Factors regulating phosphorus in drains and streams in sandy agricultural catchments on the south coast of Western Australia.

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Abstract

The eutrophication of waterways continues to be recognised as a worldwide issue due to the negative economic, environmental and social impacts of resultant algal blooms. In catchments dominated by broad acre and irrigated agriculture, nutrients such as phosphorus (P) delivered to streams are mainly considered to originate from diffuse rather than point sources (e.g. waste water treatment plant). The pathways of phosphorus (P) loss from the agricultural landscape to the stream have been well studied. Much effort and resources have been placed into reducing the amount of P being lost to waterways through implementation of best management practices (BMP’s) at a paddock, farm and catchment scale. On the south coast of Western Australia (WA), BMP’s have been implemented with little or no consideration of the role of stream sediments in the retention and release of P. Although we have a reasonable understanding of water quality patterns associated with seasonal conditions at a catchment or sub catchment scale, it is not known whether P is retained or released from drain or stream sediment under various conditions (such as intermittent or ephemeral stream flows in a Mediterranean climate) in these coastal catchments. Consequently, it remains difficult to differentiate the P retention or release from a catchment in any year or event between the agricultural landscape and the stream network.

This thesis examines factors controlling P retention and release by stream and drain (known as ‘streams’ from herein) sediments in sandy agricultural catchments to determine whether they are net immobilisers or sources of P. Internationally (in predominately temperate climates with perennial streams), key factors that affect the control of P retention and release have been identified. Based on the literature, the two key elements that influence the retention and release of P are particle size and mineralogy (specifically iron oxides). Biotic control on the retention of P in various sediment particle sizes was also found to be significant.

Using the international literature as a guide, this study of fundamental controls on P retention and release identified that mineralogy was a key driver of P retention by sediments in these catchments. When normalised by surface area rather than mass, sand material (<2mm) adsorbed considerably less P (mg m⁻²) than lateritic gravel material (>2mm). In these catchments gravel is a significant contributor to P retention and should be considered along with the <2mm fraction when determining retention and release characteristics of stream sediment. Furthermore, both the sand and gravel...
components of the sediments were considered net immobilisers of P with approximately 30% of the P added in solution retained by the sediment and 8% of the retained P then released back into stream water. While geochemical (abiotic) processes dominate the control of P retention and release, the microbial biota in sediment can play an important role in regulating P uptake. This thesis identified that mechanisms of biotic P uptake from intermittent streams in a Mediterranean climate with sandy-gravel sediments are very different from mechanisms in perennial streams in a temperate climate. In this study, sand was integral in maintaining biotic populations. A novel approach was used to separate non-phototrophic (microbial biota that does not require photosynthesis to function) and phototrophic P uptake. It was found that the ratio of photo and non-phototrophic biota was site specific. Sediments with low abiotic P sorption, such as stream sediments with poorly sorbing sands, are assisted by the presence of biota to increase their capacity to retain P.

The Mediterranean climate, specifically the drying and wetting cycle of many streams on the south coast of WA influence both biotic and abiotic controls on P retention and release. The literature suggested that given the sediment type, aging of minerals and death of biota on drying of sediment, the sediments should be a source of P to streamwater. The annual wetting and drying cycle has most likely aged the minerals in sediments on the south coast of WA. When drying of sediments occur there are minimal increases in the equilibrium phosphorus concentration (EPC₀) and negligible decreases in the P binding energy. Therefore minimal release of P from the sediment upon will occur. This is concurrent with an analysis of historic water quality and equilibrium P concentration of stream sediments reinforcing the idea/suggestion that stream sediments on the south coast of WA are net immobilisers of P and not a source of P.

Significantly, the findings of this thesis clearly identifies that in sandy catchments, stream sediments are an important component in the removal of P from stream water. This has implications for both modelling of P loss in catchments and also for the measurements of BMP efficacy implemented in the catchments. The new understanding of factors regulating P in streams on the south coast of WA may strengthen catchment models through having experimental values to input rather than suggested stream loss rates or algorithms based on factors of stream affecting P assimilation. Importantly, the understanding of sediment controls on P allows determination of the appropriate length of water quality monitoring to determine a better estimate of the beneficial effect of an implemented BMP at a catchment level.
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I dedicate this PhD thesis to my father:

Victor Russell Clarendon
1946-2014

and close friends:

Arjen & Yvonne Ryder
1960-2014

I miss you all heaps.
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Declaration

I declare that the source of all information presented in this thesis is from the work of myself, unless the source is otherwise acknowledged, and that it has not been previously presented for any degree at any university.

______________________________
Simon Clarendon
Thesis structure

This thesis is composed of six chapters. Chapter 1 introduces succinctly why P as a nutrient is required in an agricultural production system and the consequence of the over-application of P in these systems. The review identified a knowledge gap in the understanding of P movement through agricultural catchments with sandy soils, which this thesis addresses. Chapter 2 provides a detailed review of international literature on the processes involved in P retention and release by stream sediment. Chapter 2 provided guidance for the development of methodology and experiments in Chapters 3, 4 and 5. The role of particle size and mineralogy in P retention and release in the context of sandy coastal catchments is discussed in Chapter 3. Similarly, Chapter 4 identifies the contribution of sediment biota to the retention and release of P by the sediments. Chapter 5 assesses the effect that climate has on P retention and release by sediment, then draws all these elements together (particle size, mineralogy, biota and climate) to determine if stream sediments on the south coast of WA act as sources or sinks of P (or perhaps both under varying conditions). Chapter 6 provides a summary of each of the data chapters and places the new knowledge in the context of international research and discusses the ramifications of those findings for the measurement of water quality and for the efficacy of BMP’s. The conclusions provide guidance for future research based on the findings of this thesis.
Chapter 1. Introduction

Agricultural production continues to intensify to meet global food demand (Moore et al., 2010) increasing the use of fertiliser (Nguyen and Sukias, 2002; Evans and Johnes, 2004; Hoffmann et al., 2009; Palmer-Felgate et al., 2009; Gourley and Weaver, 2012). Repeated applications of fertiliser in agricultural systems in excess of agronomic demand has caused the build-up of phosphorus in soils (Sharpley and Withers, 1994; McDowell et al., 2003a; Weaver and Wong, 2011), and thus enrichment of receiving aquatic systems such as streams, rivers, lakes, estuaries, marine embayments (Hodgkin and Hamilton, 1993). This eutrophication (nutrient enrichment) of waterways is an important worldwide issue (Pote et al., 1999; Sharpley and Tunney, 2000; Nguyen and Sukias, 2002; House, 2003a; Evans and Johnes, 2004; Palmer-Felgate et al., 2009). Algal blooms are a well documented consequence of eutrophication of waterways (Chapman et al., 2001; Palmer-Felgate et al., 2009). In some cases these are toxic (Chapman et al., 2001; McDowell et al., 2004) and can lead to negative environmental (Carpenter et al., 1998; McDowell et al., 2009), economic (Carpenter et al., 1998; Nash and Halliwell, 1999; McDaniel et al., 2009) and social impacts (Carpenter et al., 1998; McDowell et al., 2004; McDaniel et al., 2009). Phosphorus (P) can be the limiting factor for the growth of algae, specifically as nitrogen and carbon, both essential to growth of aquatic biota are more dynamic, freely exchanging between the atmosphere and water (Daniel et al., 1998).

In Western Australia (WA), research has been undertaken to facilitate understanding of nutrient loss, in particular P loss from agricultural systems and the best management practices (BMPs) to minimise these losses. The catchments on the south coast of WA are dominated by sandy textured soils and have inherently low fertility, due in part to high rainfall infiltration and poor nutrient retention properties increases the leaching of nutrients to groundwater (National Land & Water Resources Audit, 2002). The topography is low in relief with 50% of the drainage basins dominated by dryland agriculture. Gully erosion is the dominant source of sediment (70%) to streams (National Land & Water Resources Audit, 2002). The Mediterranean climate (Davies and Stewart, 2013) comprises seasonal rainfall which in turn results in intermittent and ephemeral flows in most streams with a limited capacity to transport sediment (National Land & Water Resources Audit, 2002). As a result, 57% of the P load delivered to receiving waters is in dissolved form.
At a catchment level, through analysis of farm-gate nutrient budgets, there is an understanding of the amount of agricultural P use efficiencies and the associated nutrient surpluses that have the potential to be lost to the wider landscape (Gourley et al., 2007; Keipert et al., 2008). What is not well-understood is the role that drains and streams within a catchment play in regulating P lost from agriculture to receiving waters. The movement of P from the edge of paddocks in agricultural systems to the receiving waters is often considered as the weakest aspect of catchment models, thereby adding uncertainty to predicted responses by receiving waters (Haggard and Sharpley, 2007).

This thesis identifies key elements that have an influence on P retention and release by drains and streams in sandy agricultural catchments in a Mediterranean climate. The understanding from this thesis will provide insight for regional catchment P loss models and present opportunities for further research to separate retention and release of P by streams to landscapes to better understand the efficacy of best management practices (BMP’s) implemented to reduce P loss. This chapter provides background to why P loss from agricultural systems has become a water management issue, the efforts undertaken to minimise P loss from agricultural systems and an outline of the remaining thesis chapters.

Background

The requirement for phosphorus in agriculture

Phosphorus is a major nutrient essential for plant growth to provide food directly for human consumption and for consumption by animals in agricultural production systems as well as fibres (i.e. cotton) and biofuels (Sharpley and Tunney, 2000; McDowell et al., 2003b). Globally, some soils are low in native P such as in Australia and, in particular, Western Australia (Weaver et al., 2001; Bolland et al., 2003a). Soils such as these require the application of fertilisers to meet the growth requirement of pasture and crop plants and ensure agricultures economic viability (McComb and Davis, 1993; Weaver and Wong, 2011).

Phosphorus application in agricultural systems

Despite the opportunity for landowners to apply fertiliser at rates required for optimum plant growth, many farmers in southern Australia have applied P at a higher rate (e.g. annual rate of 10 – 15 kg P ha\(^{-1}\)), irrespective of the soil P status (Weaver and Wong, 2011; Rivers et al., 2013) leading to P enriched agricultural systems. This practice of
over-fertilisation has been identified as a global issue (Alley, 1991; Sharpley et al., 1994). Over-application of P is thought to be due to a “traditional” approach to fertiliser application whereby P is applied at rates generally based on those developed when the land was first cleared (annual rate of 10 kg P ha\(^{-1}\) - 15 kg P ha\(^{-1}\)) (Weaver and Prout, 1993; Yeates, 1993; Rivers et al., 2013). This has contributed to more than 50% of the soils on the south coast of WA having high P status: that is, the soils contain sufficient plant available P to be able to avoid at least one annual application of P and still provide the same pasture production (Weaver and Reed, 1998). Soils with a high P status will more likely lose P as the soils capacity to retain P diminishes with repeated application of P. Sharpley et al. (1994) identified that the amount of P lost from agricultural runoff was dependent on management factors such as time, rate and method of fertiliser application. The pathways by which excess P from agricultural systems reaches waterways are now discussed in detail.

The movement of P from agricultural production systems to waterways

**P inputs**

The main avenues of P input into agricultural systems is via fertiliser and feed (Figure 1). Unlike nitrogen, P does not have a gaseous loss phase and thus avenues of removal of P from agricultural systems are more easily identified (Gourley and Weaver, 2012). Some P is taken off the farm in produce, whilst the remaining P either accumulates in the soil or is lost via leaching or runoff.
Figure 1. Phosphorus input and movement through an agricultural system (modified after Weaver and Wong, (2011)).

**P outputs**

The export and sale of animals (e.g. beef cattle), products from an animal (wool and milk) and plant products, such as hay, silage, grain and crop are outputs that remove P from an agricultural system (Figure 1). More prevalent in the USA and Europe is the output of manure/effluent from agricultural systems (such as a piggery), which then becomes a nutrient input for another agricultural system within the same region (Kleinman et al., 2011). Alternatively, it can be redirected locally (Sharpley et al., 2001) such as within a farm to another paddock through grazing management, as occurs in Australia and New Zealand.

The remaining P that is not accounted for in outputs (removed from the agricultural system) will either accumulate in the soil, leach through the soil profile (sub-surface flow) or be removed by runoff and erosion via overland flow (Figure 1).
Accumulation of P in the soil

Mineralogy, particle size, pH, fertiliser history, temperature, time and soil-solution ratio are important factors that affect the soil’s capability to retain P (Barrow, 1974, 1983b, 1984, 1989b, 2008; Barrow et al., 2000). Geochemical processes govern much of the retention of P by soils. The adsorption of P by soil is a two-step process, initial rapid sorption by the soil followed by a slow sorption; and this is likewise for desorption (Barrow, 1983b). The fine fraction of the soil (<2mm), especially clay material, is considered to be able to retain the most P because of its surface area and mineralogy. In the finer soil fraction, multivalent cations such as Fe$^{2+}$, Ca$^{2+}$ and Al$^{3+}$ are attracted to the negative charge on clay platelets forming a bridge for the clay platelets to be held together. Phosphate ions in soil-water can bind strongly to the aluminium and iron oxides with little chance of the bond breaking (Brady and Weil, 2008). Given the extensive network of strong binding sites available for P in clay soils, in some instances annual applications of P are required for pasture growth due to the locking up of large amounts of. At the opposing end of the P-retention spectrum are soils with high sand content. Generally sandy soils have less surface area (in comparison to clays), due to larger particle size (Brady and Weil, 2008) and are low in aluminium and iron (Weaver et al., 1988) providing minimal binding sites for P. The annual applications of fertilisers to sandy soils are made for the opposite reason to clay soils, due to the high hydraulic conductivity of sand. Soils with different clay and sand content will vary in how much P they accumulate with some P being lost to the wider environment via runoff or leaching.
Surface runoff and leaching of P through soil

The flow of P through the landscape is influenced by numerous factors that will determine the form of P and its loss pathway. Rainfall duration, amount and intensity and topography are contributors to the selection of the pathway of flow of P through a landscape (Haygarth et al., 2000; McDowell et al., 2004; Buda et al., 2009b). Physical and chemical properties of soil also affect the pathway of P movement through the landscape (Haygarth et al., 2000).

Soil type and climate will determine the rate of infiltration and the dominant flow pathway through soils due to its structural components, e.g. macropores will allow flow down the soil profile (Heathwaite and Dils, 2000). In sandy soils, the dominant pathway of P movement is predominantly via subsurface flow (Ruprecht and George, 1993; Chardon and Schoumans, 2007) due to the low P binding capacity and high porosity of the soil with the principal form that enters the waterways being soluble P (Kinhill Engineers, 1988 cited in Ruprecht and George, 1993). Typically, sandy soils are categorized as having a P loss pathway via leaching unless they are seasonally inundated, in which case surface runoff (lateral leaching) can be a significant pathway of P loss. Similarly, a landscape with low relief can provide greater opportunity for infiltration of water prior to entering the stream, altering the form of P entering the stream (e.g. particulate P to soluble P). A landscape with steep slopes will have higher erodability (National Land & Water Resources Audit, 2001), which in turn will lead to a dominance of particulate P entering streams. A clay or silty soil will have higher potential for overland flow, owing to the higher probability of rainfall exceeding infiltration capacity of the soil, providing more opportunity for transfer of topsoil material eroded to streams, with P attached to the eroded particles (Summers et al., 2002). As clay soils tend to have low saturated hydraulic conductivity, the dominant pathway of P movement is via surface flow, with much of these losses being event-specific (e.g. rainfall event) (Hart et al., 2004; Chardon and Schoumans, 2007). In many regions of the world, the form of P in surface runoff is dominated by particulate P (Hartikainen et al., 2010), although in some landscapes, soluble P can form a substantial component of total P (TP) (Dougherty et al., 2004; Buda et al., 2009a). Loam soils sit between clay and sandy soils and can be dominated by either overland flow (Ruprecht and George, 1993) or subsurface flow (Kleinman et al., 2007). Rainfall-runoff is a key driver in the flow of water along a stream. Whilst topography and soil type can affect the forms of P and the energy of flow events, runoff is the carrier of nutrients. A high
rainfall intensity event, when the rate of rainfall exceeds the rate of infiltration of the soil irrespective of soil type or topography is conducive to overland flow. Rainfall intensity, soil type, topography, vegetation cover and antecedent conditions influence the dominant flow pathway (e.g. sandy soil will have high infiltration which will mean subsurface flow is the dominant pathway). Phosphorus that has accumulated in the soil, but is remobilised over time through the various pathways to the stream is identified as legacy P (Sharpley et al., 2013).

Irrespective of the pathway that P takes to the stream from the landscape the loss of P to waterways through erosion, surface and sub-surface runoff and leaching from a soil is often called a ‘diffuse’ source of pollution, that is, it does not have a specific discharge point (e.g. pipe) that P loss can be attributed to, at which remediation can be targeted.

**P loss pathways: a southwestern Australia perspective**

On the south coast of Western Australia, the long time period over which weathering has occurred means the soils can be high in silica, Fe and Al or combinations thereof (Singh and Gilkes, 1991; Weaver and Reed, 1998). Thus many of the soils on the south coast of WA are sandy. Where clay is present, the dominant form is kaolinite (Singh and Gilkes, 1992a). The soil tends to be more acidic than neutral, making the Fe and Al more readily available for sorption of P. Some duplex soils (sand over clay or rock), such as those on the coastal areas of WA contribute a quarter of the movement of P via subsurface flow and the remainder via saturated overland flow. These pathways are due to the movement of P through and over the A horizon due to the low transmissivity exhibited by the B horizon (Ruprecht and George, 1993). The dominance of sandy and sandy duplex soils on the south coast of WA leads to a dominance of soluble P, a point of difference from many areas of the world where the loss of particulate P (PP) to waterways from soil is often seen as the greatest concern in mitigating P loss from agricultural catchments (Kleinman et al., 2011). However, as observed on the south coast of WA (Ruprecht and George, 1993; McKergow et al., 2003; Weaver and Summers, 2014), it is becoming increasingly apparent that soluble P may be of similar or greater concern than PP loss from erosion in both surface and subsurface runoff (Heathwaite and Dils, 2000; Buda et al., 2009a; Weaver and Summers, 2014)
Management of nutrient loss from agriculture: a southwestern Australia perspective

To minimise the loss of P to the environment, a number of on-farm and catchment level management practices have been developed and implemented (Figure 2). Ideally management practices should have dual outcomes such as reduced environmental P loss and be cost-beneficial at a farm level (assuming the broader environmental costs have been accounted for).

Internationally, Gitau et al. (2001) (cited in McDowell et al., 2004) collated studies on effectiveness of numerous BMP’s on landscapes dominated by overland flow. The two most effective BMP’s for reducing P loss to the receiving environment were the installation of riparian forest buffers (60% reduction) and filter strips (30% reduction). Both of these management practices involve the planting of indigenous or exotic plant species to act as a barrier by entrapping particulate bound P prior to entering waterways (Weaver and Summers, 2014). Riparian plantings are generally located adjacent to the stream, whereas filter strips are located nearby but downslope of known P sources, such as an animal production facility (Dillaha et al., 1989). Management practices within animal production systems such as effluent management systems only reduced P loss to the environment by 10-15%, although some studies showed a greater loss P of 50% (McDowell et al., 2004). Effluent management systems include multiple holding ponds for ‘washdown’ water from dairy sheds with the effluent being reapplied to paddocks. Confronting the issue of excess nutrients at the source, nutrient management plans reduced the loss of dissolved P by 20% (McDowell et al., 2004). Nutrient management plans require extensive soil testing. The results of the soil test provide the basis for the targeted application of nutrients via fertilisers or effluent to minimise or alleviate the loss of excess nutrients to the environment while providing monetary benefit to the landowner through reduced fertiliser application. However, whilst particular BMP’s, such as riparian buffers are effective in reducing P loss to the greater environment in some regions of the world, they may not be effective in other regions. In the case of WA, riparian buffers are not an effective BMP tool due to the nature of soils and hydrological pathways (McKergow et al., 2003; Summers et al., 2014; Weaver and Summers, 2014). Many BMP’s have been researched and some applied in WA and are discussed in more detail.
Figure 2. The key components (circles) through which P transfers in an Australian agricultural environment, and examples of interventions (rounded rectangles). Contribution to scientific knowledge from this thesis (to the right of the dotted line). Figure adapted from Gourley and Weaver (2012).

Figure 2 illustrates the pathway of P transfer through an agricultural environment and notes examples of interventions that have been undertaken (predominantly by the WA Department of Agriculture and Food). To the right of the dotted line is the research reported in thesis: an evaluation of in-stream factors that regulate the losses of P from the terrestrial catchment to the receiving waters. Specifically, the interventions that have been undertaken within the farm boundaries to reduce P loss from agriculture including:

- **Alternative fertilisers:** the use of alternative fertilisers (Summers *et al.*, 2000), such as amended aluminium bauxite residue coated fertiliser granules. The bauxite residue coating on the superphosphate fertiliser reduces the leaching of P from the fertiliser granule over time increasing the P available for plant production.

- **Nutrient management:** improved fertiliser management through the use of soil testing to optimise P inputs (Sharpley *et al.*, 2001; Weaver *et al.*, 2011). Soil tests are used to identify the areas of nutrient excess or deficiency, enabling the landowner to tailor their fertiliser application to areas that only require P. Furthermore, less frequent use of fertilisers with reduced solubility instead of regular application of highly soluble fertilisers such as superphosphate can reduce the loss of P to the environment (Ritchie and Weaver, 1993).
• Soil amendments; the use of P-retaining material on soils to reduce loss of P from sandy soils and improve plant production (Summers et al., 2001, 2004). The P retaining function through the soil amendment having a large surface area and high P fixing capacity, thereby reducing P loss to the environment. A gypsum amended bauxite residue such as Alkaloam™ has the ability to reduce the loss of nutrients to sensitive waterways by up to 75% while increasing pasture production by up to 25% (Summers et al., 2004). Similarly, the application of chemical amendments, such as slaked lime to some manure reduced the solubility of P in the manure and soil (Sharpley et al., 2001), reducing the runoff of P.

• Perennial pastures; the introduction of perennial pastures into farm programs (Keipert et al., 2008), which have a longer growing season and are more deeply rooted compared to annual pastures allows greater P utilisation. However, recent research in WA suggests that the P requirements for these species may be low, therefore perennial pastures may not be as successful at minimising P loss under current fertiliser regimes (Rogers, 2011).

