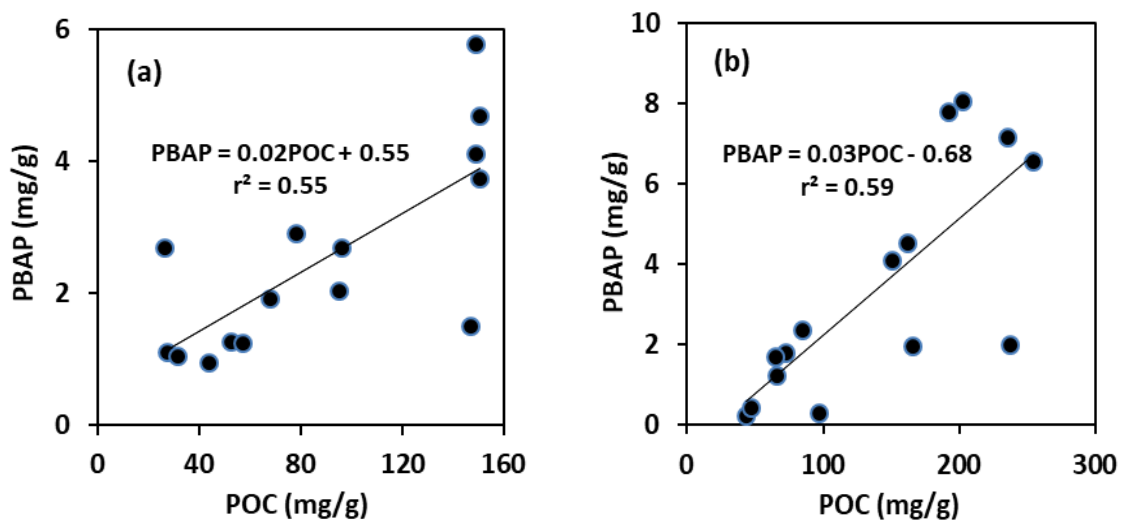
A positive and significant relationship between POC and SS could suggest delivery of allochthonous carbon from land controlled by precipitation or incorporation of aquatic organic carbon from plankton production mediated by terrestrial nutrient input, as have been observed in other studies (Canuel et al., 2012). The subtle but significant differences in the relationship between POC and SS in the rivers could possibly be related to the distribution and nature of SS in the rivers. The siting of both fluvial and anthropogenic carbon inputs in the rivers may be crucial factors together with the spatial variability in the decomposition and utilization of POC. Finer sediments comprising of mainly clay and silt occur in the agricultural river while somewhat coarser sediments occurs in the relatively low turbid urban river, where SS comprise sandier material. The positive relationship between POC and SS in both rivers also implies that SS consists of considerable POC which possibly contributes to primary productivity in the rivers.

POC to PON ratios declined to a lesser but significant extent at low flow and varied from 6.31 to 14.98 in the agricultural river, and from 5.8 to 9.27 in the urban river as shown in **Table 5.1 and 5.2**. This result was unexpected since the anticipation was that POC to PON stoichiometry would be much higher in the urban river at low flow. Nevertheless, the significant increase in POC and PON concentrations in the urban river at low flow could be an indication of organic matter loading from point sources or gradual input of organic matter originating from the forested area upstream.



In contrast, particulate organic C to N ratios increased in both rivers at high flow despite remaining relatively constant among the different high flow events. Nitrogen flows in an almost constant concentration and in proportion to the flow, while most phosphorus flows at storm flow when flow increases. Though the concentration of dissolved nutrients is almost constant in the increasing flow, particulate nutrient concentration increases at high flow with the order of increasing ratio being phosphorus followed by carbon and nitrogen (Inoue et al., 1991). The high ratios observed in the agricultural river correlate with high nutrient loading in erosion runoff from the cultivated fields in the watershed. The sustained delivery of agricultural nutrients could also explain the lack of significant variation in POC to PON ratios despite the remarkable change in SS concentration. The elevated POC to PON ratios in the urban river could possibly be due to contribution of particulate organic matter from point sources in the urban area. It has been found that large amounts of particulate N delivered from surrounding urban areas during rain events account for the particulate C to N stoichiometry (Prater et al., 2017). Furthermore, POC to PON ratios of particulate organic matter could be used to characterize the origin of organic matter in the rivers. In general, values greater than 20 can be taken as indicators of vascular plant material, those between 15 and 8 seem to represent eroded soil humus, and lower values are thought to indicate planktonic sources (Savoie et al., 2003). Hence, the nature of particulate organic matter in both rivers could have shifted from humic substances during high flow towards planktonic material during low flow. This is further supported by the relatively high Mg content in sediments from the rivers at low flow. Shimotori et al. (2019) suggested that in tracing P emanating from phytoplankton cells, the Mg content in sediments can be used as an indicator as all photosynthetic primary producers include chlorophyll a, which consists of a group of Mg coordination complexes of cyclic tetrapyrroles.