Research into reducing P loss has been applied at the catchment scale:

• Riparian management; the exclusion of stock from waterways (through fencing) and the revegetation of the riparian zone to minimise the loss of P from the landscape into the stream. Due to the dominance of subsurface and saturated flow in the coastal catchments of WA, McKergow et al. (2003) showed that instead of reducing total phosphorus (TP) loss through the revegetation of the riparian zone, the proportion of stream water TP concentration (which remained constant pre and post riparian revegetation) present as filterable reactive phosphorus (FRP) increased after riparian revegetation was established. The increase in FRP provides more bioavailable P for consumption by aquatic species including algae.

• Wetland management; the use and design of wetlands for the storage and cycling of P. Wetlands have been shown to provide limited value for retaining P in agricultural catchments (Chambers et al., 1993). While wetlands have considerable capacity for removal of nutrients from inflowing water, the inflow-
outflow of water through the wetland may change sediment chemistry and release P. If high flows of water should occur, short residence times would not allow for removal of P by wetland sediment (Chambers et al., 1993).

- Endpoint remediation; the intervention of the effect of eutrophication in the receiving water. To reduce the opportunity of algal blooms to occur in the Peel Inlet on the west coast of WA, a channel was constructed from the inlet to the ocean to increase flushing of nutrient rich water to the ocean and alter the salinity regime to inhibit algal blooms (Hodgkin and Hamilton, 1993). This saw a marked decrease in algal blooms in the estuary but an increase of algal blooms in the feeder river systems (Rose, 2003; Summers et al., 2004).

BMP’s such as those previously discussed have been in some cases, have been shown to have a negligible effect on minimizing P loss from the agricultural landscape in WA (McKergow et al., 2003). Similarly, the reduction of P by implemented BMP’s known to work at the edge-of-field is not being seen in WQ measured instream (Jarvie et al., 2013b; Rogers et al., 2013). This is a call for concern as future monetary investment by government and the private sector in reducing P loss to meet catchment nutrient reduction targets is reliant on seeing results (Sharpley et al., 2013). This disparity in levels of P identifies the lag effect of P movement through the landscape and stream network, known as legacy P (Kleinman et al., 2011; Jarvie et al., 2013b; Sharpley et al., 2013). In particular, instream legacy P is not accounted for when assessing nutrient reduction targets and the efficacy of BMP’s even though a considerable amount of P is potentially stored in stream sediment (Keipert et al., 2008). Thus, in aiming to improve WQ and reduce the amount of P entering receiving waters, factors affecting the cycling of nutrients in streams must be taken into account when considering the effectiveness of BMP’s as well as modeling of P loss through catchments.
Motivation for study

Nutrient processing within drainage networks in agriculturally-dominated catchments remains under-studied in WA, and has received limited attention in Australia though there was a small on-farm plot trial on different soils in Victoria, Australia (Barlow et al., 2003). The limited study on this topic is in spite of modelling suggesting that about 40% of the surplus total P in the catchment is lost from paddock edges to streams, and up to 80% of the P input to streams may be retained in the stream (Keipert et al., 2008). In the South West Coast Australian drainage division, only 13% of the sediment supplied to the stream was exported to the coast, indicating retention of sediment along the river course (National Land & Water Resources Audit, 2002). Thus, how streams regulate P transport in agricultural catchments dominated by sandy soils and subsurface flow requires research. Furthermore, the ancient highly weathered landscape of Western Australian provides a unique opportunity to study stream sediment retention and release of P in agriculture-dominated catchments largely consisting of ephemeral and intermittent streams.

Research challenges

The objectives of this thesis are to:

1) Identify the key elements that regulate P in drains and streams in agricultural catchments dominated by sandy (deep sand and sandy duplex) soils.

2) To better understand the contribution of streams and drains to P retention and release, with a focus on intermittent and ephemeral streams. Do the sediments act as a source or sink?

3) Provide insight for models to better estimate P loss from catchment models.
Chapter 2. Factors influencing the regulation of phosphorus by stream sediment in agricultural catchments

Introduction

Eutrophication and nuisance algal blooms are an increasing problem in aquatic environments. Consequently, understanding the processes and pathways of phosphorus (P) transfer to receiving waters is critical to the prioritisation of nutrient management practices at both a farm and catchment level. While man-made and natural drainage of agricultural lands is integral to maintaining the productivity of agricultural land (Sharpley et al., 2007), it is also the network by which water and P is transferred from landscapes to receiving waters (Needelman et al., 2007). During this transfer in the drainage network, a complex combination of abiotic and biotic processes in the sediment can regulate the movement of P (House and Warwick, 1999; Sharpley et al., 2007) and are considered important in the cycling of P along a stream ecosystem (Klotz, 1988; House and Warwick, 1999; McDowell et al., 2002; Evans et al., 2004; Haggard et al., 2007). These processes, along with inherent sediment characteristics, influence the retention or release of P to stream water.

Internationally, numerous studies have identified the individual abiotic and biotic elements that contribute to the regulation of P by sediments from streams in agricultural catchments, although the controls on their relative importance are not well understood (McDaniel et al., 2009). These elements can be assigned under overarching themes. The themes that are considered to contribute to in-stream P regulation are geological influences (Ballantine et al., 2009), physicochemical characteristics of the sediment (Klotz, 1988; Nguyen and Sukias, 2002; Haggard et al., 2007), sediment particle size (Meyer, 1979; Klotz, 1988), biotic elements (Haggard et al., 2007; Sharpley et al., 2007; McDaniel et al., 2009), chemistry of the water (Meyer, 1979; McDaniel et al., 2009), seasonal hydrological regimes (Evans et al., 2004; Simon et al., 2005; Sharpley et al., 2007; Ballantine et al., 2009) and temporal elements (Barrow, 1983b).
Geological and geomorphological influences

Depending on the parent material, soils or sediments will have different characteristics affecting how P is sorbed (Lopez et al., 1996 cited in Ballantine et al., 2009). The sediment in streams can be derived from various soil sources in the catchment landscape; topsoil via overland or tile drainage flow (Nguyen and Sukias, 2002), subsoil, stream banks and stream beds (McDowell and Wilcock, 2007). Each of these sources will vary in their contribution to sediment formation due to characteristics such as soil type, topography, hydrology, land use and management and climatic conditions (Harrod and Theurer, 2002; Walling, 2005; McDowell and Wilcock, 2007; Ballantine et al., 2009). Consequently, soil and sediment will share some characteristics that will affect the biological, chemical and physical functions of the sediment (Needelman et al., 2007). However, sediments can be dissimilar to soils in their behaviour as they have undergone particle size ‘sorting’ by fluvial processes, microbial activity within the sediment and changes in the redox reactions (Baldwin et al., 2002). In intermittent and ephemeral streams, particle size ‘sorting’ can be quite distinct with a rapid decline in grain size downstream (Dunkerley, 1992). This must be viewed in the context of the type of flow i.e. storm or base, to which the stream is exposed (Powell, 1998). Furthermore in-stream sorting can lead to geomorphological stream features forming such as riffles and pools which have different physical and chemical characteristics (Agudelo et al., 2011). The origin of the sediment will therefore, in part, determine the physico-chemical characteristics of the sediments capacity to retain and release P.

Physico-chemical characteristics

Phosphorus transfers between sediments and the water column are influenced, in part, by the physico-chemical characteristics of the sediment (Evans et al., 2004; Agudelo et al., 2011). Particle size, surface area and geochemistry of sediment are highly interlinked (Horowitz and Elrick, 1987). For example, in sediments that consist of coarser grains, the geochemistry (abiotic component) is more important than particle size as the surface area is reduced in comparison to fine grain sediment. In part, this is due to the mineralogy of the surface coating having greater effect than the size of the grain and its associated geochemistry (Horowitz and Elrick, 1987). The geochemistry that affects all sediment particle size is discussed in more detail below.
Geochemistry irrespective of particle size

The abiotic exchange of P between the water column and the sediment is generally accepted as the dominant component of P regulation in streams (Klotz, 1985; Shigaki et al., 2008). There is underlying chemistry such as the presence of Al and Fe oxides, that guides adsorption and desorption processes of P from sediment irrespective of the size of the particle. The mineralogy and geochemistry of each particle size fraction defines the maximum capacity for each fraction to adsorb and desorb P.

Phosphate ions that are readily exchanged from the water column to the sediment are negatively charged, for example, hydrogen phosphate (HPO$_4^{2-}$) and dihydrogen phosphate (H$_2$PO$_4^-$) (Barrow, 1989b; Fox, 1989). The form of the phosphate ion is pH dependent with HPO$_4^{2-}$ dominant in alkaline environments and H$_2$PO$_4^-$ in acidic environments (Barrow, 1989b; Brady and Weil, 2008). In near-neutral solutions both anions are present in similar amounts (Barrow, 1989b; Brady and Weil, 2008). Similarly, the pH of the sediment or solution will affect the adsorption or precipitation of phosphate ions from the water column. In acidic environments, such as on the south coast of WA (Gazey et al., 2013), the phosphate ion will adsorb to iron (Fe) and aluminium (Al) hydroxides but in alkaline conditions the phosphate ion will bind to calcium (Ca) (Axt and Walbridge, 1999). However for precipitation of P as calcium phosphate, the pH of the sediment and solution has to be above pH 8 (Diaz et al., 1994).

Adsorption of phosphorus by Fe and Al

Amorphous and poorly crystalline Fe and Al and to a lesser extent organic matter are an integral and dominant influence on the P sorption capacity of sediments (Horowitz and Elrick, 1987; Borggaard et al., 1990; Reddy et al., 1995; Nguyen and Sukias, 2002; Agudelo et al., 2011; Zhenhua et al., 2012). This is due in part to a poorly crystalline structure having a high specific surface area for P sorption (Borggaard et al., 1990; White, 2006; McDowell, 2009; Agudelo et al., 2011).

There are numerous mechanisms which enable the adsorption of phosphate ions onto Fe and Al oxides and oxyhydroxides and other materials. Generally it can be considered a two-step process (Froelich, 1988). The first step precipitation reaction takes minutes to hours whereby the negatively charged oxygen (O) of the phosphate ion attaches to the aluminum hydroxide (Al-OH) or iron hydroxide (Fe-OH) via the positively charged Fe or Al (Stone et al., 1995; Brady and Weil, 2008; Lair et al., 2009). Another first step
process is ion exchange, whereby the phosphate ion replaces another, attaching itself to a hydroxide. This reaction is relatively reversible (Brady and Weil, 2008).

The second step reaction is not easily reversible and occurs over a period of days to months (Barrow, 1983b; Froelich, 1988; Stone et al., 1995; Lair et al., 2009). This is ligand exchange whereby the phosphate ion replaces a pair of adjoining singly coordinated hydroxyl (-OH) groups on the Fe or Al oxide (Borggaard et al., 1990; Brady and Weil, 2008). This binds the phosphate ion tightly not allowing easy exchange with other anions. Over time, the second O in the phosphate ion may attach itself to another Fe or Al, replacing another structural -OH. A binuclear bridge is formed and the phosphate ion becomes part of the mineral structure; a process considered irreversible under “normal” conditions. Similarly, when pH of the sediment and solution is alkaline, \( \text{H}_2\text{PO}_4^- \) reacts quickly with Ca to form mono-, di- and tri-calcium phosphates, which decrease in solubility from the mono form (highly soluble) to the tri form (Stone et al., 1995; Brady and Weil, 2008).

Increased Fe and Al concentrations and to a lesser extent Ca concentration in sediment increases its capacity to bind P. The pH will affect both the form of the phosphate ion attaching and also the oxide or oxyhydroxide that the P will attach to. There is a two-step process for P sorption to sediment from solution. The first step, a rapid uptake of P, is highly to relatively reversible. The second step, considered irreversible, binds the P very strongly to the oxides, incorporating the P in the mineral structure. Organic matter (OM) alongside Fe and to a lesser extent Al can have control on P sorption by sediment.

**Organic matter and phosphate sorption**

Organic matter is the remnant of plant and animal material at various stages of decomposition and is colonized by an array of soil organisms (White, 2006). The non-water soluble components are typically categorized by size into a) particulate OM (200 - 53 µm) that is recently partly humified and, b) the humified fraction (<53 µm) which adheres strongly to mineral particles and consists of very inert OM and humus. About 60-80% of the OM is made up of humus (Brady and Weil, 2008), which includes fulvic acid, humic acid and humins. The fulvic and humic acids are predominantly alkyl and aromatic groups covalently bonded to form polymers and are absorbed onto mineral surfaces via various mechanisms (White, 2006). Horowitz and Elrick (1987) noted that OM could be found in two major forms. Firstly, as a discrete particle which is more
predominant in coarse grain sediment or secondly, as a coating on individual grains which is more common in fine grain sediments.

Organic matter in sediment can potentially decrease or increase P sorption capacity. Organic matter of a high molecular weight can inhibit crystallisation of Al and Fe oxides through complexation creating Al, Fe or Ca–humic complexes, expanding the specific surface area of the sediment particle and increasing the P sorption capacity (Borggaard et al., 1990; Axt and Walbridge, 1999; Nguyen and Sukias, 2002; McDowell, 2003; Dunne et al., 2007; Zhuan-xi et al., 2009). Conversely, if the OM has a low molecular weight it has potential to compete with phosphate sorption sites on mineral surfaces (Reddy et al., 1998; Zhuan-xi et al., 2009; Niedermeier and Robinson, 2009). The humic acids in OM with a low molecular weight are known to obstruct P sorption by forming stable complexes with Al, Ca and Fe ions (Niedermeier and Robinson, 2009). Organic matter present as a coating on the sediment can inhibit an increase in surface area (Horowitz and Elrick, 1987) and hence reduce potential P sorption sites.

A strong relationship between P sorption by sediment and OM content has been identified. Dunne et al. (2006) suggested 42% of the variability in P sorption to OM was most likely due to OM complexing with Fe and Al. Reddy et al. (1998), Nguyen and Sukias (2002), Yoo et al. (2005) and Dunne et al. (2006) all found a strong positive correlation between P sorption maximum ($S_{\text{max}}$) and OM or total organic carbon content (TOC) content suggesting that OM can play an important role in the amount of P the sediment can store. The effect that OM has on P sorption by Al and Fe are different for each metal (Borggaard et al., 1990). However, it has been noted that OM would more strongly absorb P in association with Fe than with Al (Montigny and Prairie, 1993; Nguyen and Sukias, 2002). Organic matter can also affect the equilibrium P concentration ($EPC_0$) of sediment with higher OM, decreasing the $EPC_0$ (McDaniel et al., 2009). As OM percentage increases in the sediment, so does the ability of the sediment to buffer P from solution (Smith et al., 2005). Contrary to Horowitz and Elrick's (1987) assessment of the function of the two main forms of OM (coatings on grains or as discrete particles) large grain material, (i.e. gravel) coated with OM can adsorb pollutants such as P (Gainswin et al., 2006a).

Other authors have suggested that Fe and Al govern the sorption capacity of some sediment and OM has no direct influence or even has a negative influence on P sorption by some sediments with the decrease in sorption of P onto Fe and Al oxides due to the
presence of OM (Sibanda and Young, 1986; Borggaard et al., 1990) particularly in areas with low OM (compared to global standards) such as in Western Australia (Griffin et al., 2013). Similarly McDowell and Sharpley (2003) found that OM did not limit P uptake and Ryan et al. (2007) found no relationship between OM and P uptake in both autoclaved and fresh sediments and attributed P sorption variation to changes of the silt-clay content in fine bed sediment. In some studies, OM has been identified as retaining and transporting large amounts of P (Evans et al., 2004) particularly in fine material (McDaniel et al., 2009). Organic matter can be highly competitive against P for adsorption sites (Sibanda and Young, 1986) at low pH or even leach P in coarse textured soils with high OM content due to primary drivers of P sorption (Fe and Al) being absent (Sims et al., 1998). Whilst fine OM is made up of acids, humin and humus which have effects on the sediments capacity to retain P, coarse OM such as detritus leaf material which contains P, can induce a pulse of P released upon breaking down (Reddy et al., 1995).

The effect that OM has on P sorption, be it an increase or decrease is most likely determined by other factors, such as pH, Al, Fe and Ca content, particle size and mineralogy as can be seen by the breadth of results obtained by various authors. Organic matter can be considered as providing a framework to which the Fe or Al oxides can attach and that the P sorbs to the Fe or Al oxides rather the OM itself.

Particle size and phosphate sorption

The definition of particle size

This review and subsequent research in the thesis uses the USDA/FAO textural classification and soil texture triangle for particle size analysis (PSA) of sediment based on recommendations in Minasny and McBratney, 2001 who compared particle size data between the International system (used in Australia) and the USDA/FAO system. Therefore sand is defined as 2mm – 0.05mm in size, silt is 0.05mm – 0.002mm and clay is <0.002mm. The 2mm – 20 mm size is gravel and >20mm is considered stone size (Gainswin et al., 2006b). Similar to PSA, there is variation in the literature for definitions of particle sizes. Some authors describe fine material to be <63µm (Stone and English, 1993; McDowell and Sharpley, 2003; Ballantine et al., 2006), whilst others consider a particle size of <2mm (Gainswin et al., 2006a; Lottig and Stanley, 2007; Palmer-Felgate et al., 2009) as fine grain. Herein, fine grain material is <50µm as per PSA, coarse grain (sand) is 50 µm – 2mm and gravel 2- 20mm.
Size fractions of sediment and P sorption

Sediment material will undergo particle size sorting from its origin in the landscape to its final destination through geomorphic, vertical and longitudinal hydraulic controls (Milburn et al., 2000; McDowell et al., 2004), which will determine the size and percentage of each size fraction of the sediment. For example, as stream flow increases, the fine sediment along with the adsorbed P can be remobilized and coarse material will become the dominant particle size that remains as the sediment bed (House and Denison, 2002; Ballantine et al., 2006).

The <2mm fraction of the sediment can be divided into three main size descriptors; sand, silt and clay. Clay and silt tend to be categorised together due to their particle sizing despite silt having mineralogical origins similar to the larger sand particle (White, 2006) (Table 1).

**Table 1.** Surface area of different components of sediment (taken from White, 2006).

<table>
<thead>
<tr>
<th>Sediment Component</th>
<th>Specific surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe and Al oxides and hydroxides</td>
<td>100-300</td>
</tr>
<tr>
<td>Hydrous micas (illites)</td>
<td>100-200</td>
</tr>
<tr>
<td>Kaolinites</td>
<td>5-40</td>
</tr>
<tr>
<td>Silt</td>
<td>1.0</td>
</tr>
<tr>
<td>Fine sand</td>
<td>0.1</td>
</tr>
<tr>
<td>Coarse sand</td>
<td>0.01</td>
</tr>
</tbody>
</table>

In general terms, the clay fraction is made up of two groups, crystalline material and other minerals such as oxides and hydroxides. The dominant crystalline material present in clay is phyllosilicates (e.g. kaolinite, illite) (White, 2006). Clay minerals showed varied reactivity and absorptive capacity for P. Minerals such as kaolinite and gibbsite enhance P sorption (Froelich, 1988; Stone and English, 1993). Clays such as kaolinite tend to have broken edges where ligand exchange sites exist for exposed O and -OH groups and P (Axt and Walbridge, 1999; White, 2006) whereby there is uptake by the first step P sorption mechanisms but limited P uptake thereafter (Froelich, 1988). Clays
like gibbsite contain natural oxide coatings and have a higher capacity to sorb P (Froelich, 1988).

Sand and silt are predominantly the resilient residue of weathered primary rock minerals interspersed with lesser amounts of secondary minerals, such as oxides and hydroxides, including Fe and Al (White, 2006). Primary rock minerals are predominantly silicates which have a crystalline structure (White, 2006).

Fine grain sediment being physically smaller, has a larger specific surface area in comparison to the coarse grain and gravel size components, and is consider the most reactive component of sediment and hence the dominant sorbent of P, particularly the clay material (Stone and English, 1993; Webster et al., 2001; van der Perk et al., 2006; Ryan et al., 2007; Zhuan-xi et al., 2009). Fine grain sediment may have higher proportions of Al and Fe oxides and hydroxides and clay minerals which are considered significant in removing P from solution (Horowitz and Elrick, 1987; Stone and English, 1993; Haggard et al., 1999; Zhenhua et al., 2012). These components increase the sediments’ propensity to bind P, thereby lowering the EPC$_0$ (Klotz, 1985; House and Warwick, 1999; Evans et al., 2004; Lottig and Stanley, 2007; Agudelo et al., 2011) which likely makes the sediments a P sink. Clay material can be enriched with larger amounts of bio-available forms of P (Stone et al., 1995). On the contrary, the $<$19 µm fractions significantly released sorbed P (Stone and English, 1993 in Stone et al., 1995) even though Fe, Al and Ca which all have affinity for P are generally more abundant in the very fine fraction of sediment. This may indicate that particle size is not the only driver of P retention by sediment and other factors may be relevant, such as P saturation, the portion of P binding sites covered with P. This is an important measure as it identifies the potential of P to desorb from a soil (Beauchemin and Simard, 1999) as well as accounting for mineralogy and surface area.

Irrespective of the key driver of P sorption in fine grain sediment, the fine material is considered transient storage for P in a stream. Seasonal conditions, such as altered stream flow, result in re-suspension of fine grain sediment and thus the attached P (Nguyen and Sukias, 2002; Bowes et al., 2003; Evans and Johnes, 2004; Ballantine et al., 2009). In this scenario, for a period of time, coarser material with a lower P sorption and buffering capacity (Vervier et al., 2009), and a lower P content will be the common sediment fraction on the streambed until fine material is deposited again (Agudelo et al., 2011).
In coarse grain material (sandy sediment), as for fine grain material, Al and Fe oxides can be the key adsorbents of P (Borggaard et al., 1990). Coarse grain material, such as those that occur extensively on the south coast of WA (Master, 2008, 2009) have a smaller surface area compared to fine grain material (Krøger and Moore, 2011), decreasing the Fe and Al ion concentration on the surface and lessening the capacity to adsorb P (Webster et al., 2001; Evans et al., 2004). Coarse sediments with high plant available P and lower amount of fine material have a greater capacity to desorb P compared to clayey sediments (Li et al., 2007; Zhenhua et al., 2012) suggesting that sediments which are dominated by coarse material will be more likely a source of P to the stream.

The <2mm fraction is considered the most geochemically reactive portion of the sediment and therefore gravel material, which can be present in large amounts in soils in WA (Gilkes et al., 1973), is generally not considered nor measured when determining P sorption characteristics of stream sediments. However, Gainswin et al. (2006a, 2006b) and Lottig and Stanley (2007) undertook research on P sorption by gravel and suggested that P uptake and release by gravel and stone was dominated by biotic processes and hypothesized that as particle size increases, P buffering capacity decreases and the control of P uptake changes from abiotic mechanisms to biotic mechanisms. The two mechanisms suggested for P uptake by biota in gravel material are the uptake of P by periphyton during its growth period (Withers and Jarvie, 2008; Rogers et al., 2011) and the entrapment of suspended particulate P in filamentous algae (Withers and Jarvie, 2008). Both of these mechanisms can be considered relatively short term storage of P. Upon death and decomposition of the periphyton, P will be released into the stream water (Rogers et al., 2011). Similarly under highly turbulent flows, particulate P may dislodge from the filamentous algae and be suspended in the water column (Gainswin et al., 2006b). Abiotic control of P retention has been studied in lateritic (high in Al and Fe) soils by Weaver et al. (1992). For gravels of identical mineralogy, as the gravel size increased (2-4mm up to >8mm), the ability to sorb P decreased (when compared on a mass basis) suggesting that gravel size, or surface area had an effect on P uptake. Weaver et al. (1992) also identified under laboratory conditions, that no P had been adsorbed beyond the surface of the gravel except where a crack was present with no further increase in P retention after a week of a five-week experiment.

The P retention of sediment is often considered proportional to the surface area of the particle size, the smaller the particles in the sediment, the larger the surface area for P
sorption (Horowitz and Elrick, 1987; Pailles and Moody, 1992). This has differed in other studies whereby mineralogy was found to be an important driver in P sorption rather than particle size alone (Stone and Murdoch, 1989 cited in Rogers et al., 2013; Webster et al., 2001). The review of the role of particle size suggests the greater the proportion of fine material, the greater the P retention (Nguyen and Sukias, 2002; Vervier et al., 2009) due to both chemistry and surface area. Furthermore, sediments can be affected by the P enrichment ratio (PER). This the ratio of the concentration of P in sediment to the concentration of the nutrient in the soil it has originated from (Flanagan and Foster, 1989; Brodie and Mitchell, 2005). Soil that has eroded from the landscape through various processes (e.g. surface water erosion) is sorted in size from larger particles close to the source to smaller particles further away from the source.

This selective process provides sediment to the stream, which is generally higher in P concentration than the soil in the landscape where it originated (Sharpley, 1980; Flanagan and Foster, 1989). In areas where erosion is minimal (i.e. such as a landscape with low relief), the PER ratio increases, favouring the removal of fine material such as clays and organic matter, which has generally higher P concentration due to their mineralogical composition, (Flanagan and Foster, 1989; Sharpley et al., 2001). Similarly, PER can also affect sediments with coarser textures, such as sandy loams (Sharpley, 1980). Soil material and P entering the stream via erosive pathways such as overland flow will most likely be richer in P than the soil source it originated from, which will play an important role in determining if the stream will act as a source or a sink.

**Equilibrium Phosphorus Concentration – effects of particle size and sediment geochemistry.**

The equilibrium phosphorus concentration ‘zero’ (EPC$_0$) is an empirical reference point on a P sorption curve that identifies the solution concentration at which the sediment displays the maximum capacity for buffering P from solution (Froelich, 1988). That is, the concentration of P in solution at which negligible or no net retention or release from the sediment to the water column occurs (Taylor and Kunishi, 1971; Haggard et al., 2007; Rogers et al., 2013). Therefore EPC$_0$ has a major bearing on the P concentration in solution (McDowell et al., 2002) and is governed by the individual physico-chemical characteristics previously discussed in this chapter. Similarly, the Langmuir binding-strength coefficient (K) and the P sorption maxima of the sediment (S$_{\text{max}}$) will also be affected by the factors previously discussed in this literature review.
The EPC$_0$ is positively correlated to particle size (McDowell et al., 2002). Amongst a range of particles, the relative proportions of small and large particles and their respective concentrations of P on the surface of those particles will in part determine the amount of P released from the sediment and the final concentration in solution. However, there will be inherent variability in EPC$_0$ values along a stream affected by the geological influences and hydrological controls, such as sediment mineralogy and stream flow. The EPC$_0$ of sediment increased almost two-fold under anaerobic conditions (Reddy et al., 1998). The EPC$_0$ is reported to be higher after sediments have been exposed to totally dry conditions (Kerr et al., 2010). Contrarily, Xiao et al. (2012) showed no difference between EPC$_0$ of field moist and air-dried sediment, however there was a positive correlation ($r^2$=0.7) of EPC$_0$ to OM under air-dried sediment and a negative correlation ($r^2$=0.6) under field moist conditions. Thus under dry conditions, if there are higher amounts of OM in the sediment, EPC$_0$ will increase becoming a greater source of P to the water column. Whereas, under moist conditions an increase in OM will result in lower EPC$_0$. In areas where streams are ephemeral, this suggests that rewetting of sediment may provide an increased source of P to stream water.

In sediments with nutrient runoff from agricultural land, EPC$_0$ is higher than from forested or mixed-use (forest/agriculture) catchments (McDowell et al., 2002; Sharpley et al., 2007; Smith, 2009). While this suggests that forested or mixed-use sediments are most likely to be a sink for P, agricultural sediments had a higher S$_{max}$ due to finer material which was high in Fe and Al oxides (Sharpley et al., 2007) increasing the amount of P the sediment can take up. Maintenance, such as dredging of artificial drains for efficient removal of water from the landscape can affect the EPC$_0$ of the sediment. Undredged streams have a higher EPC$_0$, suggesting they will be a source, however they also have a higher S$_{max}$ compared to dredged streams (Shigaki et al., 2008). On the contrary, Smith et al. (2006a) noted that undredged streams had lower EPC$_0$, linking the lower EPC$_0$ to the amount of extractable Al and Fe in sediments.

So in effect, the higher the sediment EPC$_0$, the more potential to be a source of P to the water column. Agudelo et al. (2011) noted some studies identified strong positive relationships between dissolved P concentrations in stream water and sediment EPC$_0$. This suggests that as sediment P increases so does the EPC$_0$, further suggesting that stream sediment has an important role to play in P cycling in catchments.

The amount of Fe present in sediment is a significant driver for increasing the capacity of sediment to adsorb P as indicated by the positive correlation of Fe with S$_{max}$.
Similarly, with higher Fe concentrations K increases. Even though EPC$_0$ is an indicator of whether sediments are a source or sink of P (Lucci et al., 2010), it must be understood in the context of other factors, such as $S_{\text{max}}$ as noted by Sharpley et al. (2007). Iron related uptake of P can be affected by the redox potential of the sediment with the EPC$_0$ sensitive to the oxic state of the sediment (House and Denison, 2000; Agudelo et al., 2011).

A common method in literature to estimate the P sorption characteristics ($S_{\text{max}}$ and K) of sediment is to use the Langmuir adsorption equation (Syers et al., 1973; Bolster and Hornberger, 2007).

Two forms of the Langmuir equation commonly used are the non-linear version (Bolster and Hornberger, 2007):

$$S = \frac{S_{\text{max}}KC}{1 + KC}$$

And the linear version:

$$\frac{C}{S} = \frac{1}{KS_{\text{max}}} + \frac{C}{S_{\text{max}}}$$

where S is the amount of P sorbed (mg kg$^{-1}$), C is the final concentration in solution (mg L$^{-1}$), $S_{\text{max}}$ is the maximum amount of P (mg kg$^{-1}$) that can be taken up by the sediment and K is the constant relating to P bonding energy (L mg$^{-1}$) which is an indication of the strength by which the P is bound to the sediment (Graetz and Nair, 1995). In the linear form of the Langmuir equation when plotting $C/S$ vs. C, the $S_{\text{max}}$ is calculated from the reciprocal of the slope of the linear relationship ($1/S_{\text{max}}$). The $S_{\text{max}}$ value refers to the sorption maxima of the initial fast reversible sorption of P (McGechan and Lewis, 2002). Similarly K is calculated from the y-intercept ($K/S_{\text{max}}$). In relation to P sorption from stream sediment, K is a relative measure of the ability of sediment to buffer P from solution (Smith et al., 2005). An increase in K suggests the sediment has a stronger ability to adsorb P from solution (Haggard et al., 2007). Organic matter content and to a lesser degree, the fine grain sediment fraction are known to strongly affect changes in K, and OM can be negatively correlated to K (Smith et al., 2005; Liu et al., 2010). Iron oxide rich sediments have high K values (Liu et al., 2010) and K diminishes under anaerobic conditions due to the reduction of Fe (III) to Fe (II) (Pant and Reddy, 2001). Phosphorus sorption measurements reported by House et al. (1995) and Webster et al.
(2001) identified coarser sandy material had a vastly lower K values than the fine material.

In some cases, the variability in $S_{\text{max}}$ has been explained in a large part by Fe in particular as well as Al (Reddy et al., 1998; Pant and Reddy, 2001; Yoo et al., 2005; Liu et al., 2010), further indicating that Fe and Al are key drivers in P retention in sediment. An increase in Al-ox and Fe-ox in the sediment will increase $S_{\text{max}}$ (Shigaki et al., 2008). Organic matter has also been positively correlated with $S_{\text{max}}$. This may be due to Fe and Al binding to the OM, and hence indirectly affecting $S_{\text{max}}$ (McDowell et al., 2003b; Reddy et al., 2005). Generally, $S_{\text{max}}$ is higher under aerobic conditions (Reddy et al., 1998) due to the amorphous and poorly crystalline iron, however the $S_{\text{max}}$ under anaerobic conditions can be largely explained by organic carbon (Pant and Reddy, 2001). The $S_{\text{max}}$ has also been negatively correlated to pH due to a change in the charge ratio on the sediment surface (Liu et al., 2010). As pH decreases, the charge on the sediment surface becomes more positive providing more binding sites for P. Yoo et al. (2005) suggested the $S_{\text{max}}$ value is positively correlated with total P, OM, extractable Al, Ca and Fe; an increase of these factors will raise the $S_{\text{max}}$. Like $S_{\text{max}}$ and K, the concentration of Fe and to a lesser extent Al in sediment are drivers of EPC$_0$ that have a large bearing on whether the sediment acts as source or sink of P.

Biotic factors and oxic/anoxic conditions affecting P sorption

Not all the processes that govern retention and release of P from sediment in streams are fully controlled by abiotic processes. Phosphorus is an essential nutrient for biota survival hence the role of biota is potentially of importance in the regulation of P in streams (McDaniel et al., 2009). The interface of the water column and the sediment provides a region of elevated growth of algal and microbial biofilms (House, 2003a).

In agricultural streams, biotic processes can account for 30-40% of the P release and retention by sediment (Haggard et al., 1999 in Chaubey et al., 2007; McDowell and Sharpley, 2003; Sharpley et al., 2007). It has been identified that at low dissolved P concentrations (<0.005 mg L$^{-1}$), the control of P release and retention is most likely regulated by biotic mechanisms (Barlow et al., 2004; Ekka et al., 2006). At higher concentrations of dissolved P, the biotic communities become ‘saturated’ with P, thus providing no control of P uptake (Mulholland et al., 1990 cited in Macrae et al., 2003). In coarse sediment such as sand where hyporheic flow is dominant, the uptake of P by
the biofilm may be significant (Webster et al., 2001). Contrarily, Lottig and Stanley (2007) found that the <2mm fraction of the sediment provided an extensive area for P sorption but was an unstable substrate for biota to establish due to its ease of resuspension and deposition (Stone et al., 1995). Streams with stone size sediment (>20mm) have a stable substrate for algae to attach, allowing temporary storage of P. Dissolved reactive P and TP are negatively correlated with the percentage of large size sediment present due to algae being a sink for P when alive (Rogers et al., 2011).

House and Denison (1997) and later Webster et al. (2001) suggested the net soluble reactive phosphorus (SRP) retention by the sediment did not account for all the loss of SRP from the water column and implied that algae and macrophytes utilised the residual amount. Moore et al. (2010) identified that both vegetated and non-vegetated waterways were able to decrease the nutrient loads to receiving waters. However, non-vegetated ditches were higher in their uptake rate of P. Similarly, Summers et al. (2014) suggested that dredging of sediments, provided fresh binding sites and therefore a greater removal of P from the stream water than the vegetated ditches. Contrarily, Smith et al. (2006a) and Smith and Pappas (2007) found that immediately after dredging, the release of P to the stream from the sediment was more rapid than prior to dredging. Biological processes contribute more to the uptake of P in agricultural drainages ditches than forested ditches (Sharpley et al., 2007). The microbial biomass of sediment can be considered a dynamic store of P, in response to increases and decreases in microbial populations (McDowell and Sharpley, 2003). However, while biotic processes have been shown to regulate up to 40% of P to and from the sediment, it may not be an overriding factor in comparison to abiotic factors regulating P in agricultural catchments (Klotz, 1988; McDowell, 2003).

The oxygen conditions at which the water-sediment interface operates are important, as sharp gradients in the concentration of oxygen can change the assemblages of microbial communities and ions sensitive to redox conditions. It has been noted that sediment categorized as silt have a higher demand for oxygen than the coarser grain material. However the oxic layer of the silt sediment may only be 1-3mm deep (House, 2003a) which in turn has a bearing on Fe and Al oxides and hence the release and retention of P. Under oxidised conditions, S\text{max} may be reduced but have a lower EPC\text{0} with P bound more strongly than under reduced conditions (Reddy et al., 2005). Also in contrast, greater removal of P from the water column by the sediment can occur under anaerobic conditions due to the reduction of ferric oxyhydroxides to more soluble forms,
increasing surface area of P binding sites and hence P sorption capacity (Patrick and Khalid, 1974 cited in Reddy et al., 1998). Ferric iron can dissolve causing the release of bound P under reducing conditions caused by warm weather and low stream flow (Reddy et al., 1995; Vaughan et al., 2007).

The hydrological regime, the effect of the spatial component of streams and the effect of water quality on P sorption

**Hydrological regime**

The flow of water through a stream is determined largely by climate, soil type and topography (Campbell et al., 1995; Haygarth et al., 2000) which are highly interlinked. The amount of rainfall influences the flow volume and energy within a stream. High rainfall (intensity and/or duration) will provide faster flow giving lower residence time of the water and hence less time for the P to interact with sediment. Contrarily, low rainfall intensity-long duration events will allow infiltration and often (under saturated conditions) provide a baseflow, enabling P in the streamflow to interact with the sediment promoting significant P retention in the stream sediment (Hill, 1982; Dorioz et al., 1998; House and Warwick, 1998; Kronvang et al., 1999; Sharpley et al., 2007; Ballantine et al., 2009; Palmer-Felgate et al., 2009; Kerr et al., 2011). Under base flow conditions, the release of P from stream sediment is influenced by particle size, sorption capacities, desorption rates and EPC0 of the sediment (McDowell et al., 2001). While the retention of P under low flow conditions provides storage of P, the ‘first flush’ at the start of the season may provide an opportunity for resuspension and remobilisation of the sediment retained nutrients (SRP and TP), providing a significant source of P (Kronvang et al., 1999; Palmer-Felgate et al., 2009). The culmination of factors affecting the hydrological regime will bring about different flows which can be allocated into three broad types; ephemeral, intermittent and perennial flows (Gordon et al., 2004; Levick et al., 2008). Ephemeral streams flow in direct response to rainfall and are not linked to the groundwater. Perennial streams are distinctly different to ephemeral streams, flowing year round and with the flow largely maintained by groundwater discharge. Intermittent streams flow continuously for a portion of the year irrespective of rainfall. They can be connected or disconnected from groundwater, such is the situation with many streams on the south coast of WA (National Land & Water
Resources Audit, 2002). The difference in flow regimes also affects how nutrients are transported to the receiving water with ephemeral flows contributing significant amounts of P during flushing (nature of ephemeral streams) during large-scale storm events, whereas perennial streams are constantly cycling P. This delivery of P however is generally not characterised in laboratory-based research or standard in-stream monitoring.

The drying out of sediment during summer conditions can lead to elevated levels of P being released upon rewetting of the sediment. This is most likely due to the reduction in the P sorption capacity of the sediment caused by increased crystallisation of Fe hydroxides upon drying, reducing potential P binding sites (Nguyen and Sukias, 2002; Schönbrunner et al., 2012). When there are fast or slow time switches between periods of wetting and drying, this affects the microbial community, potentially releasing P due to biota death (Kerr et al., 2010; Schönbrunner et al., 2012; Xiao et al., 2012). In addition, sediments that are continually exposed to wetting and drying cycles have a reduced affinity for P, compared to sediments that seldom dry out (Baldwin et al., 2000). Kerr et al. (2010) found that the degree of desiccation of the sediment may affect \( E_{PC0} \) after rewetting, with sediment that had fully desiccated having a higher \( E_{PC0} \) than sediments that had partially dried. Kerr et al. (2010) also noted that drying may transform relatively unavailable organic forms of P into available inorganic forms of P. Conversely sediments that have been air dried to simulate drained conditions could oxidise ferrous to amorphous ferric oxides, increasing \( S_{max} \) (Reddy et al., 1998). Phosphorus sorption capacity and oxalate Fe and Al were highly positively correlated under both wet and dry conditions (Reddy et al., 1998) suggesting that irrespective of the moisture content of the sediment Fe and Al are key drivers of P sorption.

Smith et al. (2006b) identified that \( E_{PC0} \) remained unaffected after fresh sediment had been deposited during a storm event, however the P buffering capacity (K) increased an order of magnitude following the deposition of fresh sediment. Sediment particle size distributions will shift with seasons affecting sediment particle composition, sediment chemistry and hence P availability (Stone et al., 1995), for example, in high flow events where selective removal of fine particles occur (Weaver and Reed, 1998) or is deposited (Ryan et al., 2007). In their research on catchments in the United Kingdom, Palmer-Felgate et al. (2009) suggested that P derived from the sediment would not pose a significant risk to eutrophication of waterways, given that there was no release of SRP to the water column in periods of high eutrophication risk such as during base flow in
spring and summer. However, Palmer-Felgate et al. (2009) did note that there was an increased risk of eutrophication of water from sediment P at sites with greater intensity of agriculture.

**Stream geomorphology**

Stream geomorphology is a function of slope, channel morphology and size and bed material (Rosgen, 1996 cited in Agudelo et al., 2011), thus water velocity and residence time of water varies along a watercourse. Consequently, a gradient occurs in streams that are made up of different sediment particle sizes (and hence abiotic capacity to remove P from stream water) with their associated biotic assemblages. Stream geomorphology also includes bed sediment features such as riffle-pool-run sequences, as well as bank sediment (Agudelo et al., 2011). Location of the stream in the catchment landscape affects P retention with increasing particulate P retention occurring as stream order increases (Strahler, 1957; Kronvang et al., 1999). Similarly, Macrae et al. (2003) recorded that first order streams did not retain substantial quantities of SRP under low flow conditions. However, they made no comparison to other stream orders. In a catchment dominated by agriculture, Weaver et al. (2001) observed that low order streams had higher TP concentrations in the water than high order streams. Other studies have noted the importance of stream order (Novak et al., 2004; McDaniel et al., 2009; Lucci et al., 2010; Agudelo et al., 2011) or used it to select study sites (McDowell, 2009), but did not provide an analysis of P regulation in streams or drains with varying stream order. The variability of when P is released or retained by streambed sediment suggests that it is dependent on local hydrology and seasonal variations (Simon et al., 2005).

**Water quality**

Factors of soil type, landscape relief, rainfall intensity, fertiliser history, fertiliser application amount and timing, plant type and growth, tillage practices and livestock management all determine the amount and form of P entering the water. The amount and form of P entering a stream is controlled by various factors along the P flow pathways (described in Chapter 1). Whilst these pathways transport, transfer and modify P forms, other factors such as slope and soil type also alter the form of P entering the stream through various mechanisms that are summarised below. Soil has a finite capacity to adsorb P and repeated application of P reduces the soils P storage capacity over time. If a soil P test is high, this indicates there is a higher risk of P loss (Sharpley
et al., 2003). In different soil types, this degree of high P levels is reached at different rates. Applied P from fertiliser can be lost if rainfall events occur soon after application (Buczko and Kuchenbuch, 2007) through leaching or overland flow. This is often called incidental loss. The amount of P remaining in soil that has the opportunity to be lost to the greater environment is also dependent on the plant type and plant growth. For example, a perennial grass such as kikuyu often has lower nutrient requirements than an annual groundcover like clover. Fertiliser applied at the rate required for annuals i.e. the traditional rate, may be surplus to the P needs of some perennial grasses, causing loss of P to the P flow pathways. The continuity of ground cover in grazing systems through livestock management and in crop rotations through conservation tillage reduces erosion (Sharpley et al., 2003; Hart and Cornish, 2012). This helps to minimise the loss of particulate P but is less efficient in reducing dissolved P entering streams (Sharpley et al., 2003; Weaver and Summers, 2014). Whilst these factors discussed previously determine the amount and form of P entering streams, sub-surface flow paths are more likely to relocate soluble species to the stream (McKergow et al., 2003). Similarly, soluble P can be a major component (up to 70%) in TP in surface flow (Dougherty et al., 2004; Buda et al., 2009a), although surface runoff typically delivers particulate P (Hartikainen et al., 2010). Labile and bioavailable P are the forms of P that will bind to sediment and be taken up by biota. Inherently, the concentration of P in the water and the pre-existing sediment P concentration governed by sediment type (Evans et al., 2004) will play a large role in whether the sediment acts as a source or sink of P. Under baseflow conditions, stream water with very low P concentrations is controlled by the sediment geochemical properties and lower water velocities (van der Perk et al., 2006; Smith, 2009).

**Literature Review Summary**

Based on the literature review, two key elements have been identified as influencing the retention and release of P, namely particle size and Fe oxides (Horowitz and Elrick, 1987). Iron oxides are a key element in sorption of P by sediment. The P sorption capacity, the ability of the sediment to act as a source or a sink and the ability of sediment to buffer P from solution are all directly influenced by the amount of Fe oxides present (Sharpley et al., 2007). The presence of Fe oxides will increase the capacity of the sediment to adsorb P tightly, reducing the opportunity to release P back
into the water column. Similarly the capacity of OM to assist in P sorption by sediment is also related to Fe oxides with OM providing sites for attachment of Fe oxides, increasing the surface area for P to sorb (Nguyen and Sukias, 2002). How Fe oxides impact P sorption by sediment is directly related to the particle size as well as the geochemistry of each fraction. Particle size alone changes the sediments capacity to provide potential P sorption sites (Kröger and Moore, 2011). As particle size decreases the surface area of the sediment increases providing an increase in potential sorption sites for P: in particular, clays having large fractions of Fe oxides, some as part of the physical structure of the clay mineral (e.g. illite). As particle size increases, Fe content tends to diminish, in part due to the silicate, crystalline nature of the coarser sediment fraction and coupled with the decrease in surface area provides fewer sites for P sorption.