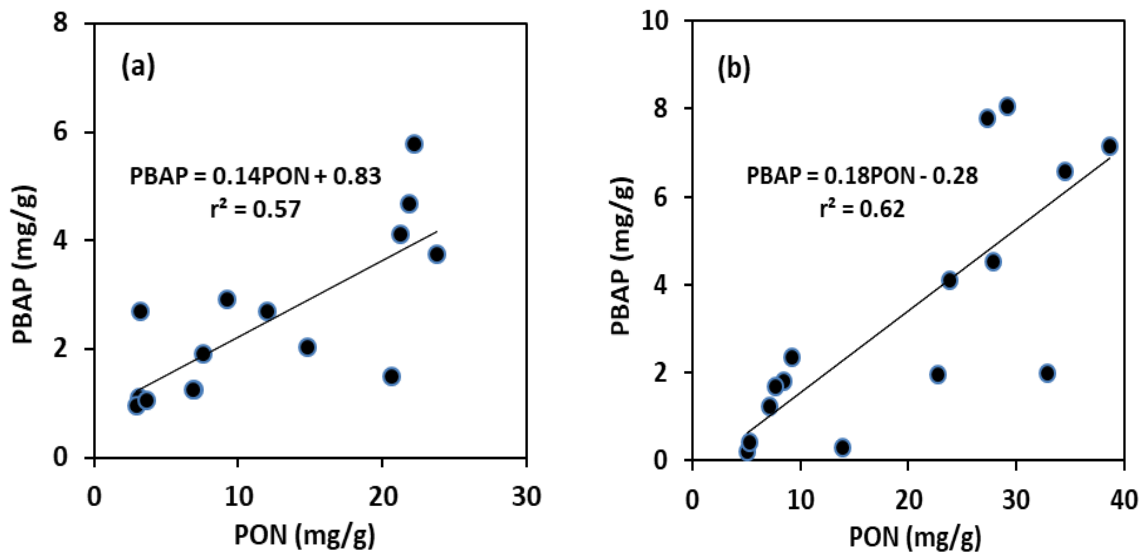
Further, a positive relationship was observed between PBAP and POC in both rivers as shown in (**Figure 5.7a and b**). Particulate organic matter in the agricultural river most likely originates from cultivated fields in the watershed since organic fertilizers such as composted poultry manure are commonly applied to support plant growth, and some fertilizers are subsequently washed off through agricultural drains during rain events.



**Figure 5.7:** Relationship between PBAP and POC; (a) agricultural river, (b) urban river

The medium correlation ( $r^2 = 0.55$ ,  $p < 0.01$ ) observed in the agricultural river implies that there are elevated bioavailable P amounts associated with eroded soil organic particulate matter. Previous research has demonstrated that inputs from agricultural field drains are critical pathways for particulate organic matter and may transport reactive phosphorus from agricultural fertilizers straight into the river channel (Cooper et al., 2015a). POC in the agricultural river could be more labile, and hence subject to a biochemical oxidation reaction which results into the release of bioavailable inorganic P which is sorbed to suspended sediments. Reynolds and Davies, (2001) reported that maintenance of decomposer biomass occurs at the expense of organic carbon in the river system but to the release of potentially bioavailable P, as a result of chemical processes like adsorption or desorption and reduction-oxidation reactions which regulate the amount of inorganic P that is sorbed to particulate matter (Ellison and Brett, 2006).

A significant relationship existed between PBAP and PON in both rivers as shown in (Figure 5.8a and b). This highlights the potential for increased primary productivity in the rivers due to contribution of PON from anthropogenic sources in the river catchments. It is also important to note that the color of recovered SS in both rivers was markedly different with the agricultural river SS exhibiting a yellowish-brown color in contrast to the urban river SS which was dark grey.