While fine sediment material is considered important in P removal from the water column, it is also highly transient due to the minimal force required to transport these particles, potentially accelerating the delivery of P to receiving waters (Bowes et al., 2003; Evans and Johnes, 2004). Similarly biotic factors, while contributing up to 40% of the P uptake by sediments can be considered a transient storage of P too, due to the life-cycle of biota (Withers and Jarvie, 2008). An example is the drying of sediment, which may cause the death of biota, releasing P back into the water column when the sediment is rewetted (Kerr et al., 2010; Schönbrunner et al., 2012). It has been suggested that as particle sizes increases, the control of P sorption is switched from abiotic to biotic elements (Lottig and Stanley, 2007).

While we have a good understanding of water quality patterns associated with seasonal conditions, it is not known the degree to which these water quality patterns are influenced by drain or stream sediment under high or low flows in the coastal catchments of Western Australia. On this basis it remains difficult to differentiate the P contributions from the agricultural landscape or stream network in a catchment for any year or event.

What is apparent is the complexity of P regulation in drains and streams. The importance of the various factors affecting P regulation by sediment discussed in the literature review is unknown for sandy and sandy duplex soils in southwestern Australia. A understanding of the study catchments provides the basis to put forward hypotheses to answer the question; what factors control the retention and release of P by stream sediment in sandy catchments dominated by agriculture in southwest WA?
On the south coast of WA, vast areas of land and stream sediments are dominated by sandy material and lateritic gravels in a Mediterranean climate, a point of difference to most other locations where studies on P retention by streams have been undertaken (Table 2).

The current international knowledge on P uptake by stream sediment suggests that because of coarse sandy material dominating the sediment on the south coast of WA together with gravel, the ability to bind P tightly will be reduced, sediment will have a low $S_{\text{max}}$ and the EPC$_0$ of the sediment will be high. This is due in part to the <2mm sediment fraction being the most geochemically reactive, particularly the clay component. This indicates that stream sediment will most likely act as a source of P. Furthermore, as it has been identified that Fe and Al are key sorbents of P under acidic conditions, abiotic processes will be the dominant driver of P uptake by stream sediment. Biotic functions in streams sediments can contribute up to 40% of P uptake, but these are limited by sandy substrates which are unstable for biota colonisation (Lottig and Stanley, 2007). The ephemeral and intermittent nature of the stream flows, does not present opportunity for algae growth (for P uptake) on the larger gravels due to biota death upon drying, removing less P. Therefore, I hypothesise that the sediments on the south coast will have little or no biotic contribution to P uptake and streams will thus be reliant on abiotic processes, which as described earlier are limited in their capacity to uptake P. The ephemeral and intermittent nature of the streams on the south coast not only affects the biotic structure of stream sediment but will also affect their geochemistry. On drying, crystallisation of Fe and Al reduce the capacity of the sediments to retain P. Therefore, upon rewetting, large amounts of P will be released into the water. Taking into consideration the current international knowledge of the factors affecting retention and release of P in stream sediments, I suggest that on the south coast of Western Australia, stream sediment will most likely be a source of P to the water column.
Table 2. Key points of difference in sediment material, climate and stream flow regime for factors affecting P uptake by stream sediments in agricultural catchments described in the international literature and for WA.

<table>
<thead>
<tr>
<th>Factor</th>
<th>International literature</th>
<th>Western Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Large presence of fine grain material</td>
<td>Sediment consists up to 50% of lateritic gravel material</td>
</tr>
<tr>
<td>Climate</td>
<td>Predominantly temperate climates</td>
<td>Mediterranean climate</td>
</tr>
<tr>
<td>Hydrological regime</td>
<td>Predominantly perennial streams</td>
<td>Predominantly ephemeral and intermittent streams</td>
</tr>
</tbody>
</table>

As there is little or no research on understanding of how stream sediments regulate P in the sandy agricultural catchments of WA, this research and thesis will bridge key knowledge gaps and extend the current knowledge of P movement through catchments. Specifically it will test the following hypotheses:

1) Sediment material <2mm in size is the most reactive component of a sediment in relation to P retention.
2) Abiotic processes dominate the retention and release of P in an Australian agricultural catchment dominated by sandy soils.
3) Intermittent flow (the repeated drying) in streams decreases the capacity for retention of P in streams sediments.
4) In a Mediterranean (dryland) climate (intermittent/ephemeral streams), stream sediment will act as a source of P to the stream water. Thus sediments in catchments on the south coast will act as a source of P to stream water.
Chapter 3. The influence of particle size and mineralogy on P retention and release by streambed materials

Abstract

In some areas of the world including the south coast of Western Australia, gravel (>2mm) can contribute >50% of the sediment mass in streams. Most analysis and interpretation of sediment phosphorus (P) qualities is measured on the less <2mm fraction as previous research has identified this fraction as the most geochemically reactive. Due to the presence of lateritic (iron rich) gravel in stream sediment on the south coast of Western Australia, this chapter takes into account the P sorption of both the <2mm material and >2mm sediment fractions. Using a fluvarium (simulated stream environment) and P sorption batch experiments, mineralogy of these sediments was identified to be the key driver of P removal from solution rather than particle size. Using a novel analysis method, presenting the amount of P sorbed as mg m^{-2} (area based) rather than the commonly used weight based measurement of mg kg^{-1}, helped elucidate that mineralogy, not particle size, was the key driver of P retention by sediment. The stream sediments analysed from the south coast were identified as net immobilisers of P with approximately 30% of the P added in solution adsorbed by the sediment and 8% of the P sorbed released back into stream water. The exclusion of larger material, i.e. gravel, in determining the capacity of stream sediment to remove P from stream water may underestimate the capacity of sediment to uptake and retain P.

Introduction

Phosphorus (P) is an essential macro nutrient for plant growth to provide food for consumption by humans and by animals in agricultural production systems (Sharpley and Tunney, 2000; McDowell et al., 2003b). Repeated applications of P over time can lead to P fertility in excess of agronomic requirements (Sharpley et al., 1994, 2013; Buczko and Kuchenbuch, 2007; Weaver and Wong, 2011). The accumulation of P in some soils has led to losses from these soils leading to the eutrophication of receiving waters.
The P transport pathways by which these losses occur have been identified in agricultural systems (Haygarth and Jarvis, 1999; McDowell et al., 2004; Gourley and Weaver, 2012). Research to date has shown that sediment in drains and streams can either retain or release P indicating that the sediment is an important component in nutrient cycling in agricultural catchments (Sharpley et al., 2007). However, little emphasis has been placed on the relevance of the different size particles of stream sediment on the cycling of P.

Most research on the retention and release of P from stream bed materials has focused on the <2mm fraction as it is considered the most reactive sedimentary component under natural conditions (Lucci et al., 2010). The measurement of P sorption curves and the EPC₀ (the concentration at which P is neither sorbed nor desorbed by the sediment) has typically used material that was exclusively <2mm (Kovar and Pierzynski, 2009). In some regions of the world, such as the south west of Western Australia and northwestern Arkansas in the USA (Rogers et al., 2011), the >2mm fraction can represent significant amounts (~ 30-50%) of the stream sediment mass. It has been a long held convention that particle size is a key factor that affects the P sorption in sediments, whereby smaller particle sizes, have greater surface areas per unit mass of material and hence sorb more P. However, more recently some authors have suggested that sediment mineralogy may be as important if not more so than particle size as a key determinant of P sorption (Stone and Murdoch, 1989; Rogers et al., 2013). Given that a large proportion of some sedimentary materials can be >2mm size (Rogers et al., 2013), this material may have one of two effects on P sorption, dependent on its mineralogy:

1) If the >2mm fraction of a sediment is inert relative to the <2mm fraction, the >2mm fraction will occupy volume, diluting the capacity of the <2mm fraction to retain or release P, since fewer binding or releasing sites will be available, or

2) If the >2mm fraction of sediment is P reactive (e.g. lateritic gravels), the >2mm fraction may provide P sorption sites in addition to the <2mm material, as well as acting as a partial diluent (Weaver et al., 1992) and contribute to overall P retention or release by the sediment.

In addition, it is universally accepted that P sorption by sediment or soil is evaluated and expressed in terms of mass (milligrams of P sorbed per kilogram (mg P kg⁻¹)) of material. This may not be appropriate where the >2mm fraction is concerned since only the outer surface of such fractions may react with P (Weaver et al., 1992). Measuring
the P sorbed by sediment in units of mg P kg$^{-1}$ does not account for surface area which is important when you compare two different size fractions such as >2mm and <2mm with differing mineralogy. Inherently, larger particles will have less surface area and less P sorbed for the same experimental mass as finer textured soils. In these cases, normalising by area rather than mass may be more appropriate. Where sediment material mineralogy is uniform across the whole sediment, small particles (<2mm) will have more surface area and hence more potential for P sorption than large particles (>2mm). The relative importance of mineralogy might be better explored by considering P mass sorbed per unit of surface area (mg P m$^{-2}$) in addition to mg P kg$^{-1}$ as measuring in mg P kg$^{-1}$ takes into account mass but not surface area. Holding one of the variables of mineralogy or particle size constant is problematic when using materials from most natural systems, however, clearer insights can be gained from experimental work in the soil sciences that controls particle size. Figure 3 displays P sorption isotherms where P sorbed is expressed as mg P kg$^{-1}$ for >2mm fractions of the same mineralogy but where different proportions of each size fraction were present (Weaver et al., 1992). When measured as mg P kg$^{-1}$, Figure 3 suggests that soil that has proportionally greater fine material adsorbs the most P.

![Figure 3](image-url)

**Figure 3.** P sorbed for mineralogically constant lateritic gravel material from (Weaver et al., 1992) presented as mg P kg$^{-1}$. Gravel groups were composed of different proportions of 2-2.8mm, 2.8-4mm, 4-5.6mm, 5.6-8mm and >8mm sizes. Proportions (%) were as follows respectively •- solid line: 2.7, 4, 7.3, 15.6 and 70.4. -long & short dash: 4.6, 8.1, 16.7, 29.5, and 41. ▲ - medium dash: 12.1, 21.4, 31.5, 22.5 and 12.4. ◆ - short dash: 39.3, 43.7, 15.9, 1 and 0. Equilibrium $P_{5\text{ weeks}}$ is P concentration measured after 5 weeks of contact with soil samples.
Assuming that individual sediment particles are spherical (Walling, 2005) and smaller particles provide more particles per kilogram, the mineralogically constant data of Weaver et al., (1992) can be recalculated and normalised for surface area P Sorbed_{NSSA} rather than mass. This results in the P sorbed falling on the same curve, irrespective of the particle size (Figure 4); indicating the importance of mineralogy in P sorption. Scatter around the curve in Figure 4 is maybe due to assumptions made in reworking the data, including the number of particles per size group, bulk density of the gravel and regularity of the gravel. The results of normalising for surface area (mg P m$^{-2}$) may contribute to a better understanding of P sorption by sediment rather than considering mass alone (mg P kg$^{-1}$). Taking into account the surface area of sediment, this can be applied to all particle sizes and mineralogy.

**Figure 4.** Mineralogically constant lateritic gravel material from Weaver et al. (1992), reanalyzed as mg P kg$^{-1}$_{NSSA}. Gravel groups were composed of different proportions of $>$8mm, 5.6-8mm, 4-5.6mm, 2.8-4mm and 2-2.8mm sizes. Proportions (%) were as follows respectively • -70.4, 15.6, 7.3, 4 and 2.7. ■ - 41, 29.5, 16.7, 8.1 and 4.6. ▲ - 12.4, 22.5, 31.5, 21.4 and 12.1. ♦ - 0, 1, 15.9, 43.7 and 39.3.

This understanding of mineralogy becomes of particular importance in regions with highly weathered soils, such as on the south coast of WA where Fe and Al can be abundant in soils. Streambed sediment can be derived from a range of sources including
selective erosion of fine particulate matter from surface soils, as well as from stream banks with exposed subsoil profiles. In the latter case, material from subsoils, including >2mm fractions comprised of lateritic gravels can ingress into streams and can represent a large proportion of the sediment. It is therefore important to understand the contribution that both the <2mm and >2mm material in streambed sediments have on regulating P within a stream reach.

Studies outside of south west Australia suggest that particulate P contributed up to 94% of total P (TP) load exported from catchments (Ballantine et al., 2009), with surface runoff and erosion of topsoils being the main contributor. In contrast, catchments on the south coast of Western Australia (WA) are shown to be dominated by subsurface transport of soluble P (McKergow et al., 2003; Weaver and Summers, 2014). The prevalence of soluble P in these systems highlights the importance of the role of stream sediment in the control of P transfers from landscapes to receiving water.

This paper aims to explore the potential for both the <2mm and >2mm fractions to retain and release P from streams in agricultural-dominated catchments on the south coast of WA.

**Site Description**

Located on the southern coast of WA immediately to the west of the regional city of Albany (35.0228° S, 117.8814° E), the Wilson Inlet Catchment (WIC) is approximately 263 000ha with rainfall ranging from an average of 710mm per annum in the northern reaches of the catchment to a mean of 940mm per annum in the south (Figure 5). The catchment is dominated by sandy surfaced soils (52%) with both deep sands and sandy duplex soil classification. The remaining soils are made up of small pockets of different soil types: e.g. stony or waterlogged soils. The WIC drains into the Wilson Inlet, a 48km² freshwater inlet (Brearly, 2005) that is annually breached by the creation of a channel to flush the inlet and mix the contents with seawater. The Cuppup Creek sub-catchment drains a flood prone area where cattle grazing is the dominant agricultural enterprise. The sample site (Site A, Figure 5 and Figure 6) is located 3 km upstream of the entrance to the inlet. Cuppup Creek is an intermittent stream. Using the USDA soil texture triangle as a reference, 78% of the total sediment weight was identified as sand (92% sand; 7.5% clay; 0.5% silt) for the <2mm fraction with the remainder (i.e. 22%) constituting gravel.
The Oyster Harbour Catchment (OHC) is located adjacent to the WIC to the east. The OHC is approximately 536 000 ha (Weaver and Reed, 1998) and extends over a large range of rainfall zones, from 500mm per annum in the north to 950mm per annum in the south (Master, 2008). The OHC drains into Oyster Harbour, a permanently open estuary, 15.6km² in area (Hillman et al., 1990). Two major rivers flow into Oyster Harbour; the Kalgan River (130 km in length) and the smaller King River (Brearly, 2005). The sample site (Site B, Figure 5 and Figure 6) is located approximately 3.6 km from the headwater of this intermittent stream on an unnamed tributary (8 km in length) that feeds into the upper Kalgan River. Both grazing and cropping are undertaken in this sub-catchment. The <2mm sediment (64% of the total sediment weight) was identified as a sand (93.6% sand; 5.3% clay; 1.1% silt) with 30% gravel (30% content w/w) making up the rest of the sediment.

Figure 5. Left: Map of Western Australia showing the location of the study region (near Albany) approximately 420 km south east of Perth, the capital city of WA. Right: The study catchments, WIC and OHC. Catchment boundaries (thick solid lines), stream network (greyed solid lines), rainfall isohyets (solid dash-dot lines), major towns (solid circles) and study sites A and B (solid stars).
Materials and Methods

Sediment Sample Collection and Processing

Experiment 1. P sorption and $EPC_0$ estimation

Air-dried sediment was passed through a 2mm sieve and the <2mm (known as ‘sand’ from hereon) and >2mm fraction (known as ‘gravel’ from hereon) were separated. The gravel was thoroughly washed with tap water to remove traces of the fine sediment from the surface of the gravel. The sediments used for this experiment were artificially combined (i.e. mixed from sand and gravel sieved material), such that the ‘whole’ sediment samples consisted of the measured percentages of sand and gravel material (Table 3).

In triplicate, each sediment (Table 3) was left in contact with P concentrations of 0, 0.5, 1, 2, 5 and 10 mg L$^{-1}$ in a potassium chloride (KCl – see below) solution at a sediment solution ratio of 1:20 for 24 hours prior to a sub sample being taken for P analysis.
Table 3. Percentage of sediment material that makes up experimental sediments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Gravel</th>
<th>% Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravel – Site A or B</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>75% Gravel – Site A or B</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>Whole Sediment – Site A</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td>Whole Sediment – Site B</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>Sand – Site A or B</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Calcium chloride (CaCl₂) is often used in sediment P sorption experiments to mimic the ionic concentration of the streamwater that the sediment came from (Lucci et al., 2010). In this experiment KCl was used as Allen (pers. comm.) determined that due to the higher concentrations of K cations in WA soils, KCl was preferred over CaCl₂.

A 0.0005 M KCl solution was used for Site A and a 0.02M KCl solution for Site B. This increase in molarity of KCl for Site B was made to improve laboratory processes such as filtration (<0.45 µm) by settling out of sediment from water more efficiently upon centrifuging. Experiments undertaken in this research project (or by me) on P desorption from 10 different streambed sediments in the presence of deionised water, 0.02M KCl and 0.0005M KCl showed no statistically significant difference between the different electrolyte solutions.

Samples were agitated gently by hand for 30 seconds at 1 hour, 3 hours and 23 hours to avoid abrasion of gravel surfaces (Barrow and Shaw, 1979; Stone and Murdoch, 1989) minimise the possibility of creating fresh binding sites on abraded gravels that could artificially increase P uptake for these highly weathered soils.

Water samples were extracted at 24 hours from the jars and filtered through a 0.45µm mesh filter, prior to measurement of Filterable Reactive P (FRP).
**Experiment 2. Phosphorus sorption by crushed material**

To determine the maximum potential to adsorb P that different sediment materials had, mineralogically distinct sediment components were ground to a powder in a Rocklabs ring mill. These components were selected visually and included sand (<2mm) and gravel consisting of both iron coloured material (>2mm) and non-iron coloured material (>2mm) from both Site A and B (Table 4). Ground materials were shaken end over end for 20 hours at a material solution ratio of 1:20 with P concentrations of 0, 0.25, 0.5, 1, 2, 5, 10 and 100 mg L\(^{-1}\). The samples were then centrifuged at 2300 rpm for 20 minutes and filtered through a 0.45μm mesh filter and stored in refrigeration at 3°C prior to analysis.

**Table 4. Crushed sediment material colour identification.**

<table>
<thead>
<tr>
<th>Site</th>
<th>Sediment material</th>
<th>Munsell colour</th>
<th>Colour descriptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Sand (&lt;2mm)</td>
<td>10YR 7/4</td>
<td>Very pale brown</td>
</tr>
<tr>
<td></td>
<td>Gravel non- iron coloured (&gt;2mm)</td>
<td>2.5Y 7/3</td>
<td>Pale yellow</td>
</tr>
<tr>
<td></td>
<td>Gravel iron coloured material (&gt;2mm)</td>
<td>5YR 4/6 - 7.5YR 4/6</td>
<td>Yellowish red to strong brown</td>
</tr>
<tr>
<td>B</td>
<td>Sand (&lt;2mm)</td>
<td>10YR 7/4</td>
<td>Very pale brown</td>
</tr>
<tr>
<td></td>
<td>Gravel non-iron coloured (&gt;2mm)</td>
<td>10YR 7/6</td>
<td>Yellow</td>
</tr>
<tr>
<td></td>
<td>Gravel iron coloured (&gt;2mm)</td>
<td>7.5YR 4/6</td>
<td>Strong brown</td>
</tr>
</tbody>
</table>

**Experiment 3. Simulated stream conditions using fluvariums**

To understand the ability of sediment to uptake P in moving water, a simulated flowing stream was setup using a fluvarium apparatus (Figure 7). At each site, the top 3cm of sediment was collected randomly using a shovel/ manually along a 75m transect on the streambed and combined to represent a composite sample. Composite samples were laid out on plastic sheets to air dry. A subsample was passed through a 2mm sieve to determine the percentage of gravel and sand by weight. A portion of the remaining composite sample was sieved using a 2mm sieve to provide a gravel and sand subsample for each site. The gravel subsample was washed with municipal tap water to
remove fine particles. This resulted in a gravel, sand and whole sediment subsample for each site.

Purpose built fluvariums based on the design by McDowell and Sharpley (2003) (Figure 7) were filled to 3 cm with sedimentary materials, one with gravel, one with sand and two with whole sediments from each site (Figure 8). Sediments were tampered down and the slopes of the fluvarium troughs were set to 1% to simulate the slope at each sample site.

![Figure 7](image7.png)

**Figure 7.** Fluvarium design based on McDowell and Sharpley (2003). Drawing by F. Robinson.

![Figure 8](image8.png)

**Figure 8.** Left: Fluvarium channel filled with gravel and sand material from Site A. Right: front-on view of fluvarium with water flowing over the flumes. Note the automatic sampler at left of picture used to collect samples over the experiment period.

There were two phases in this experiment that were repeated multiple times for each site; The uptake phase, KH$_2$PO$_4$ was added to 396L of rainwater to give a starting concentration of 2.5-3 mg L$^{-1}$ FRP and this solution flowed over the sediment for 48 hrs. The second phase was a release phase; 396L of rainwater (median FRP of 0.06 mg L$^{-1}$) was cycled over the sediment that had sorbed P in the previous uptake phases. At the end of each 48hr phase, the starting 396L of water was removed, and replenished with water of the appropriate concentration (that is with added P or no added P) to represent the starting conditions of the uptake or release phase. The Site A sediments were
exposed to 10 consecutive uptake phases, followed by 4 release phases, a further single uptake phase and finally a release phase. The sediments from Site B were exposed to 5 consecutive uptake phases, 2 release phases followed by a further uptake phase. During each phase samples were automatically collected using an ISCO 6712 portable autosampler (Teledyne ISCO, Lincoln, NE, USA) at 0, 5, 10, 15, 45 minutes and 1, 4, 8, 10, 12, 20, 24, 32, 36 and 48 hrs. The flow rate for the experiments was approximately 1 L s\(^{-1}\), measured on each fluvarium channel through 0.5 ft H-flumes. To determine the background P concentration in the rainwater prior to addition of P, a grab sample was taken. Similarly after the addition of the P solution, a grab sample was taken to determine the concentration of P for the experiment run.

**Sample analysis**

All filtered (≤0.45µm) water samples for each experiment were analysed for FRP using a modified molybdenum blue method of Murphy and Riley (1962). The colour was measured at 728 nm wavelength on a Shimadzu UV-1800 manual spectrophotometer.