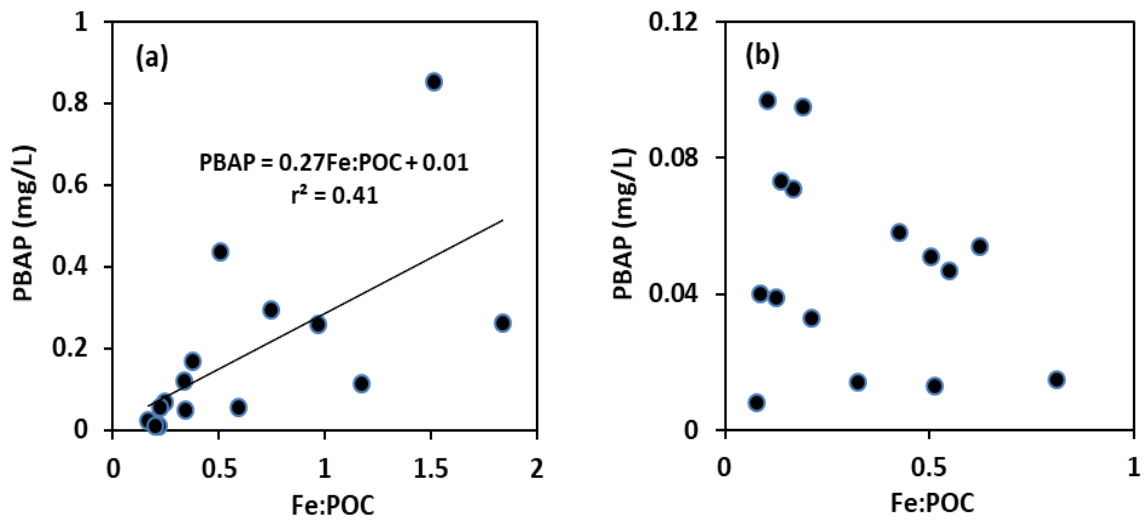


**Figure 5.8:** Correlation between PBAP and PON; (a) agricultural river, (b) urban river

The color of agricultural river SS points to the dominance of iron-bound compounds associated with clay particles and organic matter in SS originating from the agricultural watershed. Iron may significantly contribute to P bioavailability in sediments by increasing the cationic exchange capacity and reducing P fixation (Long and James, 2002), and the binding of P to Fe may take place in the oxidized SS and also by precipitation from the overlying waters (Baken et al., 2015; Ribeiro et al., 2008).

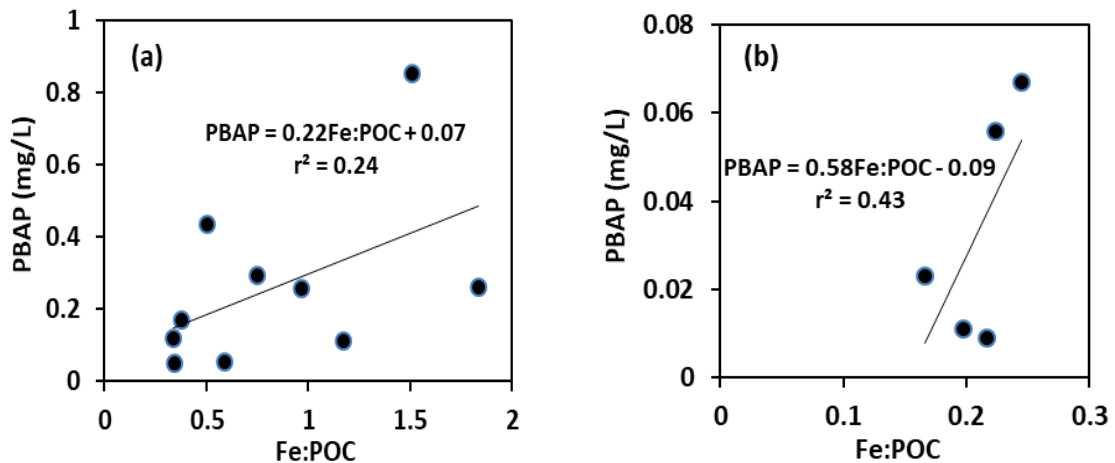
### 5.2.5 PBAP concentration and Fe to POC ratios in suspended sediments

**Figure 5.9** represents the relationship between PBAP and Fe to POC ratios in the agricultural and urban river. As the Fe to POC ratio increased in the agricultural river, PBAP concentration showed an increasing trend (**Figure 5.9a**). This behavior was in contrast to the urban river where no predictive trend was observed between Fe to POC ratio and PBAP (**Figure 5.9b**). Previous studies suggested that the phosphate binding strength to Fe-rich particles increases with elevated Fe to POC ratio due to reduced competition between phosphate and POC for binding on Fe or Fe(oxy)hydroxides phases (Weng et al., 2008; Lehrona et al., 2015). The results from this study reveal contrasting relationships between Fe, POC and PBAP.



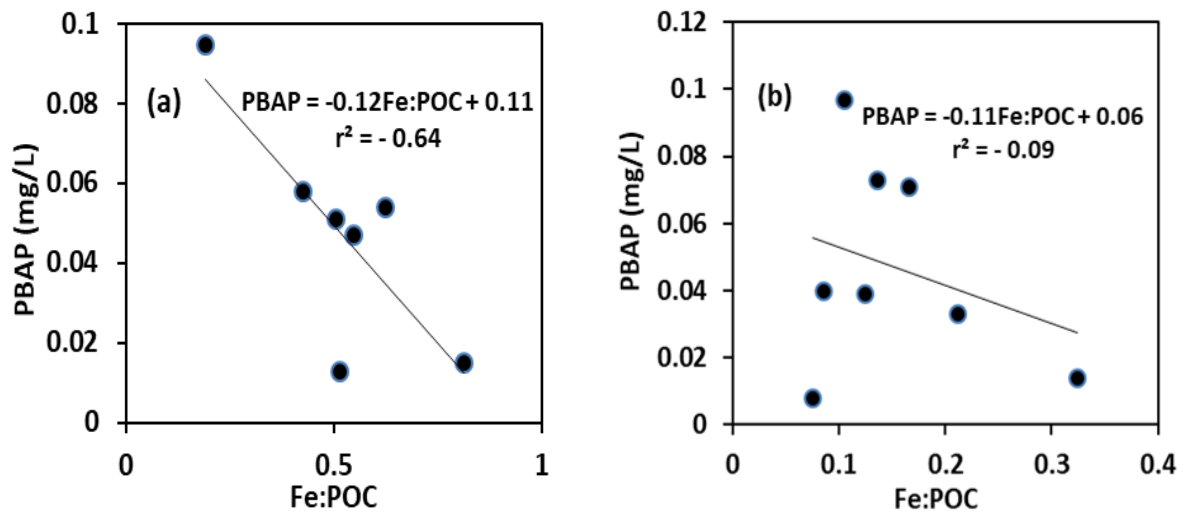
**Figure 5.9:** Fe to POC ratio influence on PBAP concentration; (a) agricultural river, (b) urban river

When PBAP and Fe to POC relationships for river runoff are assessed separately at both high and low flow conditions, a positive correlation was maintained in the agricultural river whereas the correlation tended to be negative in the urban river (Figure 5.10 and 5.11). As noted earlier, POC concentration was much higher in the urban river than the agricultural river especially at low flow, potentially indicating that POC exerts a strong influence on PBAP in the urban river by sorption on Fe oxides in sediments.



**Figure 5.10:** Consistent positive correlation between PBAP and Fe to POC ratio in the agricultural river.

(a) high flow; (b) low flow



**Figure 5.11:** Negative correlation between PBAP and Fe to POC ratio maintained in the urban river. (a) at high flow; (b) at low flow

Hence, the separation of flow events into high and low categories in this study, has proven useful as a simple way of understanding how variable hydrological conditions may influence particulate organic matter constituents, sediment elemental composition and bioavailable phosphorus.

### 5.3 Conclusions

The relationship between PBAP, POC and PON was assessed in two rivers flowing through urban and agricultural catchments at varying flow conditions. Elevated POC and PON concentrations in both rivers were associated with low flow. POC and PON concentrations in both rivers declined at high flow, and it was hypothesized that increasing flow alters the particulate organic matter composition. POC was significantly correlated with SS in both rivers and the POC to PON ratios reveal the change in the nature of particulate organic matter in river runoff at varying flow conditions. PBAP exhibited a positive relationship with POC and PON concentration in both rivers, an indication that particulate organic matter contributes to bioavailable phosphorus in the rivers. The sediment mineral elements revealed the composition of runoff SS in both rivers, with clay minerals potentially abundant in the agricultural river due to the apparent correlation between the Na and Mg elements.

Additionally, Fe was the most abundant element in the sediments from both rivers, and it was found that increasing Fe to POC ratio affects the PBAP concentration in the agricultural river, hence revealing that POC and PBAP compete for binding with Fe in sediments.

## References

- Antelo, J., Arce, F., Avena, M., Fiol, S., López, R. and Macías, F., 2007. Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma*, 138(1-2), pp.12-19.
- Auer, M.T., Tomasko, K.A., Babiera, M.J., Needham, M.L., Effler, S.W., Owens, E.M. and Hansen, J.M., 1998. Phosphorus bioavailability and P-cycling in Cannonsville Reservoir. *Lake and Reservoir Management*; 14(2-3), pp.278-89. <https://doi.org/10.1080/07438149809354337>
- Baken, S., Verbeeck, M., Verheyen, D., Diels, J. and Smolders, E., 2015., Phosphorus losses from agricultural land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches. *Water Research*, 71, pp.160-170. <https://doi.org/10.1016/j.watres.2015.01.008>
- Baker, D.B, Confesor R, Ewing, D.E., Johnson, L.T., Kramer, J.W. and Merryfield B.J., 2014. Phosphorus loading to Lake Erie from the Maumee, Sandusky and Cuyahoga rivers: The importance of bioavailability. *Journal of Great Lakes Research*, 40(3), pp.502-17,
- Bin Omar, A. and Bin MatJafri, M., 2009. Turbidimeter design and analysis: a review on optical fiber sensors for the measurement of water turbidity. *Sensors*, 9(10), pp.8311-8335.
- Bortleson, G.C., 1974. Phosphorus, iron and manganese distribution in sediment cores of six Wisconsin lakes. *Limnology and Oceanography*, 19, pp.794–801.
- Canuel, E.A, Cammer, S.S, McIntosh H. A. and Pondell C.R., 2012. Climate change impacts on the organic carbon cycle at the land-ocean interface. *Annual Review of Earth and Planetary Sciences*, 40, pp.685-711. [10.1146/annurev-earth-042711-105511](https://doi.org/10.1146/annurev-earth-042711-105511)
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth. R.W., Sharpley, A.N. and Smith V.H., 1998. Non-point pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*, 8(3), pp.559-68. [https://doi.org/10.1890/1051-0761\(1998\)008\[0559:NPOSWW\]2.0.CO;2](https://doi.org/10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2)
- Cooper, R.J., Krueger, T., Hiscock, K.M. and Rawlins B.G., 2015a. High-temporal resolution fluvial sediment source fingerprinting with uncertainty: a Bayesian approach. *Earth Surface Processes and Landforms*, 40(1), pp.78-92. <https://doi.org/10.1002/esp.3621>
- Cooper, R.J., Rawlins, B.G., Krueger, T., Lézé, B., Hiscock, K.M. and Pedentchouk, N., 2015b. Contrasting controls on the phosphorus concentration of suspended particulate matter under baseflow and storm event conditions in agricultural headwater streams. *Science of the Total Environment*, 533, pp.49-59.