Semi-quantitative analysis using X-ray diffraction of samples greater than 2mm (ground) was carried out on using a Panalytical Xpert Pro with a PIXCEL 1D detector, angular range of 5° to 110° with \(\frac{1}{2}\)° & 1° fixed slits. Radiation used was Co k\(\alpha\) 1.788965 with a 45Kv 40Ma generator.

**Analysis and calculations**

Equilibrium Phosphorus Concentration (EPC\(_0\)) (Taylor and Kunishi, 1971; Froelich, 1988) was determined for samples in Experiment 1. The EPC\(_0\) is most often calculated using the lowest points on the sorption isotherm (Lucci *et al.*, 2010) where the sorption isotherm is linear. The three or four concentrations below 2 mg L\(^{-1}\) (0, 0.25, 0.5, 1 mg L\(^{-1}\)) were used to calculate the EPC\(_0\) for the sediment. The following linear equation on a plot of initial FRP in solution vs. P sorbed (mg kg\(^{-1}\)) was used to determine the EPC\(_0\).

\[
S = m C_i + c
\]

Where \(S = \text{P sorbed or desorbed (mg kg}^{-1}\))
\(m = \text{slope}, \ c = \text{y-intercept}\)

\(C_i = \text{initial starting concentration}\)
On a plot of final FRP vs. P sorbed, the linear version of the Langmuir equation (Syers et al., 1973) was used to calculate the P binding energy of the sediment and the maximum P adsorption capacity.

Using the linear Langmuir equation:

\[
\frac{C}{S} = \frac{1}{K_{S_{\text{max}}}} + \frac{C}{S_{\text{max}}}
\]

where \( S \) is the amount of P sorbed (mg kg\(^{-1}\)), \( C \) is the final concentration in solution (mg L\(^{-1}\)), \( S_{\text{max}} \) is the maximum amount of P (mg kg\(^{-1}\)) that can be taken up by the sediment and \( K \) is the constant relating to P bonding energy (L mg\(^{-1}\)) which is an indication of the strength with which the P is bound to the sediment (Graetz and Nair, 1995). When plotting \( C/S \) vs. \( C \), the \( S_{\text{max}} \) is calculated from the reciprocal of a slope of the linear relationship \( (1/S_{\text{max}}) \), similarly \( K \) is estimated from the y-intercept divided by the slope \( (K/S_{\text{max}}) \) (Shigaki et al., 2008).

The following approach was used to estimate surface area of different size classes of sediment for P retention and release as mg P m\(^{-2}\) in Experiment 2. The mass of material in a known volume of each of the size classes of sediment was determined by weighing. The weight in a known volume was extrapolated out to the fluvarium channel dimensions and the total weight of sediment in each fluvarium was estimated.

A subsample of gravel was passed through a 50, 31.5, 20, 4, 2.8 and a 2 mm sieve (shaken by hand) concurrently. Surface area of particles were determined using the assumption that all particles were spherical (Ballantine et al., 2009) with measurements of size (mm) determined using a ruler and radius (r) being calculated. The median of these subsamples for each size group was used to calculate the surface area. Where particles could not be measured, i.e. <4mm, the middle value was used (e.g. 2-2.8 mm = 2.4 mm).

To calculate the surface area of the fractions of gravel or sand in the fluvarium, the following equation was used:

\[
A_f = \left[ \frac{1000}{W_{\text{size}} / n} \right] \times \%_{\text{size}} \times 4\pi r^2
\]

\( W_{\text{size}} = \) total weight (g) of counted particles for a size group
\( n = \) number of particles counted for a size group
\[ \%_{\text{size}} = \text{is the } \% \text{ (by weight) of a size group of the whole sediment.} \]

\[ A_f = \text{surface area (m}^2\text{) of the size fraction} \]

To calculate the total surface area of the combined fractions in the fluvarium channel, \[ A_{f_{\text{flu}}ry} = \text{Sum of } A_f \text{ from each size fraction.} \]

**Statistical analysis**

An ANOVA was used to statistically determine if there was any significant difference between the P sorbed by each type of sediment at each site and to determine if there were statistically significant differences between the EPC\(_0\) of the different sediments (at p<0.05).

**Results**

Experiment 1. P Sorption and EPC\(_0\) estimation

When P sorbed was expressed as mg kg\(^{-1}\), the sediment consisting of 100% sand at Site A and B had the highest uptake of P (up to 65 mg P kg\(^{-1}\)) whereas 100% gravel had the lowest uptake of P (up to 30 mg P kg\(^{-1}\)) at both sites (Figure 9a, b). The sediment used in these experiments produced linear relationships between initial P concentration in solution and P sorbed, providing a good fit (\(r^2\): 88-99%) for calculating EPC\(_0\). There were no significant differences between EPC\(_0\) values with varying gravel proportions at both Site A and B (p>0.05). However, the EPC\(_0\) at Site A, increased from 0.03 mg L\(^{-1}\) to 0.07 mg L\(^{-1}\) as the proportion of gravel in the sediment increased (Table 5).

It is commonly reported that P sorption increases with a reduction in particle size (Haggard *et al.*, 2007) due to an increase in surface area (Evans *et al.*, 2004). This same trend appears to be occurring at Site A when particles >2mm are included. No similar consistent relationship with particle size was found at Site B with 100% gravel having an EPC\(_0\) of 0.15 mg L\(^{-1}\), 75% gravel with an EPC\(_0\) of 0.12 mg L\(^{-1}\) and increasing again to 0.17 mg L\(^{-1}\) for 30% gravel (Table 5).
Table 5. The calculated P sorption variables for the sediments from Experiment 1.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Site</th>
<th>&lt;2mm (%)</th>
<th>&gt;2mm (%)</th>
<th>EPC₀ (mg L⁻¹)</th>
<th>Sₘₐₓ (mg kg⁻¹)</th>
<th>K (L mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Gravel</td>
<td>A</td>
<td>0</td>
<td>100</td>
<td>0.07</td>
<td>20.4</td>
<td>0.315</td>
</tr>
<tr>
<td>75% Gravel</td>
<td>A</td>
<td>25</td>
<td>75</td>
<td>0.03</td>
<td>52.4</td>
<td>0.295</td>
</tr>
<tr>
<td>22% Gravel</td>
<td>A</td>
<td>78</td>
<td>22</td>
<td>0.02</td>
<td>86.4</td>
<td>0.299</td>
</tr>
<tr>
<td>0% Gravel</td>
<td>A</td>
<td>100</td>
<td>0</td>
<td>0.03</td>
<td>62.1</td>
<td>1.277</td>
</tr>
<tr>
<td>100% Gravel</td>
<td>B</td>
<td>0</td>
<td>100</td>
<td>0.15</td>
<td>22.2</td>
<td>0.317</td>
</tr>
<tr>
<td>75% Gravel</td>
<td>B</td>
<td>25</td>
<td>75</td>
<td>0.12</td>
<td>55.8</td>
<td>0.262</td>
</tr>
<tr>
<td>30% Gravel</td>
<td>B</td>
<td>70</td>
<td>30</td>
<td>0.17</td>
<td>83.6</td>
<td>0.333</td>
</tr>
<tr>
<td>0% Gravel</td>
<td>B</td>
<td>100</td>
<td>0</td>
<td>0.13</td>
<td>61.6</td>
<td>1.293</td>
</tr>
</tbody>
</table>
Figure 9. P sorbed (mg kg\(^{-1}\)) from different types of sediment at (a) Site A and (b) Site B. • - small dash: 100% sand, - long & short dash: whole sediment (22% gravel) (A), whole sediment (30% gravel) (B), ▲ - medium dash: 75% gravel, ● - solid line: 100% gravel.
Experiment 2. Crushed material experiment

Mineralogy of the sediment can be a key driver in the sorption of P, and in some cases can be more important than particle size (Stone and Murdoch, 1989; Rogers et al., 2013). This became evident when the sedimentary materials selected here were ground to a uniform size and P sorption was compared. Iron coloured (Munsell colour: 5YR 4/6 - 7.5YR 4/6) gravel material ($S_{\text{max}} = 1073 \text{ mg kg}^{-1}$) at Site A sorbed more than four times the P than the sand (Munsell colour: 10YR 7/4) and the non-iron coloured gravel material (Munsell colour: 2.5Y 7/3) (Figure 10 and Figure 11).

The non-iron coloured (Munsell colour: 10YR 7/6) gravel material at Site B (Figure 11) was greater in its adsorption capacity ($S_{\text{max}} = 722 \text{ mg kg}^{-1}$) of P relative to the iron coloured (Munsell colour: 7.5YR 7/6) material at over half the adsorption ($S_{\text{max}} = 1229 \text{ mg kg}^{-1}$). At Site A (Figure 10) iron coloured gravel with a $S_{\text{max}}$ of 1073 mg kg$^{-1}$ was 10 times higher than the non-iron coloured gravel a $S_{\text{max}}$ of 102 mg kg$^{-1}$. The non-iron coloured material had a greater sorption capacity at Site B than Site A relative to the iron coloured material at each site (Figure 10 and Figure 11).

![Figure 10. The P adsorbed by the uniformly ground material from Site A sediment; gravel ironstone material (● - solid line), <2mm material (● - large dash) and the gravel non-ironstone material (●- small dash) plotted against the P in solution.](image-url)
Figure 11. The P adsorbed by the uniformly ground material from Site B sediment; gravel ironstone material (■ - solid line), < 2mm material (● - large dash) and the gravel non-ironstone material (◆- small dash) plotted against the P in solution.

The X-ray diffraction analysis of a mixed (iron and non-iron coloured material) gravel sample from each site identified their mineralogy and relative proportions of each of the minerals (Table 6). The major P sorbing minerals present in higher amounts at both sites were the iron oxides, hematite (α-Fe₂O₃) and goethite (α-FeO(OH)) which is consistent with the analysis of iron oxides in soils in southwest WA (Singh and Gilkes, 1992b).
Table 6. Mineral composition (X-ray diffraction analysis) of the <2mm and >2mm material of sediments from Site A and B.

<table>
<thead>
<tr>
<th></th>
<th>Site A</th>
<th>Site B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>&lt;2mm material (clay fraction)-unground</strong></td>
<td>Kaolinite (major)</td>
<td>Kaolinite (major)</td>
</tr>
<tr>
<td></td>
<td>Smectite (minor)</td>
<td>Smectite</td>
</tr>
<tr>
<td></td>
<td>Vermiculite (minor)</td>
<td>Traces of:</td>
</tr>
<tr>
<td></td>
<td>Traces of:</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>Muscovite (mica)</td>
</tr>
<tr>
<td></td>
<td>Albite (feldspar)</td>
<td>Albite (feldspar)</td>
</tr>
<tr>
<td><strong>&lt;2mm material (bulk mineral composition)</strong></td>
<td>Quartz</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>Sanidine (feldspar)</td>
<td>Goethite</td>
</tr>
<tr>
<td></td>
<td>Gibbsite</td>
<td>Gibbsite</td>
</tr>
<tr>
<td><strong>&lt;2mm material (clay mineral composition)</strong></td>
<td>Quartz</td>
<td>Kaolinite</td>
</tr>
<tr>
<td></td>
<td>Goethite</td>
<td>Kaolinite</td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Minor Vermiculite</td>
</tr>
<tr>
<td></td>
<td>Minor Vermiculite</td>
<td>Minor Muscovite (mica)</td>
</tr>
<tr>
<td></td>
<td>Minor Muscovite (mica)</td>
<td></td>
</tr>
<tr>
<td><strong>&gt;2mm ground</strong></td>
<td>Quartz (&gt;50%)</td>
<td>Quartz (&gt;50%)</td>
</tr>
<tr>
<td></td>
<td>Kaolinite (5-15%)</td>
<td>Kaolinite (5-15%)</td>
</tr>
<tr>
<td></td>
<td>Goethite (10-20%)</td>
<td>Goethite (1-10%)</td>
</tr>
<tr>
<td></td>
<td>Plagioclase (1-5%)</td>
<td>Plagioclase (5-15%)</td>
</tr>
<tr>
<td></td>
<td>Gibbsite (&lt;1%)</td>
<td>Gibbsite (&lt;5%)</td>
</tr>
<tr>
<td></td>
<td>Hematite (1-5%)</td>
<td>Hematite (10-20%)</td>
</tr>
<tr>
<td></td>
<td>K-Feldspar (5-15%)</td>
<td>K-Feldspar (1-10%)</td>
</tr>
</tbody>
</table>

Experiment 3. Simulated stream using a fluvarium

The decay curves of FRP normalised to % FRP left in solution over time display the P uptake by the sediment during each run of the fluvarium after the initial addition of a known quantity of P (Figure 12 and Figure 13). The rate of P uptake by sediment did not remain constant with sequential applications of P. The uptake rate reduced upon repeated applications of P as noted by the run number sequence on each chart in Figure 12 and Figure 13. This may in part be due to some of the P over time being adsorbed tightly to the sediment (Barrow, 1974, 2008). After concurrent release runs of P, during which between 3%-6% of the P sorbed at Site A and 9%-15% of the P sorbed at Site B
(Table 7) was returned to streamwater, the uptake of P in most sediments was ‘reset’ to the equivalent of the third uptake phase (Figure 12, run 11 and Figure 13, run 6).

In the fluvarium, the sediment material at Site A removed 71% to 84% of the P added whereas Site B removed between 29% to 46% of the P added after the first run (Figure 14). With the P retained data was presented as mg kg\(^{-1}\) at Site A and B (Figure 14), the 100% gravel material was the second most absorbent material beside the 100% sand material. The gravel material from Site B required approximately 5 runs of 2.5-3 mg L\(^{-1}\) P addition to be able sorb the amount of the first run at Site A.

Over the multiple P uptake and release phases, most of the sediments adsorbed approximately 30% of the P added (Table 7). Of the P adsorbed by the sediments, Site A released 3-6% and Site B released 9% -15% into the water (Table 7). As discussed in the introduction to this chapter (Figure 4) when P sorbed is normalised for specific surface area, irrespective of particle size the soil material with the same mineralogy sits along the same curve. This identifies mineralogy as an important differentiator in P sorption rather than particle size alone. Based on the understanding that limited P has penetrated beyond the surface of the gravel material (Weaver et al., 1992), the P sorbed data is presented as mg m\(^{-2}\). The Site A gravel material adsorbed 6 times more mg P m\(^{-2}\) of surface area than the sand sediment and the whole sediments (Figure 15). The Site B gravel material adsorbed 14 times more than the whole sediment and sand material (Figure 15). This is a conservative estimate of P sorbed by gravel, as not all the material is iron coloured with an estimated 20% of the gravel non-iron in colour. When expressed as mg P m\(^{-2}\) the sand and the two whole sediments would require > 5 runs to adsorb the same amount of P as gravel on its on the first run at Site A for their respective sediments.
Figure 12. Normalised (% FRP) P uptake data for Site A sediments: (a) 100% Gravel (b) 100% sand (c) whole sediment 1 (d) whole sediment 2. Numbers in the box represent the sequence of experimental runs.

Figure 13. Normalised (% FRP) uptake data for Site B sediments: (a) 100% Gravel (b) 100% sand (c) whole sediment 1 (d) whole sediment 2. Numbers in the box represent the sequence of experimental runs.
Figure 14. The cumulative P sorbed (mg kg\(^{-1}\)) by sediment at Site A and B. WS = whole sediment.

Figure 15. The cumulative P sorbed (mg m\(^{-2}\)) by sediment at Site A and B. WS = whole sediment.
Table 7. The percentage of P sorbed (mg kg\(^{-1}\)) with sequential uptake phases (10 for Site A, 5 for Site B) and P desorbed in sequential release phases (5 for Site A, 2 for Site B) immediately following uptake phases.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sediment</th>
<th>P adsorbed (% of P added)</th>
<th>P desorbed (% of P adsorbed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Gravel 100%</td>
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<td>6%</td>
</tr>
<tr>
<td>A</td>
<td>Sand 100%</td>
<td>27%</td>
<td>6%</td>
</tr>
<tr>
<td>A</td>
<td>Whole Sediment 1</td>
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<td>3%</td>
</tr>
<tr>
<td>A</td>
<td>Whole Sediment 2</td>
<td>30%</td>
<td>3%</td>
</tr>
<tr>
<td>B</td>
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<td>Sand 100%</td>
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<tr>
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<td>9%</td>
</tr>
<tr>
<td>B</td>
<td>Whole Sediment 2</td>
<td>21%</td>
<td>15%</td>
</tr>
</tbody>
</table>

**Discussion**

**Experiment 1. P Sorption and EPC\(_0\) estimation**

The greater P sorption in the 100% sand sediment compared to the 100% gravel (Figure 9) is likely due to the high surface area of the sand compared to the gravel and differences in mineralogical composition of those surfaces. The inconsistency of an increase in the EPC\(_0\) values with increasing gravel proportions (Table 5) suggest that mineralogy of the gravel fraction may be as important as particle size in regulating P sorption and desorption. This is in contradiction to findings of McDowell *et al.* (2002) who identified that an increase in the proportion of sand size particles would increase the EPC\(_0\) of the sediment. The measurement of EPC\(_0\) when including gravel (simulating the sediment) potentially alters the uniformity in increasing EPC\(_0\) observed by McDowell *et al.* (2002). On a much finer fraction of the sediment (<0.5mm), Stone and Murdoch (1989) suggested that the key factors controlling adsorption of P onto the sediment were chemical composition and mineralogy.
Experiment 2. Crushed material experiment

All the material at Site B has a higher potential to adsorb P than the material from Site A (Figure 10, Figure 11), particularly the sand material due to the occurrence of the mineral goethite (α-FeO(OH)) (Torrent et al., 1992) and to a lesser extent kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) (Table 6). In the bulk mineral composition at Site A, the P binding material present is gibbsite (Al(OH)$_3$) (Torrent et al., 1994) with the inert sanidine and quartz. Iron is often considered important in the sorption of P (Murphy, 1939; Borggaard, 1983; Haggard et al., 1999; Kröger and Moore, 2011), this is reflected in the difference between the two sites in their potential for the sand material to sorb P. The lateritic gravel material at both sites has a far greater potential to adsorb P than the <2mm material when the surfaces are more fully exposed by grinding (Figure 10 and Figure 11). This potential is diminished within streams as the natural gravels are largely intact, limiting P sorption to the exposed outer surface (Weaver et al., 1992).

Experiment 3. Simulated stream using a fluvarium

To better understand P retention and release characteristics of gravel in a simulated stream environment compared to other materials, a fluvarium experiment was undertaken. The rate of P uptake by sediment not remaining constant with sequential P applications is possibly due to displacement of singly coordinated hydroxyl groups by the P ion (Barrow, 1983a; Froelich, 1988; Stone et al., 1995; Lair et al., 2009), which removes binding sites available for the next addition of P (Barrow, 1974). Another explanation presented by Barrow et al., (1998) identified that rather than a decrease in available binding sites, the increased presence of phosphate ions which are negatively charged provides a negative charge to the surface of the sediment particle. The presence of the negative charge decreases the electric potential of the sediment particle and thus reduces the capacity of the sediment to hold more P. Desorption of smaller amounts of P after concurrent release phases suggests that while a small amount of P has been desorbed, the majority of P is retained within the sediment. Barrow (1989b) identified that the desorption process which is the reversal of the diffusive adsorption process by soils is much slower. There could be potential over time for more P to be released due to the slow nature of the desorption of P, however other factors need to be taken into account, such as stream water concentration and sediment EPC$_0$.

Rogers et al. (2013) identified that the sediment in their study removed 85-96% of the P. While Sharpley et al. (2007) obtained similar results, this previous research only
included one uptake phase. In the initial uptake phase in Experiment 3, the amount of P removed from Site A is similar to that of Sharpley *et al.* (2007) and Rogers *et al.*, (2013). The more P released back into stream water from sediment at Site B indicates that Site B is more likely to be a source of P into stream water. Like soils, the percentage of P sorbed decreased with sequential applications of P as well as decreasing the P buffering capacity of the sediment which is identified by systematic changes in FRP decay curves (Figure 12 and Figure 13) (Barrow, 1974; Barrow *et al.*, 1998). This finding is pertinent to both future research on sediments and instream P transfer modelling as it identified that stream sediment P uptake is dynamic. The capacity of the sediment to remove P changes and the use of a single P uptake curve to describe a sediments capacity to adsorb P may overestimate the actual P retention capacity. When modelling, consideration must be taken to include the decrease in the buffering capacity of the sediment.

When expressed as mg P m$^{-2}$ the gravel adsorbs considerably more P than both the sand and the whole sediments (Figure 15) indicating that mineralogy of the sediment is an important factor in the uptake of P irrespective of the particle size. Sorbed P varies for materials within a site, as well as between sites (Figure 15). The gravel material from Site B required approximately 5 runs of 2.5-3 mg L$^{-1}$ P addition to be able sorb the amount of the first run at Site A which could be linked to the greater abundance of the iron oxide (hematite) at Site B which has a lower affinity and slower uptake of P (Torrent *et al.*, 1994) compared to goethite which was in higher amounts at Site A.

To better understand how stream sediments consisting of sand and lateritic gravel remove P from stream water, it is appropriate to discuss aspects of each of the experiments together. At Site A in Experiment 1 (batch experiment), the sand material adsorbed the most P (mg kg$^{-1}$) (Figure 9) whereas the sand material in Experiment 3 (fluvarium experiment) adsorbs the least amount of P (Figure 14). The lesser P sorption under simulated stream conditions is possibly due to reduced time of contact between the sand and P in Experiment 3 compared to Experiment 1. Once the pore space of sand is saturated with water, the surface area of the sand that is in constant contact with the flowing water lessens as water flows over the top, reducing its capacity to adsorb P. On the other hand, gravel has substantially larger pore spaces due its to particle size, and water can flow through these pore spaces, interacting with a greater surface area of the gravel. The amount of P sorbed in Experiment 3 (Figure 14) was greater than the estimated S$_{\max}$ calculated from Experiment 1. A soil: solution ratio of 1:20 was used in
Experiment 1, compared with the 1:4 ratio used in Experiment 3. Barrow and Shaw (1979) identified that a lower soil solution ratio (i.e. 1:4) will adsorb more P.