- Day JW, Crump BC, Kemp WM. and Alejandro YA., 2013. *Estuarine Ecology*, Wiley-Blackwell, Hoboken, New Jersey, United States, 2nd ed. DOI:10.1002/9781118412787
- DePinto, J.V., Young, T.C. and Martin S.C., 1981. Algal-available phosphorus in suspended sediments from lower Great Lakes tributaries. *Journal of Great Lakes Research*, 7(3), pp.311-25.
- Dodds, W.K., 2003. Misuse of inorganic N and soluble reactive P concentrations to indicate nutrient status of surface waters. *Journal of the North American Benthological Society*, 22(2), pp.171-181.
- Dorich, R.A, Nelson, D.W. and Sommers, L.E., 1980. Algal availability of sediment phosphorus in drainage water of the Black Creek watershed. *Journal of Environmental Quality*, 9(4), pp.557-563
- Ellison, M.E. and Brett, M.T., 2006. Particulate phosphorus bioavailability as a function of stream flow and land cover. *Water Research*, 40, pp.1258-1268. <https://doi.org/10.1016/j.watres.2006.01.016>
- Environmental Protection Agency, USA, Method 3050B., 1996. Acid digestion of sediments, sludges and soils. Available online <https://www.epa.gov/sites/production/files/2015-06/documents/epa-3050b.pdf> accessed on 22 March 2018.
- Gottselig, N., Nischwitz, V., Meyn, T., Amelung, W., Bol, R., Halle, C., Vereecken, H., Siemens, J. and Klumpp, E., 2017. Phosphorus binding to nanoparticles and colloids in forest stream waters. *Vadose Zone Journal*, 16(3).
- Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J.A., Elmgren R., Caraco, N., Jordan T. and Berendse F., 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. In Howarth R.W. (eds): *Nitrogen cycling in the North Atlantic Ocean and its watersheds*. Springer, Dordrecht, pp. 75-139. [https://doi.org/10.1007/978-94-009-1776-7\\_3](https://doi.org/10.1007/978-94-009-1776-7_3)
- Inoue T. and Ebise S., 1991. Runoff characteristics of COD, BOD, C, N and P loadings from rivers to enclosed coastal seas. *Marine Pollution Bulletin*, 23, pp.11-14.
- Jarvie, H.P., Smith, D.R., Norton, L.R., Edwards, F.K., Bowes, M.J., King, S.M., Scarlett P., Davies et al., 2018. Phosphorus and nitrogen limitation and impairment of headwater streams relative to rivers in Great Britain: A national perspective on eutrophication. *Science of the Total Environment*, 621, pp.849-62. <https://doi.org/10.1016/j.scitotenv.2017.11.128>
- Jarvie, H.P., Sharpley, A.N., Flaten, D., Kleinman, P.J., Jenkins, A. and Simmons, T., 2015. The pivotal role of phosphorus in a resilient water–energy–food security nexus. *Journal of Environmental Quality*, 44(4), pp.1049-1062. doi:10.2134/jeq2015.01.0030
- Jensen, H.S., Kristensen, P., Jeppesen, E. and Skytthe, A., 1992. Iron:phosphorus ratio in surface sediments as an indicator of phosphate release from aerobic sediments in shallow lakes. *Hydrobiologia*, 235–236, pp.731–743
- Jung, B.J., Jeanneau, L., Alewell, C., Kim, B. and Park J.H., 2015. Downstream alteration of the composition and biodegradability of particulate organic carbon in a mountainous, mixed landuse watershed. *Biogeochemistry*, 122(1), pp.79-99. <https://doi.org/10.1007/s10533-014-0032-9>

- Kaiser, K. and Guggenberger, G. 2003. Mineral surfaces and soil organic matter. *European Journal of Soil Science*, 54, pp. 219-236, 10.1046/j.1365-2389.2003.00544.x
- Large, D.J., Fortey, N.J., Milodowski, A.E., Christy, A.G. and Dodd, J. 2001. Petrographic observations of iron, copper, and zinc sulphides in freshwater canal sediment. *Journal of Sediment Research*, 71, pp.61-69, 10.1306/052600710061
- Lehtoranta, J., Ekholm, P., Wahlström, S., Tallberg, P. and Uusitalo, R., 2015. Labile organic carbon regulates phosphorus release from eroded soil transported into anaerobic coastal systems. *Ambio*, 44(2), pp.263-273.
- Lukkari, K., Hartikainen, H. and Leivuori, M., 2007. Fractionation of sediment phosphorus revisited. I: Fractionation steps and their biogeochemical basis. *Limnology and Oceanography: Methods*, 5(12), pp.433-44. <https://doi.org/10.4319/lom.2007.5.433>
- Long, N. and James, S., 2002. Phosphorus fractions and retention in drainage ditch sediments receiving surface runoff and subsurface drainage from agricultural catchments in the North Island, New Zealand. *Agriculture Ecosystem and Environment*, 92, pp.49–69
- Mbabazi, J., Inoue, T., Yokota, K. and Saga, M., 2019. Phosphorus bioavailability in rivers flowing through contrasting land uses. *Journal of Environmental Chemical Engineering*, 7(2), p.102960. <https://doi.org/10.1016/j.jece.2019.102960>
- Miller, W.E. and Greene, J.C., 1978. The *Selenastrum capricornutum* Printz algal assay bottle test: Experimental design, application, and data interpretation protocol, *Environmental Protection Agency*, Office of Research and Development, Corvallis Environmental Research Laboratory; 78(18), Oregon, USA.
- Murphy, J.A. and Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, 27, pp.31-36.
- Naden, P.S., 2010. The Fine-Sediment Cascade. In *Sediment cascades: an integrated approach*, Burt, T., Allison, R (eds.): John Wiley & Sons: Oxford, UK, ISBN: 978-0-470-84962-0, pp. 271–306.
- Neal, C., Williams, R.J., Bowes, M.J., Harrass, M.C., Neal, M., Rowland, P., Wickham, H., Thacker et al., 2010. Decreasing boron concentrations in UK rivers: Insights into reductions in detergent formulations since the 1990s and within-catchment storage issues. *Science of the Total Environment*, 408(6), pp.1374-1385.
- Ngoc, N.M., Inoue, T. and Yokota, K., 2017. Ultrasonic extraction method for quantifying bioavailable phosphorus in particulate form. *Journal of Environmental Chemical Engineering*, 5(3), pp.2498-2507. <https://doi.org/10.1016/j.jece.2017.04.047>
- Ngoc NM, Inoue T. and Yokota K., 2016. Ultrasonic treatment for quantification of bioavailable phosphorus in soils and suspended sediments. *Water Science and Technology: Water Supply*; 16(6), pp.1745-1752. <https://doi.org/10.2166/ws.2016.100>



- Onstad, G.D., Canfield, D.E., Quay, P.D. and Hedges, J.I., 2000. Sources of particulate organic matter in rivers from the continental USA: lignin phenol and stable carbon isotope compositions. *Geochimica et Cosmochimica Acta*, 64(20), pp.3539-46. [https://doi.org/10.1016/S0016-7037\(00\)00451-8](https://doi.org/10.1016/S0016-7037(00)00451-8)
- Pacini, N. and Gächter, R., 2009. Speciation of riverine particulate phosphorus during rain events. *Biogeochemistry*, 47(1), pp.87-109. <https://doi.org/10.1007/BF00993098>
- Poirier, S.C., Whalen, J.K. and Michaud A.R., 2012. Bioavailable phosphorus in fine-sized sediments transported from agricultural fields. *Soil Science Society of America Journal*, 76(1), pp.258-267. doi:10.2136/sssaj2010.0441
- Prater, C., Frost, P.C., Howell, E.T., Watson, S.B., Zastepa, A., King, S.S., Vogt, R.J. and Xenopoulos, M.A., 2017. Variation in particulate C: N: P stoichiometry across the Lake Erie watershed from tributaries to its outflow. *Limnology and Oceanography*, 62(S1), S194-S206.
- Rabalais, N.N., Turner R.E. and Wiseman, W.J., 2001. Hypoxia in the Gulf of Mexico. *Journal of Environmental Quality*, 30, pp.320-29. doi:10.2134/jeq2001.302320x
- Rasul, E., Inoue, T., Aoki, S., Yokota, K., Matsumoto, Y. and Okubo Y., 2013. Nutrient enrichment and physical environmental effects caused by typhoons in a semi-enclosed bay. *Journal of Ecotechnology Research*, 17(3-4), pp.107-114. <https://doi.org/10.11190/jer.17.107>
- Reynolds, C.S. and Davies, P.S., 2001. Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. *Biological Reviews*, 76(1):27-64.
- Ribeiro, D.C., Martins, G., Nogueira, R., Cruz, J.V. and Brito, A.G., 2008. Phosphorus fractionation in volcanic lake sediments (Azores- Portugal). *Chemosphere*, 70, pp.1256-1263
- Ruttenberg, K.C., 2003. The global phosphorus cycle. In: Holland HD, Turekian KK (eds) *Treatise on geochemistry*, 2nd edn. Elsevier, Amsterdam, pp.499-558
- Saunders, J.F. and Lewis, W.M., 1998. Transport of phosphorus, nitrogen, and carbon by the Apure River, Venezuela. *Biogeochemistry*, 5(3), pp.323-342. <https://doi.org/10.1007/BF02180071>
- Savoie, N., Aminot, A., Treguer, P., Fontugne, M., Naulet, N. and Kérouel, R., 2003 Dynamics of particulate organic matter  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  during spring phytoplankton blooms in a macrotidal ecosystem (Bay of Seine, France). *Marine Ecology Progress series*, 255, pp.27-41.
- Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E. and Orihel DM. 2016. Reducing phosphorus to curb lake eutrophication is a success. *Environmental Science and Technology*, 50(17), pp.8923-8929.
- Sharpley, A.N., Robinson, J.S. and Smith, S.J., 1995. Bioavailable phosphorus dynamics in agricultural soils and effects on water quality. *Geoderma*, 67(1-2), pp.1-15.
- Sharpley, A.N., Troeger, W.W. and Smith, S.J., 1991. The measurement of bioavailable phosphorus in agricultural runoff. *Journal of Environmental Quality*, 20(1), pp.235-38.