In the batch experiment (Experiment 1), the intact gravel material from Site B sorbed more P than the gravel material from Site A. In the fluvarium experiment, this was the opposite (Figure 14). However in the crushed material experiment (Experiment 2), the gravel material at Site B had a higher S_{max} than Site A and sorbed more. Torrent et al. (1994) noted that hemaites had a slower sorption of P and reduced affinity for P in comparison to goethite, which could be the reason for the less P being sorbed at Site B in Experiments 1 and 3, which had a higher content of hematite than goethite to that of Site A (Table 6). This however does not account for the higher sorption of gravel in Experiment 2 from Site B in relation to Site A. The difference is the material in Experiment 2 was ground, suggesting that the physical structure of the gravel may have had a role to play in the sorption of P. In Experiment 1, the 100% gravel material at Site A and Site B adsorbed approximately 18 and 27 mg P kg^{-1} respectively (Figure 9). In Experiment 2, with the 100% gravel material crushed, the Site A sample adsorbed approximately 1000 mg P kg^{-1} and Site B, approximately 1200 mg P kg^{-1} (Figure 10 and Figure 11). Similarly, the 100% crushed sand material at both sites adsorbed more P than the uncrushed material from Experiment 1 (Figure 9, Figure 10 and Figure 11). The difference of P sorbed by crushed and uncrushed material clearly reinforces that P is only sorbed to the exterior surface of the material as identified by Weaver et al. (1992).

In Experiment 1 (batch P sorption experiment), there was not a consistent effect of increasing gravel content on the EPC_0, this differed to McDowell et al., 2002 who found the EPC_0 became higher with increasing particle size. The results from Experiment 1 suggest that mineralogy may be more important than particle size. Similarly in Experiment 2, if the lateritic gravel material and the <2mm material were the same particle size, the lateritic gravel material has higher P sorption capacity. This identified that gravel is an important part of the stream sediment for the retention of P.

The experiments conducted here suggest that both sites are net immobilisers of P (mg kg^{-1}) that is adsorbed from solution (Table 7) with the ‘whole’ sediments generally retaining more P in these experiments. The gravel material adsorbs a higher percentage of the P added than the sand and releases a similar amount to the sand when expressed in mg P m^{-2}. Rogers et al. (2013) noted a similar trend in net P retention with the sediment over a single uptake and release phase.
The net P retention by sediments examined here confirms suggestions of net P retention by streams from modeling P flows and stores by Keipert et al. (2008) and Rivers et al. (2011) in a sandy agricultural catchment in the south west region of Western Australia. These authors suggested that up to 80% of the P lost to from the catchment to the streams may be stored by the sediment. Mineralogy and particle size play a role in the capacity of sediment to uptake and retain P. Contrary to previous findings suggesting the <2mm fraction is the most reactive (Stone and English, 1993; Webster et al., 2001; van der Perk et al., 2006; Ryan et al., 2007; Zhuan-xi et al., 2009), the gravel fraction can retain significant quantities of P.

**Conclusions**

This chapter has identified key factors that affect P sorption by sediment that have not previously been studied in detail and reinforced some findings by other studies elsewhere.

Gravel can be an important component of stream sediment influencing the retention and release of P. It can be a high absorber of P if it has appropriate mineralogy and should be considered when estimating sediment characteristics such as EPC$_0$. Measuring only the <2mm fraction in a sediment containing lateritic gravels may underestimate the sediment’s capacity to adsorb P, particularly when the <2mm fraction is sand with little P retention capacity. On the contrary if a sediment has gravel which is relative inert to P, measuring the uptake and release of only the <2mm fraction may provide an overestimate of the sediment P retention capacity. This is because the inert material occupies volume, which is not accounted for in measuring only the < 2mm fraction.

The mineralogy of both the <2mm and >2mm fractions is important to consider in estimating the ability of stream sediment to retain and release P, and can be of greater importance than particle size. If the <2mm fraction has poor P retention qualities, then it may contribute to the re-release of P previously sorbed by the sediment, irrespective of its particle size. The >2mm fraction, if its mineralogy supports P retention appears to provide a long-term store for P sorbed by the sediment.

The sediments tested here appear to be net immobilisers of P. Depending on the stream P concentration coming into contact with the sediment, the sediments retain more P than they release.
The results of this chapter may also inform future experimental work on P uptake by sediment to better identify the contribution of sedimentary components to remove P from the water column.

In a similar way to soils, P sorption by sediment diminishes with repeated P applications. Therefore single uptake experiments will not adequately describe the long-term potential of sediment to retain or release P as sorbed P accumulates.

It is useful to consider expressing P sorbed as mg P m\(^{-2}\) and mg P kg\(^{-1}\) when exploring the potential for sedimentary components to retain P.
Chapter 4. The influence of microbial functions in sediment on the uptake of P in stream sediments in south coastal West Australian catchments

Abstract

Having identified that the geochemistry of stream sediment plays an integral role in the capacity for stream sediment to uptake and retain P, this chapter examines the role of microbial biota in the uptake of P from sandy sediments in a Mediterranean climate on the south coast of Western Australia (WA). Based on existing knowledge of biotic contribution in perennial streams, the sand component of sediment may be too unstable a substrate for colonisation of microbial biota, and biotic controls on P uptake switch from abiotic to biotic as particle size increases. Streams with intermittent flows on the south coast of WA differ with sand being a key influence in the biotic uptake of P. A novel approach was used to determine if the separation between non-phototrophic and phototrophic P uptake could be identified to determine biotic uptake of P under conditions not conducive to photosynthesis. The contribution of non-phototrophic uptake of P varied between sites. Batch experiments were undertaken to determine if there was a difference between biotic and abiotic controls on sediment for P sorption characteristics. Whilst biotic controls on P uptake by sediments are not dominant (>50%) in relation to the geochemical processes, the biota were found to be important in increasing the maximum P sorption capacity ($S_{\text{max}}$) of sediment with a low abiotic (geochemical) $S_{\text{max}}$. Similarly the binding efficiency (K) increased in the presence of biota. This is particularly important for sediment in sandy catchments with a low geochemical capacity to sorb P.

Introduction

The geochemistry and mineralogy of stream sediments play an important role in the retention and release of phosphorus (P) from sediment into stream water (Stone and Murdoch, 1989; Chapter 3). This is exacerbated in highly weathered landscapes such as in Western Australia (WA) where lateritic gravels are mixed with low P sorbing sands
(Bolland et al., 2003a; Weaver and Summers, 2014; Chapter 3). As streams are natural biological systems, there will be interactions of P in the stream water with biotic activity in the sediment which could include vascular plants, microbes (House et al., 1995; McDaniel et al., 2009) and algae (Lottig and Stanley, 2007).

The contribution of microbial or algal biotic processes within sediment to the uptake of P was shown in literature to range from 0% up to 53%, with the contribution typically between 20% and 40% (Klotz, 1985; Haggard et al., 1999; McDowell and Sharpley, 2003; Lottig and Stanley, 2007; Sharpley et al., 2007; McDaniel et al., 2009). Much of this previous work identified the contribution of biotic functions to P uptake by sediment through the measurement of the phosphorus sorption index (PSI), initially developed by Bache and Williams (1971). The PSI is a one-point measurement made after the addition of a known amount of P to a solution-sediment mix. The greater the PSI value the more P can be retained by the sediment without releasing it into the water (Klotz, 1985). When sediment is treated to inhibit P retention by the biotic component, a reduction in the PSI value is expected. The difference between untreated and treated sediment can be explained as the contribution to P uptake by the biota. Using the PSI method, Lottig and Stanley (2007) identified that there was no biotic P uptake by sand whilst large gravel contributed 53% to biotic P uptake. Consequently, they suggested that when sediment particle size increased, the controls on P uptake by the sediment ‘switched’ from abiotic to biotic.

The majority of streams in the lower south coast region of Western Australia are intermittent or ephemeral (National Land & Water Resources Audit, 2002) and consequently sediments are exposed to seasonal wetting and drying cycles. This may inhibit the formation of phototrophic biota such as algae on larger gravels (>2mm) and thus little contribution of biotic uptake maybe observed. However, some forms of biota such as algae and some cyanobacteria are able to survive periods of desiccation through refuges, such as permanent pools or leaf packs (Robson et al., 2008). By contrast, if the fine material (<2mm) does not have the physical structure necessary for colonisation of biota (Lottig and Stanley, 2007) then sediment uptake of P may be dominated by abiotic processes.

The purpose of this study is to determine the contribution of microbial biota to P uptake in intermittent stream sediments and their individual size fractions in the south coastal region of WA.
Site Description

Ten study sites were located on the south coast in two adjoining catchments, the Oyster Harbour Catchment and the Wilson Inlet Catchment (Figure 16). Both catchments are dominated by agriculture with cropping and sheep grazing in the northern parts of the catchment and cattle grazing in the south (Master, 2008, 2009). Sites A and B are described in detail in Chapter 3. The remaining sites (C- J) are located in watercourses ranging in stream order (Strahler, 1957) from 1 to 4 in the same catchments as sites A & B. Streams sample were predominantly intermittent. No sites had macrophytes growing within the streambed where the studies were undertaken.

Figure 16. Left: Map of Western Australia showing location of study region (near Albany) approximately 420 km south east of Perth, the capital city of WA. Right: The study catchments, WIC and OHC. Catchment boundaries (thick solid lines), stream network (greyed solid lines), rainfall isohyets (solid dash-dot lines), major towns (solid circles) and study sites A to J (solid stars).

Methods

The role of microbial biota in the uptake of P by intermittent streams was investigated using two experiments. Experiment 1 aimed to identify the contribution of microbial biota to uptake of P by sediment consisting of different sized material, <2mm, >2mm and the sediment as a whole (<2mm plus >2mm). It also took a novel approach to determine if the contribution of phototrophic and non-phototrophic biotic uptake can be separated. Sites A and B (as per Chapter 3) were selected for this experiment.
(Figure 16). Experiment 2 took sediment from different locations within the catchments (sites A to J) to test the contribution of biota to values of EPC₀, K and Sₘₐₓ.

**Sample collection**

Samples for Experiment 1 were collected in areas of no-flow (exposed to air) using a shovel to remove the top 3cm of sediment along a 75m transect. Sediment for Experiment 1 was air dried and stored as described in Chapter 3.

Samples at each site for Experiment 2 were taken using a 50mm PVC core tapped into the sediment to a depth of 3cm, capped and removed; sub-samples were collected randomly within a 10m² transect in the stream and combined. Samples were stored in the dark at 3-4 °C until required for the experiment. A water sample was collected if the stream was flowing.

**Experiment 1. Particle size influence on biotic uptake**

Air-dried sediment was passed through a 2mm sieve and the sand (<2mm) and gravel (>2mm) fractions separated. The gravel was washed to remove fine material from the gravel surface. Intact sample sediments used in the experiment that had not been fractionated are known as ‘whole’ sediments. The sediment materials were submerged in unfiltered rainwater for four days prior to treatment. The three treatments were as follows:

*Nil treatment* – Control sediment, no treatment applied

*Autoclave treatment* – Using a similar method to that described in McDaniel et al. (2009), a sub sample was autoclaved at 121°C at a pressure of 134 kPa for a sterilization period of 20 minutes. In the autoclaved sediment all biological function is assumed to have ceased. There is some potential for P to be released due to cell lysis in this process. Potential P release due to cell lysis was estimated by the inclusion of an autoclaved sample with no P added. Values of P retained were then adjusted for cell lysis.

*Algaecide Treatment* – The algaecide used in this experiment has the active constituent 5g/L Diuron which is an inhibitor of the photosynthetic cycle (Sumpono et al., 2003). The algaecide applied at the rate recommended on the product package was 5mL Diuron to 300L of water. An amount of 0.13 mL was added to 800mL of deionised water. Diuron kills phototrophic biota but does not kill off non-phototrophic bacteria
(Sumpono et al., 2003), which may influence P retention. Potential P release due to cell lysis was estimated by the inclusion of an untreated and an algaecide treated sample with no P added.

A 3mg P L$^{-1}$ (KH$_2$PO$_4$ in deionised water) solution was added to each treatment in triplicate at 1:4 water-sediment ratio (see Chapter 3, Experiment 3) for 48 hours without shaking the sediment and solution. Single subsamples of 30 mL were collected at 2, 5, 21, 24, 45 and 48 hrs from each sample. Water samples were centrifuged and filtered through a 0.45µm cellulose nitrate filter prior to analysis for FRP using a modified molybdenum blue method of Murphy and Riley (1958).

The average P sorbed for each sample at each time was calculated and plotted as cumulative P sorbed against cumulative time. A regression-by-group analysis was done on these values with treatment as a discrete variable and time as a continuous variable.

For clarity in reading this chapter, definitions that are interchangeable have been noted:
untreated sediment = biotic P uptake (non-phototrophic plus phototrophic biota),
algaecide treated sediment = non-phototrophic biotic P uptake and autoclaved treated sediment = abiotic P sorption.

Autoclaving sediment killed living biota in the sediment (photo- and non-phototrophic biota) and the addition of a photosynthesis inhibitor kills only phototrophic biota. The total amount of P retained by non-phototrophic and phototrophic biota ($P_{N+P}$) was calculated as the final P retained by untreated sediment minus the final P retained by the autoclaved sediment (Figure 17). The total amount of P uptake contributed to phototrophic biota ($P_P$) is the untreated sediment minus the algaecide treated sediment. Therefore $P_{N+P} - P_P$ is the P taken up by non-phototrophic biota ($P_N$).

Two-sample t-tests were undertaken for key P sorption measures with the sites combined to test for significant differences. To determine if the abiotic vs. biotic regression was significantly different from 1 (1:1 line), the t-ratio was calculated first. The $t$-ratio = (best fit slope – hypothetical slope) / standard error of slope. The t-ratio and the degrees of freedom (n-2) for 95% confidence were checked against a critical t-value table and the regression was determined if significantly different from 1.

To determine the biotic contribution to sediment, the abiotic value measured ($S_{max}$ or $K$) and modeled values was divided by the gradient of the abiotic vs biotic regression ($S_{max}$ or $K$).
Figure 17. Conceptual model of the contribution of phototrophic biota to the uptake of P by a sediment (solid line = untreated sediment, dashed line = algaecide treated sediment and dotted line = autoclaved sediment). As not all biota has been killed by the algaecide, the value of $P_P$ will be less than the $P_{N+P}$, enabling the calculation of the contribution of both $P_P$ and $P_N$ to total P uptake by sediment.

Experiment 2: Biotic influences on commonly measured P uptake parameters of sediment

Moist sediment from sites A to J were used in this experiment (Figure 16). One set of moist subsamples was autoclaved (121°C @ 134 kPa) to kill of living biota and one set remained untreated. Using a 1:20 sediment:solution ratio, a known P concentration was added; 0, 0.5, 1, 2, 5 and 10mg L$^{-1}$ in a 0.02 M KCl solution. Each concentration was in triplicate. Samples were agitated for 30 seconds at 2hr and 23hr and a subsample of water collected at 24hr. End over end shaking was not used, as it may affect the results due to the abrasion of ironstone materials providing new bindings sites for P, artificially inflating the sediments capacity to adsorb P (Stone and Murdoch, 1989; Barrow, 2008).

Water samples were filtered through a 0.45µm cellulose nitrate filter prior to analysis for FRP using the modified moly blue method of Murphy and Riley (1962). A single blank was provided for each starting concentration for each treatment. The blank consisted of the P solution without the addition of sediment. The median of the blank
for each concentration was calculated and used to determine the mg P kg\(^{-1}\) sorbed by each sample.

The Equilibrium P Concentration (EPC\(_0\)) is a measurement of the concentration at which there is no net uptake or release of P by the sediment (Taylor and Kunishi, 1971; Froelich, 1988; Rogers et al., 2013). To determine the EPC\(_0\) of the treated and untreated sediments, a linear equation (\(S = mC_i + c\)) was calculated from a plot of initial concentrations vs. P sorbed on values <2 mg L\(^{-1}\) where S=0. The value of S is the amount of P sorbed (mg kg\(^{-1}\)) and C\(_i\) (mg L\(^{-1}\)) is the initial concentration of P in solution whilst c and m are the y-intercept and gradient respectively.

P sorption maxima (\(S_{\text{max}}\)) and P bonding energy (K) were calculated using the linear version of the Langmuir isotherm equation from a plot of C/S vs. C:

The linear Langmuir isotherm equation is as follows (Syers et al., 1973):

\[
\frac{C}{S} = \frac{1}{KS_{\text{max}}} + \frac{C}{S_{\text{max}}}
\]

where S is the amount of P sorbed (mg kg\(^{-1}\), C is the final concentration in solution (mg L\(^{-1}\)), \(S_{\text{max}}\) is the maximum amount of P (mg kg\(^{-1}\)) that can be taken up by the sediment and K is the constant relating to P bonding energy (L mg\(^{-1}\)) which is an indication of the strength of which the P is bound to the sediment (Graetz and Nair, 1995). When plotting C/S vs. C, the \(S_{\text{max}}\) is calculated from reciprocal of the slope of the linear relationship (1/\(S_{\text{max}}\)), similarly K is calculated from the y-intercept (K/\(S_{\text{max}}\)).

Other factors used in analysis and to further describe sample sites included stream order as described by Strahler (1957). Loss on ignition (LOI) is commonly used as a quantifier of organic matter in sediments. The LOI was determined gravimetrically at 550\(^\circ\)C (Kerr et al., 2010). Particle size of the <2mm material was determined using the hydrometer method with separation of particles into sand, silt and clay. Gravel content of the sediment was determined gravimetrically by separating the <2mm from the >2mm material using a 2mm sieve.
Results

Particle size effect on P uptake by biota in sediment

Figure 18. (a) Site A and (b) Site B: P uptake by whole sediment over time. Untreated sediment (solid line - ⋄); Autoclaved sediment (short dash, - ■); Algaecide treated sediments (large dash - ▲).
**Whole sediment**

At Site A, the untreated sediment retained significantly more P than the autoclave sediment (Figure 18a) (p<0.05). There was no significant difference between the amount of P sorbed by the algaecide treated sediment and the untreated sediment.

At Site B (Figure 18b) similar to the response at Site A, the untreated sediment absorbed significantly more P than the autoclaved sediment. However at Site B, there was a significant difference (p<0.05) in P adsorbed by the algaecide treated sediment between both the untreated and autoclaved sediment.

**Gravel component of sediment**

No significant difference in P uptake between the untreated and autoclaved gravel was found at Site A (Figure 19a) suggesting that there is very little biological activity occurring on the gravel. However, there was a statistically significant difference between the algaecide treated sediment and both the untreated and autoclaved gravel. At Site B (Figure 19b) there was no significant difference between any of the treatments for P uptake on the gravel.
Figure 19. (a) Site A and (b) Site B: P uptake by gravel over time. Untreated sediment (solid line - ●); Autoclaved sediment (short dash, - ■); Algaecide treated sediments (large dash, - ▲).
Figure 20. (a) Site A and (b) Site B: P uptake by sand over time. Untreated sediment (solid line, -●); Autoclaved sediment (short dash, - ■); Algaecide treated sediments (large dash, - ▲).
Sand component of the sediment

At Site A (Figure 20a) and B (Figure 20b) in the sand, the untreated sediment retained significantly more P than the autoclaved sediment. There was no statistically significant difference between the P sorbed by the algaecide treated sediment and the untreated sediment at Sites A and B.

Table 8. P uptake by the biotic component of the sediment at Site A and B.

<table>
<thead>
<tr>
<th>Site</th>
<th>Whole P uptake</th>
<th>Gravel P uptake</th>
<th>Sand P uptake</th>
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<td>A</td>
<td>18% s</td>
<td>0% ns</td>
<td>41% s</td>
<td>Unt - Auto Alg</td>
</tr>
<tr>
<td></td>
<td>0% ns</td>
<td>0% s</td>
<td>15% ns</td>
<td>Unt - Auto Alg</td>
</tr>
<tr>
<td></td>
<td>100% ns</td>
<td>0% s</td>
<td>85% s</td>
<td>Unt - Alg</td>
</tr>
<tr>
<td>B</td>
<td>15% s</td>
<td>11% ns</td>
<td>30% s</td>
<td>Unt - Auto Alg</td>
</tr>
<tr>
<td></td>
<td>69% s</td>
<td>30% ns</td>
<td>75% ns</td>
<td>Unt - Auto Alg</td>
</tr>
<tr>
<td></td>
<td>31% s</td>
<td>70% ns</td>
<td>25% s</td>
<td>Unt - Alg</td>
</tr>
</tbody>
</table>

Based on the statistical analysis of the regression of the sediment treatments over time (Figure 18, Figure 19 and Figure 20), there is no evidence to suggest that there is a difference between the P retained for algaecide treated and untreated sediment for the sand fraction and the whole sediment at Site A. Similarly, there was no difference between sand and gravel at Site B. Therefore a contribution of 0% from phototrophic sediment (untreated-algaecide) could be assumed for these cases However while not significant, some treatments had differences and these are presented in Table 8. These differences give an indication of whether the biotic processes assisting in the retention of P are dominated by non-phototrophic or phototrophic biota.

Of the P solution added to the whole sediment at Site A, 18% of the P removed by the sediment was attributed to non-phototrophic biotic controls contributing to the P uptake (Table 8). At Site B, 15% of the P taken up was attributed to biotic processes with the P uptake dominated by phototrophic biota (Table 8).
Results of the statistical analysis of the P uptake over time for gravel material indicated no significant difference between materials at Site B. While no significant difference was found between treatments in the gravel at Site B, 11% of the P uptake was attributed to predominantly non-phototrophic biota. The difference in P uptake by gravel at Site A between the algaecide and both the autoclaved and untreated sediments was significant. This may be due to an increase in population by some bacteria with the addition of Diuron (Sumpono et al., 2003). The biota had a significant impact on P retention in the sand sediments with 30-41% of P retained attributed to biotic uptake at both sites.

**Biotic influences on commonly measured P uptake parameters of sediment**

To determine if there is a significant effect on biotic P uptake on commonly measured P sorption characteristics, the EPC₀, Sₘₐₓ and P binding energy (K) (Klotz, 1988; McDowell and Sharpley, 2003; Haggard et al., 2007) were tested for statistically significant differences between untreated sediment and autoclaved sediment.

There was no significant difference in the EPC₀ (paired t-test p>0.05) between the autoclaved and untreated sediment for combined sites (Figure 21a). Generally, the EPC₀ of the untreated sediment is lower than the autoclaved/killed sediments (Lottig and Stanley, 2007; Sharpley et al., 2007) due to the presence of biota increasing the sediments ability to retain P. Surprisingly, the EPC₀ of the untreated sediment samples at sites C, D, E and G was greater than the autoclaved samples, whilst for the remaining sites, autoclaved samples had higher EPC₀ than the untreated samples (Table 9).
Figure 21. Box-percentile plot (with distribution shape) of untreated and autoclaved sediments (sites combined) (a) EPC\(_0\) (b) K and (c) S\(_{\text{max}}\). The solid lines are the median values and the dotted lines are the 25\(^{\text{th}}\) and 75\(^{\text{th}}\) percentiles.
The binding energy for the autoclaved and untreated sediment was significantly different as measured by a paired t-tests (p<0.05) (Figure 21b). The autoclaved sediment $S_{\text{max}}$ was significantly different to the untreated sediment $S_{\text{max}}$ (paired t-test p<0.05) (Figure 21c). The untreated $S_{\text{max}}$ is the abiotic $S_{\text{max}}$ plus the biotic $S_{\text{max}}$. The autoclaved $S_{\text{max}}$ represents the $S_{\text{max}}$ of the sediment in the absence of biota (abiotic $S_{\text{max}}$). This is the same for K. The regression lines for both K ($r^2=0.59$) and $S_{\text{max}}$ ($r^2=0.46$) were tested for significant difference from 1 (the 1:1 line) and were not significantly different. The $S_{\text{max}}$ autoclaved plotted against the untreated $S_{\text{max}}$ (Figure 22b) was correlated (Table 10) indicating that bitoa present was increasing the capacity for the sediment to hold P.

Figure 22. Autoclaved sediment plotted against untreated sediment for (a) K (binding energy) and (b) $S_{\text{max}}$. The solid red line is the regression line for the measured values. The dotted black line is the 1:1 line where $x=y$. 

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Statistical analysis of $S_{\text{max}}$ and K for autoclaved and untreated sediments (Figure 21b, c) identified significant differences; hence biota has an impact on the K and $S_{\text{max}}$ of the sediment. The lack of significant difference between the slope of the regression lines for untreated vs. autoclaved sediment $S_{\text{max}}$ (solid line) and the exact correspondence (1:1 line, the dash-dot line) in Figure 22a indicates that the increase in the $S_{\text{max}}$ of untreated sediment is proportional to the increase of the $S_{\text{max}}$ in the autoclave sediment. The proportional relationship of biotic contribution, plotted in Figure 23 indicates that sediment with a low abiotic K or $S_{\text{max}}$ is reliant on biotic contribution to increase the $S_{\text{max}}$ or K of the sediment.

![Graph a](image)

**Figure 23.** The effect of biotic contribution to the abiotic (autoclaved) (a) K and (b) $S_{\text{max}}$. 
Table 9. Abiotic and biotic P sorption parameters (EPC$_0$, $S_{\text{max}}$ and K) and general characteristics (particle size, LOI, and stream order) for study sediments collected from 10 sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>EPC$_0$</th>
<th>$S_{\text{max}}$(mg kg$^{-1}$)</th>
<th>K (mL g$^{-1}$)</th>
<th>Particle size (%)</th>
<th>Gravel w/w %</th>
<th>LOI %</th>
<th>Stream order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated</td>
<td>Autoclaved</td>
<td>Untreated</td>
<td>Autoclaved</td>
<td>Untreated</td>
<td>Autoclaved</td>
<td>Sand</td>
</tr>
<tr>
<td>A</td>
<td>0.01</td>
<td>0.04</td>
<td>107</td>
<td>105</td>
<td>0.97</td>
<td>0.62</td>
<td>91.3</td>
</tr>
<tr>
<td>B</td>
<td>0.10</td>
<td>0.29</td>
<td>326</td>
<td>283</td>
<td>0.04</td>
<td>0.04</td>
<td>93.6</td>
</tr>
<tr>
<td>C</td>
<td>0.09</td>
<td>0.05</td>
<td>95</td>
<td>69</td>
<td>1.53</td>
<td>1.70</td>
<td>84.5</td>
</tr>
<tr>
<td>D</td>
<td>0.09</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>87.4</td>
</tr>
<tr>
<td>E</td>
<td>0.06</td>
<td>0.04</td>
<td>141</td>
<td>44</td>
<td>1.85</td>
<td>1.38</td>
<td>92.7</td>
</tr>
<tr>
<td>F</td>
<td>0.01</td>
<td>0.02</td>
<td>149</td>
<td>133</td>
<td>0.76</td>
<td>0.50</td>
<td>62.1</td>
</tr>
<tr>
<td>G</td>
<td>0.05</td>
<td>0.01</td>
<td>45</td>
<td>43</td>
<td>0.94</td>
<td>0.52</td>
<td>88.0</td>
</tr>
<tr>
<td>H</td>
<td>0.04</td>
<td>0.06</td>
<td>44</td>
<td>29</td>
<td>2.55</td>
<td>1.22</td>
<td>98.0</td>
</tr>
<tr>
<td>I</td>
<td>0.02</td>
<td>0.04</td>
<td>106</td>
<td>99</td>
<td>0.47</td>
<td>0.33</td>
<td>92.0</td>
</tr>
<tr>
<td>J</td>
<td>0.03</td>
<td>0.04</td>
<td>68</td>
<td>41</td>
<td>1.55</td>
<td>0.94</td>
<td>90.8</td>
</tr>
</tbody>
</table>

Table 10. Pearson Product-Moment correlation for parameters in Table 9. Correlations in bold are discussed in this chapter. Au. = autoclaved, Un. = Untreated. The star (*) identified high correlation due to leverage of a single data point.

<table>
<thead>
<tr>
<th>Un. EPC$_0$</th>
<th>Au. EPC$_0$</th>
<th>Un. $S_{\text{max}}$</th>
<th>Au. $S_{\text{max}}$</th>
<th>Un. K</th>
<th>Au. K</th>
<th>% sand</th>
<th>% silt</th>
<th>% clay</th>
<th>% gravel</th>
<th>LOI %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au. EPC$_0$</td>
<td>0.584</td>
<td>-0.202</td>
<td>0.681</td>
<td>-0.746*</td>
<td>0.767</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Un. $S_{\text{max}}$</td>
<td>-0.527</td>
<td>0.662</td>
<td>-0.305</td>
<td>0.457</td>
<td>0.624</td>
<td>-0.368</td>
<td>-0.056</td>
<td>-0.532</td>
<td>0.003</td>
<td>0.610</td>
</tr>
<tr>
<td>Au. $S_{\text{max}}$</td>
<td>-0.572</td>
<td>0.005</td>
<td>0.036</td>
<td>0.477</td>
<td>0.265</td>
<td>0.447</td>
<td>0.477</td>
<td>0.265</td>
<td>0.447</td>
<td>0.477</td>
</tr>
<tr>
<td>Un. K</td>
<td>0.802*</td>
<td>0.624</td>
<td>-0.368</td>
<td>0.447</td>
<td>0.477</td>
<td>0.447</td>
<td>0.477</td>
<td>0.265</td>
<td>0.447</td>
<td>0.477</td>
</tr>
<tr>
<td>Au. K</td>
<td>0.670*</td>
<td>0.624</td>
<td>-0.368</td>
<td>0.447</td>
<td>0.477</td>
<td>0.447</td>
<td>0.477</td>
<td>0.265</td>
<td>0.447</td>
<td>0.477</td>
</tr>
<tr>
<td>% sand</td>
<td>0.244</td>
<td>0.288</td>
<td>-0.553</td>
<td>-0.695*</td>
<td>0.477</td>
<td>0.265</td>
<td>0.477</td>
<td>0.265</td>
<td>0.447</td>
<td>0.477</td>
</tr>
<tr>
<td>% silt</td>
<td>-0.208</td>
<td>-0.259</td>
<td>0.447</td>
<td>0.599*</td>
<td>-0.374</td>
<td>-0.25</td>
<td>-0.981*</td>
<td>0.624</td>
<td>0.477</td>
<td>0.265</td>
</tr>
<tr>
<td>% clay</td>
<td>-0.286</td>
<td>-0.312</td>
<td>0.696</td>
<td>0.805</td>
<td>-0.632*</td>
<td>-0.265</td>
<td>-0.919*</td>
<td>0.825*</td>
<td>0.477</td>
<td>0.265</td>
</tr>
<tr>
<td>% gravel</td>
<td>0.012</td>
<td>0.005</td>
<td>0.106</td>
<td>-0.202</td>
<td>-0.24</td>
<td>-0.036</td>
<td>0.451</td>
<td>-0.514</td>
<td>-0.273</td>
<td></td>
</tr>
<tr>
<td>LOI %</td>
<td>-0.291</td>
<td>-0.468</td>
<td>0.208</td>
<td>0.003</td>
<td>-0.408</td>
<td>-0.34</td>
<td>0.137</td>
<td>-0.216</td>
<td>0.039</td>
<td>0.610</td>
</tr>
<tr>
<td>Stream order</td>
<td>-0.43</td>
<td>-0.475</td>
<td>0.231</td>
<td>0.117</td>
<td>-0.112</td>
<td>-0.015</td>
<td>0.2</td>
<td>-0.237</td>
<td>-0.113</td>
<td>0.608</td>
</tr>
</tbody>
</table>
Discussion

*Particle size influence on biotic P uptake*

Biota has a significant effect on P uptake (30-41% attributed to biota) by sediments in sandy catchments in agricultural areas on the south coast irrespective of flow regime (i.e. intermittent or perennial flow). Out of three sediment types tested for P uptake by biota, the untreated sand fraction from both sites incorporated significantly more P than sand that had been autoclaved. This suggests that the sand fraction is important for P uptake by biota. The findings of this study contrast with results reported by Lottig and Stanley (2007) who found no significant difference between untreated and treated sediment with 100% sand sized particles for the measurement of EPC₀, sediment phosphorus uptake (SPU) and PSI. They suggested that sand was a relatively unstable substrate for the establishment of biota. The results from Experiment 1 indicated that biological activity did not significantly contribute to the uptake of P in gravels. In contrast, Lottig and Stanley (2007) noted that the P retention and release in material >2mm was controlled by biological processes, in particular algal growth attached to the gravel fraction. This difference from Lottig and Stanley (2007) may be due in part to the streams at Site A and B (in this study) being intermittent and the streams studied by Lottig and Stanley (2007) were perennial (Stanley *et al.*, 2007). A stream with a perennial flow and larger size sediment material may have more suitable substrata and conditions conducive to phototrophic biota existing and colonizing (such as filamentous algae as described in Lottig and Stanley (2007). Intermittent streams, such as those in this study can be dry for extended periods, reducing the opportunity for colonization of algae on gravel as seen in Lottig and Stanley (2007). The individual genera or species of the biota in Experiment 1 were not identified, however some forms of biota are resistant to desiccation (Baldwin *et al.*, 2000; Robson *et al.*, 2008) and can colonize in sandy substrate (Romaní and Sabater, 2001; Robson *et al.*, 2008), as seen by the uptake of P in the sand (Table 8).

*Phototrophic biota contribution to P uptake by sediment*

Further to determining the overall contribution of biotic uptake to P retention by sediment, the biotic uptake can be further assessed and used to infer the contribution that phototrophic or non-phototrophic biota have to P uptake by sediment.
Algae and some bacteria are classed as phototrophic (Sumpono et al., 2003). Adding an interrupter to the photosynthesis process such as the algaecide Diuron will kill phototrophic biota, leaving only non-phototrophic biota to take up P in solution. This may provide an indication of the stable “biotic population” for uptake of P from sediments that will not fluctuate with conditions such as light availability in streams, which can be a limiting factor in phototrophic biota growth (Chaubey et al., 2007).

The algaecide killed phototrophic biota such as algae but caused minimal destruction to other non-phototrophic biota such as certain bacteria. The contribution of phototrophic biota to the uptake of P at Site A is insignificant (Table 8) in the sand and whole sediments. The non-phototrophic biota are dominant contributors to P uptake by biota at Site A. This differs to Site B where much of the biotic P uptake is attributed to the phototrophic biota (Table 8) for both sand and whole sediment. The difference in the relative presence of non-phototrophic biota between sites suggests that a site where non-phototrophic biota are dominant may well be more resilient to fluctuations in climatic conditions that affect phototrophic biota such as light availability. The non-phototrophic bacteria are not reliant on photosynthesis for function thus light availability will not alter this biotic contribution to P uptake. The contribution of phototrophic biota to the uptake of P is most likely site specific. However care must be taken in reaching this conclusion as stream morphology and habitat along with seasonal effects such as light availability, and temperature may also be key determinants in the ratio of assemblages of phototrophic to non-phototrophic biota. Similarly there may be changes along a stream due to redistribution of sediments during flow (i.e. large areas of gravel) which would alter the contribution of biotic uptake; more gravel will provide less biotic control on P uptake.

**Biota and common P sorption parameters**

The $S_{\text{max}}$ and $EPC_0$ are frequently discussed in literature as identifiers of the sediments potential capacity to retain or release P. Predominantly $EPC_0$ is discussed as being an indicator of whether or not the sediment may act as a source or sink for P with $S_{\text{max}}$ an estimate of the maximum store of P (mg kg$^{-1}$) by the sediment (Pant and Reddy, 2001; Smith et al., 2006a; Lucci et al., 2010). The biotic processes in the sediment significantly affects the maximum retention capacity of P. Removal of biota reduced the $S_{\text{max}}$ by between 7 to 42%. Similarly, Sharpley et al. (2007) found the $S_{\text{max}}$ decreased by
The ability of sediment to buffer P from the water column is significantly influenced by biota, increasing the capacity of sediment with a poor ability, such as a sand, to buffer and store P. The proportional relationship (Figure 23a, b) between the biotic contribution to $S_{\text{max}}$ and K suggests that sediments with a low geochemical (abiotic) $S_{\text{max}}$ and K (i.e., poorly P retentive sand), will be heavily reliant on biota to increase their ability to store and retain P.

The biotic contribution (%) to P uptake by sediment at each site were assessed and used to infer the biotic contribution for each starting P concentration from Experiment 2 and are presented as boxplots (Figure 24). The biotic contribution (%) to P uptake by sediment located in agricultural streams in other research worldwide (Klotz, 1985; Haggard et al., 1999; McDowell and Sharpley, 2003; Lottig and Stanley, 2007; Sharpley et al., 2007; McDaniel et al., 2009) was plotted with the mean of these values and the minimum and maximum % biotic contribution identified (greyed area). The median and mean values for biotic contribution P uptake at study sites (A-J) were within the range of other studies worldwide.

![Figure 24](image-url)

**Figure 24.** Contribution of biota to P uptake at sites A-J (boxplots). The greyed area is the range of biotic uptake identified in international studies; the dotted line is the mean of the values of these international studies.
Conclusion

Biota in sediments from sandy agricultural catchments, such as those present on the south coast of WA play, an important role in the amount of P retained by sediment. Sand appears important in maintaining biotic communities in intermittent streams, which in turn significantly enhances the maximum capacity of the sediment to uptake and buffer P from the water column. Sediments with a low abiotic maximum capacity to store and buffer P will rely significantly on biota to increase their capacity to adsorb and retain P. The contribution of phototrophic and non-phototrophic biota to the uptake of P is site specific.

While biotic uptake of P is not the dominant mechanism of P retention from stream water for sediments on the south coast, biota is very important in increasing the capacity of the sediment to uptake P, especially in the low P sorbing sands characteristic of sandy catchments located in these agricultural regions.
Chapter 5. Seasonal influences on P retention or release by streambed sediment

Abstract

Mediterranean climates provide a distinct wetting-drying cycle for many streams resulting in intermittent and ephemeral flows. The drying of sediment provides the opportunity for minerals (iron oxides) in the sediment to ‘age’ through exposure to air, becoming more crystalline, making the sediment less conducive to retaining P. Similarly, there may be substantial death of biota upon drying releasing P into stream water upon rewetting. Batch experiments were undertaken to compare moist sediment to air-dry sediment to observe if drying had any affects on P sorption parameters. No significant effects of drying on key P sorption parameters (EPC₀, K and Sₘ₃ₙₐₓ) of sediment were observed. This indicates that the sediments reached equilibrium in relation to the aging of minerals and persistence of drying tolerant biota. Using historical water quality data, stream sediments on the south coast were shown to be net immobilisers of P, therefore contributing to the mitigation of P loss to the receiving waters.

Introduction

Abiotic factors such as mineralogy and geochemistry play an important role in determining how sediment exchanges P with the water column (Stone and Murdoch, 1989; Webster et al., 2001; Chapter 3). Biota such as microbes and algae contribute significantly to the capacity of sediment to retain P (Sharpley et al., 2007; Chapter 4). However, the hydrology of the catchment underpins the movement of P (Rivers et al., 2013), connecting the wider catchment to the stream network (Bernal et al., 2013). Driven by climatic conditions, stream flows will alter and hence the flow of P through stream networks will vary, for example; Mediterranean climate = intermittent flows. Climate does not only affect the type of flow (i.e. intermittent) but also the rate of water flowing within a stream. This has a bearing on contact time of P in solution with sediment and the opportunity for P to be immobilised or released.
Furthermore, the type of flow that occurs in a stream can have an impact on P uptake by altering biotic communities and the structure of Fe oxides (Baldwin and Mitchell, 2000; Baldwin et al., 2000). Gordon et al. (2004) and Levick et al. (2008) categorized streams loosely into three types of flow:

Perennial flow - the stream flows all year round, due to baseflow that is fed by groundwater interactions.

Intermittent flow – is affected by runoff from precipitation and shallow groundwater interactions. There will be no flow in dry periods when precipitation ceases and the shallow groundwater detaches from the stream.

Ephemeral flow - is strongly linked to precipitation with stream flow occurring as a direct result of rainfall. These are generally ‘flashy’, unpredictable flows.

Drying of sediment occurs regularly or episodically in ephemeral and intermittent streams and occasionally in perennial streams under extreme drought conditions. Drying of sediment under oxidised conditions affects both biological and geochemical controls on P uptake. This has been shown to significantly alter the sediments affinity for P, depending on the length of the drying period by increasing the crystallinity of the Fe and reducing P binding sites (Sah et al., 1989; Baldwin and Mitchell, 2000; Baldwin et al., 2000).

The drying of sediment affects biotic communities involved with the uptake of P from the water column (Schönbrunner et al., 2012). Upon partial desiccation of the sediment, extensive death of microbial populations can occur (Qiu and McComb, 1994; Watts, 2000) providing a pulse of P back to the water column upon rewetting (McDowell, 2009). However it has been suggested that repeated wetting and drying cycles may cause a shift in community to biota that are resistant to long periods of dry as they have developed drought resistant resting stages, thus minimising biota death and consequently potential P release (Baldwin et al., 2000).

Geochemically, amorphous and poorly crystalline Fe and Al are a dominant influence on P sorption by sediment (Borggaard et al., 1990; Reddy et al., 1995; Nguyen and Sukias, 2002; Agudelo et al., 2011; Zhenhua et al., 2012). Drying of the surface sediment under oxidised conditions, causes the mineral aging of oxyhydroxides, specifically Fe, causing its form to become more crystalline, therefore reducing binding sites available for P attachment (Baldwin, 1996; McDowell, 2003). Consequently the P
sorption capacity of the sediment after rewetting is decreased (Qiu and McComb, 1994, 2002). The crystallisation of the oxyhydroxides also decreases the P binding energy of the sediment, which is a possible reason for a significant reduction seen in the sorption energy coefficient (K) (Xiao et al., 2012). Furthermore, greater amounts of loosely sorbed P has been in sediment that has undergone some degree of desiccation (Kerr et al., 2010) suggests a large amount of P will be readily available to the water column upon rewetting (Schönbrunner et al., 2012). On the contrary, it has also been found that sediments previously submerged indefinitely will, upon partial drying increase their capacity to adsorb P due to ferrous sulphides in the previously saturated anoxic zone rapidly converting to amorphous ferric oxyhydroxides (De Groot and Van Wijck, 1993; Baldwin and Mitchell, 2000) giving much larger surface area for P to bind. However as conditions become more oxic and sediment dries, increased crystallisation of Fe occurs, reducing the sediment affinity for P (Sah et al., 1989; Baldwin and Mitchell, 2000). If more than 80% water content was lost on drying, P loss was found to be more pronounced (Schönbrunner et al., 2012). Sediments that are rarely subjected to desiccation will more likely show a pronounced effect on their ability to uptake and release P (Baldwin et al., 2000). Kerr et al. (2010) identified that in partially desiccated sediments P sorption characteristics would not change substantially compared to those of sediment that is rarely dried. However, loosely bound P was present in higher amounts in partially desiccated sediment, providing more opportunity for loss of P to the water column upon rewetting.

As drying of sediment affects geochemical controls on P sorption, it will alter the equilibrium phosphorus concentration (EPC₀) of the sediment. Kerr et al.,(2010) identified that across a stream transect, sediment EPC₀ in desiccated sediment is higher than in partially desiccated sediment. Furthermore, the fully submerged sediment has a lower EPC₀ than the partially dry sediment. Similarly, Klotz (1988) found a two-fold increase in sediment EPC₀ upon drying.

The degree of desiccation and regularity of drying has a major effect on both the geochemical processes and biotic assemblages controlling the release of P from the sediment upon rewetting. It has been suggested that sediments that rarely dry out (see Klotz, 1988) release more P upon rewetting due to the limited aging of P sorbing minerals and the death of biota which is not resistant to drying (Baldwin et al., 2000).

On the south coast of Western Australia, many streams are intermittent or ephemeral with only larger rivers including the Denmark, Hay, Kalgan and King being perennial,
suggesting that the sediments exposed to periods of dry will have a higher EPC$_0$ (Klotz, 1988; Kerr et al., 2010). Furthermore, the soils on the south coast of Western Australia are commonly identified as predominantly low P sorbing sands (Bolland et al., 2003b; Weaver and Summers, 2014). Given the wetting-drying climate, and increase in the sediments capacity to buffer P from the water, this suggests that stream sediments in catchments located on the south coast of Western Australia will be a source of P to the water column rather than a sink.

This study tests the following hypotheses:

1) the intermittence of flow (the repeated drying) in streams decreases the capacity for retention of P in streams sediments.

2) sediments in catchments on the south coast of Western Australia will act as a source of P to stream water.