- Sharpley, A.N. and Menzel, R.G., 1987. The impact of soil and fertilizer phosphorus on the environment. *Advances in Agronomy*, 41, pp.297-324, [https://doi.org/10.1016/S0065-2113\(08\)60807-X](https://doi.org/10.1016/S0065-2113(08)60807-X)
- Shimotori, K., Imai, A., Kohzu, A., Komatsu, K., Koshikawa, M.K., Hayashi, S. and Watanabe, M., 2019. Long-term observations of the vertical distributions of mineral elements and phosphorus dynamics in sediments in a shallow eutrophic lake in Japan. *Journal of Soils and Sediments* 19(3), pp.1566-1575. <https://doi.org/10.1007/s11368-018-2159-0>
- Smith, V.H. and Schindler, D.W., 2009. Eutrophication science: where do we go from here?, *Trends in Ecology and Evolution*, 24(4), pp.201-207. <https://doi.org/10.1016/j.tree.2008.11.009>
- Uusitalo, R., Yli-halla, M. and Turtola E., 2000. Suspended soil as a source of potentially bioavailable phosphorus in surface runoff water from clay soil. *Water Research*, 34(9), pp.2477-2482. [https://doi.org/10.1016/S0043-1354\(99\)00419-4](https://doi.org/10.1016/S0043-1354(99)00419-4)
- Wagai, R., Mayer, L.M., Kitayama, K. and Shirato Y., 2013. Association of organic matter with iron and aluminium across a range of soils determined via selective dissolution techniques coupled with dissolved nitrogen analysis. *Biogeochemistry*, 112, pp. 95-109, [10.1007/s10533-011-9652-5](https://doi.org/10.1007/s10533-011-9652-5)
- Weng, L., van Riemsdijk, W.H. and Hiemstra, T., 2008. Humic nanoparticles at the oxide-water interface: Interactions with phosphate ion adsorption. *Environmental Science and Technology*, 42, pp.8747–8752.
- Young TC, DePinto JV, Flint SE, Switzenbaum MS and Edzwald JK., 1982. Algal availability of phosphorus in municipal wastewater. *Journal of Water Pollution Control Federation*; 54(11), pp. 1505-1516



## **Chapter 6      General conclusions**

### **6.1 Recall of thesis objectives**

The conclusions and implications of this work are highlighted below, using the initial research objectives as a framework. The objectives of the study were: (i) to estimate PBAP in runoff from agricultural and urban rivers in order to assess whether the PBAP content was markedly different in the rivers at high and low flow; (ii) to determine the BAP proportion in river runoff, and to clarify its relationship with TP in the rivers; and (iii) compare the relationship between PBAP, POC and PON, and to relate this to the elemental composition of SS from the rivers.

### **6.2 Summary of conclusions**

Phosphorus bioavailability in samples collected from two rivers flowing through contrasting land use was investigated. PP was the dominant fraction during high flow in both rivers and between 6 to 79% of PP was found to be potentially bioavailable. PBAP was strongly correlated with SS in the agricultural river unlike in the urban river where no obvious correlation existed between PBAP and SS, possibly an indication of differing particle size and SS composition in both rivers. BAP varied significantly in both rivers, and at low flow, BAP amount in the urban river was high presumably due to resuspension of bed sediment which releases bioavailable P to the water column. A strong correlation was observed between BAP and TP in the urban river, implying that BAP could be used in place of TP as a conservative measure of the eutrophication potential of runoff. In contrast, a significant but not strong relationship observed between BAP and TP in the agricultural river points to the decreased bioavailability of PP at high flow when elevated TP concentration is impacted by PP associated with runoff suspended sediment.

Furthermore, high POC and PON concentrations in both rivers were associated with low flow. POC and PON concentrations in both rivers declined at high flow, and it is hypothesized that increasing flow alters the particulate organic matter composition.

POC was significantly correlated with SS in both rivers and the POC to PON ratios reveal the change in the nature of particulate organic matter in river runoff at varying flow conditions. PBAP exhibited a positive relationship with POC and PON concentration in both rivers, an indication that particulate organic matter contributes to bioavailable phosphorus in the rivers.

The PBAP concentration in the agricultural river depicted an increasing trend in concert with the increase in Fe to POC ratio in SS whereas no obvious relationship was observed in the urban river between PBAP and Fe to POC ratio. This result reveals that as the Fe to POC ratio increases in the agricultural river, there is potentially an abundance of sorption sites for PBAP on Fe oxyhydroxide phase in sediments due to reduced competition with POC. In the urban river sediments, Fe is most likely saturated with POC resulting in low PBAP content in runoff sediment as compared to the agricultural river. Hence, understanding of the potential bioavailability of phosphorus associated with suspended sediments, and the contribution of particulate organic matter constituents to the overall bioavailability is critical for the effective implementation of best management practices to combat the eutrophication phenomenon in the aquatic ecosystem.

### **6.3 Implications for future work**

In the present study, the significant differences in SS, POC, PON and P concentrations in both the agricultural and urban river likely relates to localized in-river primary production and inputs from agricultural field drains which could be the important pathways for SS and may account for phosphate transport from agricultural fertilizers directly into the river channel.

Further research is needed so as to identify the source of the fine sediment in runoff and associated PBAP coupled with organic matter. The areas in the catchment susceptible to erosion during rain events and which have a high connectivity with the river channels can provide a good starting point. Such areas include the cultivated field top soils, damaged road verges near the river, channel banks and proximal agricultural field drains.

It is also critical to determine the sediment particle sizes and the corresponding mineral element compositions among the different particle size ranges. Previous research has suggested that fine sediments and colloids have high specific surface area than coarse sediments, and therefore are significant vectors for water contaminants and nutrients such as phosphorus (Gottselig et al., 2017). The size distribution of sediments including clay (0.45–4  $\mu\text{m}$ ), silt (4–63  $\mu\text{m}$ ), and sand fractions (63–500  $\mu\text{m}$ ) can be determined using a laser diffraction particle size analyzer (Han et al., 2011). Further, insights regarding P binding to metal elements can be obtained through measurement of the mean diameter and specific surface area of river sediments, for example using a Malvern Mastersizer 2000 (Emelko et al., 2015).

In addition to the sediment metal elements assessed in this study, additional elements such as Al, Mn, Si and their corresponding oxides or compounds such as Fe sulphides, would provide information regarding the key geochemical mechanisms affecting the P forms and particulate organic matter. In this study, it was found that in some cases elevated Fe content in sediments did not translate into higher sediment PBAP concentration. This may in part be due to the prevalence of a range of poorly crystalline Fe and /or Al oxides and oxyhydroxides that have vastly different P sorption capacities.

Further work is needed to assess the impact of different hydrological conditions on POC and PON concentrations in the rivers. In this study, continuous monitoring of a storm event in the agricultural river revealed significant fluctuations in POC and PON concentrations due to dilution and mixing processes occurring in the river channel. The source of organic material can change over a flow hydrograph, and may differ between base flow and event flow (Gomez et al., 2003; Coynel et al., 2005; Wheatcroft et al., 2010), potentially explaining the lack of any sustained response of particulate organic matter to rising flow-depth and the observed variability of POC and PON over declining flow-depth in the agricultural river. Accordingly, more intensive river sampling should be conducted during different seasons such as March to May (transition from winter to spring) and August to October (transition from summer to Autumn), during high and low flow. Several factors contribute to the variability in particulate organic matter concentrations under baseflow.

Under some circumstances there may be flushing and dilution effects due to hydrological responses, and seasonality may affect what particulate form (either organic or inorganic) dominates the suspended material. However, the data from this study suggests that high flow events do not necessarily lead to high POC concentrations, and therefore POC in these rivers likely reflects the availability of particulate organic material, rather than storm characteristics.

Further work is needed in both river catchments to determine the sources of particulate organic matter (especially POC) and how these sources are attenuated during storm events. More experimental techniques such as lignin phenol and stable isotope compositions ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ), can reveal precisely whether POC associated with SS is allochthonous (sourced from outside the river channel) or autochthonous (sourced from within the river channel), and whether POC is a sensitive indicator of soil and land alterations.

## References

- Coynel, A., Etcheber, H., Abril, G., Maneux, E., Dumas, J. and Hurtrez, J.E. 2005. Contribution of small mountainous rivers to particulate organic carbon input in the Bay of Biscay. *Biogeochemistry*, 74, pp.151-171.
- Emelko, M.B., Stone, M., Silins, U., Allin, D., Collins, A.L., Williams, C.H., Martens, A.M. and Bladon, K.D., 2016. Sediment-phosphorus dynamics can shift aquatic ecology and cause downstream legacy effects after wildfire in large river systems. *Global Change Biology*, 22(3), pp.1168-1184.
- Gomez, B., Trustrum, N.A., Hicks, D.M., Rogers, K.M., Page, M.J. and Tate, K.R. 2003. Production, storage, and output of particulate organic carbon: Waipaoa River basin, New Zealand. *Water Resources Research*, 39, doi:10.1029/2002WR001619, 6.
- Gottselig, N., Nischwitz, V., Meyn, T., Amelung, W., Bol, R., Halle, C., Vereecken, H., Siemens, J. and Klumpp, E., 2017. Phosphorus binding to nanoparticles and colloids in forest stream waters. *Vadose Zone Journal*, 16(3).
- Han, L., Huang, S., Stanley, C. D. and Osborne, T. Z., 2011. Phosphorus fractionation in core sediments from Haihe River Mainstream, China. *Soil and Sediment Contamination* 20(1), pp.30–53.
- Wheatcroft, R.A., Goni, M.A., Hatten, J.A., Pasternack, G.P. and Warrick, J.A. 2010. The role of effective discharge in the ocean delivery of particulate organic carbon by small, mountainous river systems. *Limnology and Oceanography*, 55(1), pp.161-171.