**Site description**

The sample sites for these experiments are located on the south coast of WA. The Mediterranean climate of southern Western Australia is characterized by an annual cycle of wetting and drying (Gasith and Resh, 1999; Davies and Stewart, 2013). Much of the annual rainfall (65-80%) is delivered over a three month winter period with stream flows occurring as a response (Weaver et al., 1994; Gasith and Resh, 1999). The catchments in which the sample sites were located are the Oyster Harbour (OHC) and Wilson Inlet catchments (WIC) (Figure 25). Both the WIC and OHC are dominated by agriculture with cropping and sheep grazing in the northern reaches of the catchment and cattle grazing in the south (Master, 2008, 2009). There is a significant rainfall gradient across these catchments increasing from 500mm in the most northern extent to 950mm on the coast (Master, 2008, 2009). This contributes to intermittent flows over a season (Finlayson and McMahon, 1988; Weaver et al., 1994; National Land & Water Resources Audit, 2002; Brodie and Mitchell, 2005).
Figure 25. Left: Map of Western Australia showing location of study region (near Albany) approximately 420 km south east of Perth, the capital city of WA. Right: Study catchments, WIC and OHC. Catchment boundaries (thick solid lines), stream network (greyed solid lines), rainfall isohyets (solid dash-dot lines), major towns (solid circles) and study sites A to J (solid stars).

Methods

Experiment 1: The effect of air-drying sediment on P retention

Moist sediment used in this experiment from sites A to J were collected using a hand trowel from the top 3 cm of sediment were used in this experiment (Figure 25). The moist samples were transported and stored in refrigeration until experiments were undertaken. One set of subsamples was dried at 40°C in an oven over two days which is considered the standard in Australia for ‘air dry’ soil (Rayment and Lyons, 2011). The other set of subsamples remained untreated and undried. In a 1:20 sediment:solution ratio, P concentrations (as KH₂PO₄) of 0, 0.5, 1, 2, 5 and 10 mg L⁻¹ were added to a 0.02 M KCl solution. Each sample was in triplicate. Samples were agitated for 30 secs at 2 hrs and 23 hrs and a water sample taken at 24 hrs. End over end shaking was not used, as it may affect the results due to the abrasion of ironstone materials providing new binding sites for P, artificially inflating the sediments capacity to adsorb P (Stone and Murdoch, 1989; Barrow, 2008).

A single blank was provided for each starting concentration for each treatment. The blank consisted of the P solution without the addition of sediment. The median of the
blank for each concentration was calculated and used to determine the mg P kg\(^{-1}\) sorbed by each sample. All samples were filtered through a 0.45 \(\mu\)m cellulose nitrate filter prior to analysis for FRP using the modified molybdenum blue method of Murphy and Riley (1962).

The equilibrium P concentration (EPC\(_{0}\)), is the concentration (mg L\(^{-1}\)) at which no net P is retained or released by sediment (Taylor and Kunishi, 1971). This was determined using a plot of initial concentrations vs. P sorbed on values \(\leq 2\) mg L\(^{-1}\) of initial P concentration added to solution.

Phosphorus sorption maxima (S\(_{\text{max}}\)) and P bonding energy (K) were calculated using the linear version of the Langmuir isotherm equation from a plot of C/S vs. C (Syers et al., 1973):

The linear Langmuir isotherm equation is as follows:

\[
\frac{C}{S} = \frac{1}{K S_{\text{max}}} + \frac{C}{S_{\text{max}}}
\]

Where S is the amount of P sorbed (mg kg\(^{-1}\)), C is the final concentration in solution (mg L\(^{-1}\)), S\(_{\text{max}}\) is the maximum amount of P (mg kg\(^{-1}\)) that can be taken up by the sediment and K is the constant relating to P bonding energy in L mg\(^{-1}\), which is an indication of the strength with which P is bound to the sediment (Graetz and Nair, 1995). When plotting C/S vs. C, S\(_{\text{max}}\) is calculated from the reciprocal of the slope of the linear relationship \((1/S_{\text{max}})\), similarly K is calculated from the y-intercept \((K/S_{\text{max}})\).

**Experiment 2: EPC\(_{0}\) and historical water quality.**

In previous studies (Haggard et al., 2007; McDaniel et al., 2009; Palmer-Felgate et al., 2009), FRP had been measured in stream water that had been collected at the same time as sediment for the measure of EPC\(_{0}\). In some cases, this is not achievable, due to intermittency of flow. In a different approach, McDowell (2015) used both historic base flow and entire flow (baseflow + stormflow) FRP records (FRP\(_{\text{H}}\)) to see if there was a relationship between FRP\(_{\text{H}}\) and the EPC\(_{0}\) of sediments. In this assessment, historic water quality values were plotted against EPC\(_{0}\) of sediments to determine if 1) median FRP\(_{\text{H}}\) values in intermittent/ephemeral streams sediments are associated with EPC\(_{0}\) of the sediments and 2) whether the sediments on the south coast of WA are more likely to be a source or a sink of P. The average biotic EPC\(_{0}\) from Experiment 1 and Chapter 4 were calculated and plotted against median FRP\(_{\text{H}}\) data that was analysed from stream
sites within a 6 km² area of the current sediment sample sites (Figure 16) and of the same stream order. Sites that did not have an adequate number of water quality measurements, that is, <5 data points in total, were not included in the analysis.

**Experiment 3: Effect of flow on P retention by sediment**

To determine the effect of flow on P uptake, the whole (sand and gravel) sediments from Site B as described in Chapter 3 were used. Fluvarium slopes were set at 1%, and flow rates of 1 L s⁻¹ and 2.8 L s⁻¹. A solution of 3mg P L⁻¹ was cycled over the whole sediment for 48 hrs. Samples were automatically collected using an ISCO 6712 portable autosampler (Teledyne ISCO, Lincoln, NE, USA) at 0, 5, 10, 15, 45 minutes and 1, 4, 8, 10, 12, 20, 24, 32, 36 and 48 hrs. Samples were filtered through a 0.45µm cellulose nitrate filter prior to analysis for FRP using a modified moly blue method of Murphy and Riley (1958).

Two-sample t-tests between the untreated and dried sediment were undertaken for key P sorption measures with the sites combined to test for significant differences. To determine if the untreated vs. dried sediment regression was significantly different from 1 (1:1 line), the t-ratio was calculated first. The t-ratio = (best fit slope – hypothetical slope) / standard error of slope. The t-ratio and the degrees of freedom (n-2) for 95% confidence were checked against a critical t-value table and the regression was determined if significantly different from 1.

To calculate the %FRP removed, the final P concentration in water at 48hrs was subtracted from the initial P concentration, providing the concentration of FRP taken up by sediment. The FRP concentration taken up by sediment was divided by initial concentration, giving the % FRP taken up. The P sorbed (mg kg⁻¹) per m of sediment traversed was calculated by, determining the time (s) required for one pass of P by dividing the velocity (m/s) of the flowing water by the length (m) of the fluvarium. The total number of passes in 48hrs was then calculated by the time (s) of experiment divided by the time (s) for a single pass. A single pass equals 10m. The number of passes was multiplied by 10 and P sorbed was divided by this value to obtain the P sorbed per m of sediment. Distance traveled by P was calculated by multiplying the number of passes by the length of the fluvarium (10m).
Results

Experiment 1

Figure 26. Box-percentile plot (with distribution shape) of untreated and dried sediments combined for sites) (a) EPC$_0$ (b) K and (c) $S_{\text{max}}$. The solid lines are the median values and the dotted lines are the 25$^{\text{th}}$ and 75$^{\text{th}}$ percentiles.
The drying process removed 28 to 98% (data not presented) of the total moisture from the sediments (based on oven dried (@105°C sediment removing all moisture). Neither the EPC₀, the P binding coefficient or S_max were significantly different (paired t-test, P>0.05) between the moist and air dried sediments (Figure 26a, b, c). Whilst K and EPC₀ values were not significantly different between the dry and moist sediments (Figure 26a, b), there was a strong linear relationship (Figure 27a, b). The EPC₀ values sit to the left of the 1:1 line indicating the general trend that drying of sediment increases the EPC₀.
Figure 27. The (a) $\text{EPC}_0$, (b) $K$ and (c) $S_{\text{max}}$ of dried sediment plotted against untreated sediment.
Using the method applied by McDowell (2015), the historic water quality median $\text{FRP}_H$ values were strongly correlated with each site ($r^2=0.62$) (Figure 28). The values were to the left of the 1:1 line, suggesting that the median $\text{FRP}_H$ were higher than the $EPC_0$ of the sediment. There was no significant difference (paired t-test $p>0.05$) in the amount of $P$ (mg kg$^{-1}$) released between the moist sediment and sediment subject to air drying (Figure 29).

**Figure 28.** The $EPC_0$ of study sites plotted against median $\text{FRP}_H$ data.

**Figure 29.** Box-percentile plot (with distribution shape) of untreated and dried sediments with no $P$ added to solution. The solid lines are the median values and the dotted lines are the 25$^{th}$ and 75$^{th}$ percentiles.
Experiment 3

Figure 30. (a) P sorption curve of different flow rates on Site B whole sediment. (b) FRP left in solution after 48 hrs. The solid line is the flow rate set at 1 L s\(^{-1}\) and the dashed line is the flow rate set at 2.8 L s\(^{-1}\).

Table 11. Comparison of P uptake by sediment at different flow rates.

<table>
<thead>
<tr>
<th>Flow rate (L s(^{-1}))</th>
<th>FRP removed (mg L(^{-1}))</th>
<th>FRP removed (%)</th>
<th>P sorbed (mg kg(^{-1}))</th>
<th>P sorbed (mg kg(^{-1})) per m of sediment traversed</th>
<th>Distance traveled by P (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.86</td>
<td>30</td>
<td>3.07</td>
<td>1.99 x 10(^{-4})</td>
<td>15420</td>
</tr>
<tr>
<td>2.8</td>
<td>1.01</td>
<td>38</td>
<td>3.86</td>
<td>1.42 x 10(^{-4})</td>
<td>27180</td>
</tr>
</tbody>
</table>

In Experiment 3, the simulated stream flow at 1 L s\(^{-1}\) adsorbed more P per m of sediment traversed than the faster flow rate of 2.8 L s\(^{-1}\) (Table 11). The P in the fluvarium with the higher flow rate travelled further and adsorbed more P lowering the P concentration in the water (Figure 30, Table 11).
While there was no significant difference between the EPC$_0$ of the wet and air-dried sediment, most of the site’s EPC$_0$ were to the left of the 1:1 line (Figure 27a), indicating partial desiccation of the sediment will possibly increase its EPC$_0$, thereby increasing the sediments potential to be a source of P. Similarly, while not statistically significant, drying of sediment tends to decrease the bonding strength, K, as noted by values to the right of the 1:1 line. This is indicative of reduced binding sites for P to adhere to, possibly due to increased crystallinity of the Fe oxyhydroxides. That is, due to the annual drying and rewetting cycle, the minerals have aged further and therefore there will be a minimal effect of drying, increasing the EPC$_0$ and reducing K (Baldwin and Mitchell, 2000).

In this study, S$_{max}$ of the dry sediment was not significantly correlated with the S$_{max}$ of the untreated sediment, which suggests that changes in the total amount of P that can be adsorbed by the sediment were controlled by factors other than the drying of sediment. Factors controlling S$_{max}$ include the presence of biota, which has a significant effect on S$_{max}$ (Chapter 4). In this study, if drying had an effect on biota of these sediments, a significant reduction in S$_{max}$ on drying of sediment should have been observed but this was not the case. These results indicate that these sediments may have microbial populations resistant to desiccation consistent with the findings of Baldwin et al., (2000).

There was no significant difference between the P released by the wet and dry sediments (Figure 29), indicating a negligible amount of P being released into stream water upon rewetting. This result was contrary to Schönbrunner et al. (2012) who found that P release was greater in sediments undergoing repeated wetting and drying. However, the description of the site used by Schönbrunner et al. (2012) suggests that their sediment was submerged in shallow water and had not undergone repeated annual drying. This further reinforces the notion that streams which rarely dry out will show the biggest change in the sediments capacity to remove P from the water column and the biggest opportunity to release a large pulse of P into the water column upon rewetting (Baldwin et al., 2000).

As there was not a significant effect of drying on the EPC$_0$ of sediments, this study used the EPC$_0$ of moist sediment across the seasonal FRP$_{H}$ data. Using the median of the FRP$_{H}$ concentration reduces variability of seasonal water quality measurements.
(McDowell, 2015). The strong correlation and regression shown in Figure 28 of FRP_H and the EPC_0 of sediments in this study is in agreement with a similar regression in McDowell (2015) who measured EPC_0 on sediments in streams with high baseflow. The results of this study indicate that the method employed by McDowell (2015) using median FRP_H data (entire flow) plotted against the EPC_0 of the sediments is valid in streams that are intermittent and ephemeral.

All of the data points used in the analysis of the median FRP_H vs. EPC_0 were to the left of the 1:1 line, suggesting they were acting as a sink of P. Therefore, it is most likely that the streams in the WIC and OHC are net immobilisers of P. In Chapter 3 where 27-30% of P added to solution was removed and only 7-14% of the retained P was released back into solution: a further indication these sediments will be net immobilisers of P. However, during the high flow periods (increase in the flow rate), there may be a reduction in the ability of sediment to retain P due to the lower residence time of P as sediment in a stream with a lower flow rate will adsorb more P per length of stream travelled (Table 11). If the cumulative P sorbed is taken into account (Figure 30.), the sediment with the faster flow rate has adsorbed more P than the slower flowing water in the fluvarium as it has covered more distance over the sediment in the same period of time (Table 11). The increased P sorbed of the faster flowing water is due to the continual recycling of water over the sediment. These results indicate that distance along a stream may be important for gross reductions, whilst time seems more important to maximize the potential of the sediment to interact and reduce P. While a decrease in water residence time will reduce the ability of sediment to retain P, other factors not addressed in this study must be taken into consideration. These include temporal effects on sediment P storage capacity and variation in P concentration of runoff during a rainfall event. In Mediterranean climates, the timing of major events is critical to P retention and discharge into the coastal waters/estuary as a large portion of the rainfall and stream flow can be attributed to a few storm events during the period of flow (Gasith and Resh, 1999).

**Conclusion**

Desiccation or partial desiccation affects the ability of stream sediment to retain P from the water column, reducing their affinity for P and increasing the capacity of sediment to act as a source of P. However, the vast majority of the stream sediments in the Oyster Harbour and Wilson Inlet catchments are subjected to a degree of desiccation annually,
potentially ‘irreversibly aging’ their minerals (Baldwin et al., 2000) so that drying will only provide a negligible increase in EPC₀ and decrease in P binding energy, resulting in negligible release of P upon rewetting. This study shows the sediments in the Oyster Harbour and Wilson Inlet catchment stream networks are net immobilisers of P and therefore contribute to limiting P export to their respective estuaries.

However, like soils, sediments have a finite capacity to remove and retain P (Barrow, 1989a and Holford, 1989 cited in Nash and Halliwell, 1999). Sediment has a P equilibrium (EPC₀), which is affected in part by the geochemistry and moisture of the sediment. Should the stream water P concentration be below the EPC₀ of the sediment, the sediment will release P to the water column. However, if the EPC₀ of the sediment, is below stream water P concentration, it will act to retain P. Continual additions of P from the water column to the sediment will erode the capacity of the stream sediment to retain P (Chapter 3). Eventually the P storage capacity in sediments will be reduced and the concentration of P in the stream water will increase to be similar to that coming off the landscape, as the stream sediment buffering capacity will be diminished. For the stream sediment to sorb more P, greater concentrations of P would need to be leaving the landscape. However, best management practices can be implemented at a catchment and farm scale to reduce P loss and P concentrations from the agricultural landscapes. This will result in a reduction in the concentration of P entering the stream, and at this point stream sediment may become a P source rather than a sink.
Chapter 6. Synthesis

Recap of motivation for study

Globally the increased loading of P into natural systems, in part due to agriculture (Nguyen and Sukias, 2002; Evans and Johnes, 2004; Hoffmann et al., 2009; Palmer-Felgate et al., 2009; Gourley and Weaver, 2012), has led to the eutrophication of receiving waters. Worldwide, eutrophication has been identified as a major impairment of surface water quality (Pote et al., 1999; Sharpley and Tunney, 2000; Nguyen and Sukias, 2002; House, 2003a; Evans and Johnes, 2004; Palmer-Felgate et al., 2009) and gives rise to algal blooms and subsequent negative environmental, economic and social impacts (Carpenter et al., 1998; Nash and Halliwell, 1999; Sharpley et al., 2001; McDowell et al., 2004; McDaniel et al., 2009).

Having identified the various pathways by which P loss occurs from land to the waterways, much effort and resources have been placed into mitigating the loss of P through, for example through soil amendments (Sharpley et al., 2001; Summers et al., 2004), soil testing (Sharpley et al., 2001; Weaver et al., 2011) and riparian buffers (Gitau et al., 2001; McKergow et al., 2003). Success of these management strategies varies (Gitau et al., 2001; McKergow et al., 2003; Weaver and Summers, 2014), for example, riparian buffers appear to have limited effectiveness in sandy landscapes (McKergow et al., 2003; Summers et al., 2014; Weaver and Summers, 2014). Once nutrients ‘leave’ the landscape, they can be further modified, transformed, retained or released by stream sediment. Stream sediment has some control over the retention and release of P and the impact is influenced largely by particle size (Stone and English, 1993; Webster et al., 2001; van der Perk et al., 2006; Ryan et al., 2007; Zhuan-xi et al., 2009), mineralogy (Borggaard et al., 1990; Reddy et al., 1995; Nguyen and Sukias, 2002; Agudelo et al., 2011; Zhenhua et al., 2012) and biological components of the substrate (Lottig and Stanley, 2007; Sharpely et al., 2007). Furthermore, it has been identified that in catchment scale models of P loss to receiving waters, the stream component is often not adequately modelled (Haggard and Sharpely, 2007; Rivers et al., 2013). This is in part due to the complexity of P movement through streams because of influences of sediment properties and flow variability (Sharpley, 2007). Identifying stream controls should improve the stream component of catchment P models, providing a better estimate of P loss from agricultural catchments.
The evidence for the influences on P retention and release in streams is mostly-derived from temperate climates with perennial stream flows (Klotz, 1988; Reddy et al., 1995; Nguyen and Sukias, 2002; House, 2003b; McDowell, 2003; Sharpney et al., 2007; McDaniel et al., 2009; Palmer-Felgate et al., 2009; Rogers et al., 2013). The role of sediment on P in streams in catchments with sandy soils and a Mediterranean climate has received limited attention though a study by Marti and Sabater (1996) identified spatial and temporal variability in nutrient retention by streams in Spain.

This thesis sought to better understand the role of sediment on P retention and release under the aforementioned conditions.

Summary of chapters

The impetus for this study was to provide information about how streams regulate P in sandy coastal catchments in Western Australia (WA). This was a knowledge gap in our current understanding of P movement through these catchments. The outcomes of this research provided fundamental information about how streams in sandy catchments release and retain P. These results reinforced and added to current international knowledge on the topic, indicating that irrespective of geographical location or climate, some key drivers of P retention and release by stream sediment remain constant. However, it is important to consider this new knowledge in the context of the catchments for which it has relevance: i.e. sandy catchments. A summary of these significant results are discussed below:

Particle size and mineralogy (Chapter 3)

Iron oxides were identified as a key factor in the uptake of P by stream sediment and were present in both the gravel and the sand fraction of stream sediments. It has been documented that the fine material is the most reactive fraction of the sediment (Horowitz and Elrick, 1987; Stone and English, 1993; Webster et al., 2001; van der Perk et al., 2006; Ryan et al., 2007; Zhuan-xi et al., 2009). However, given that the catchments located on the south coast of Western Australia are dominated by relatively inert sand and can also have considerable gravel content, I sought to determine if the gravel fraction contributed to the uptake of P contrary to other locations around the world where fine material was the most P reactive sediment fraction. Outcomes from this research provided new knowledge on controls of P uptake by stream sediment and
also provided additional measures that could be considered when evaluating P retained by sediment.

The major findings of this research on particle size and mineralogy were:

- Irrespective of particle size, mineralogy of sediment material is important in P uptake by sediment.
- Mineralogy is of key importance in stream sediment catchments dominated by sand.
- Whole sediments and individual components of sediments (<2mm or >2mm) were net immobilisers of P in a simulated stream environment.
- In terms of sediment P uptake capacity, stream sediments behave like soils. Repeated applications of P diminish the streams ability to uptake P.
- Calculating P retention normalised by surface area (mg P m\(^{-2}\)) is a useful adjunct to P retention normalised by mass of sediment (mg kg\(^{-1}\)) as it places emphasis on the key drivers of surface area and mineralogy that influence P retention by these materials.

**Biological function in stream sediment on P uptake (Chapter 4)**

In agricultural catchments, up to 40% of the P uptake by stream sediment has been attributed to biotic controls (Klotz, 1985; Haggard *et al.*, 1999; McDowell and Sharpley, 2003; Lottig and Stanley, 2007; Sharples *et al.*, 2007; McDaniel *et al.*, 2009). Of particular interest, Lottig and Stanley (2007) undertook a detailed study of biotic contribution to P retention in different particle size groups of sediment in perennial streams. They found that abiotic processes controlled P uptake in sand and biotic processes dominated P uptake for gravel. They developed a conceptual model and suggested that as particle size increased, the controls on P uptake shifted from abiotic to biotic. I hypothesized that given the climate (Mediterranean) and sediment material (sand with gravel) on the south coast of WA, current knowledge suggests that biota would have minimal impact on P uptake.
The major findings of this research on biological function were:

- In intermittent streams, sand is important in maintaining biotic communities that contribute to P uptake.
- Biota enhances the maximum capacity of the sediment to adsorb P ($S_{\text{max}}$) and the P binding energy of the sediment.
- Non-phototrophic biota can dominate the total biotic P uptake by sediment. This suggests that irrespective of physical conditions that affect phototrophic biota, the biota will contribute to P uptake by sediment.

**Seasonal influences on P retention and release (Chapter 5)**

Chapter 3 (particle size and mineralogy) and Chapter 4 (biological function) targeted the important factors of P retention and release by stream sediments as identified in the literature review (Chapter 2) for catchments located on the south coast of WA. Seasonal factors affecting P retention and release inherently take into consideration the biotic and abiotic controls on P uptake. The desiccation or partial desiccation of sediment can reduce their affinity for P and increase the capacity of sediment to act as a source of P (Baldwin, 1996; McDowell and Sharpley, 2003). This suggests that sediments located in a Mediterranean climate (wetting-drying cycle), could act as a source of P upon rewetting each year. If this were the case, sediments in the OHC and WIC would be a net source of P to streams. Using a method developed by McDowell (2015) of coupling $EPC_{0}$ of sediments with historic water quality data, sediments in the OHC and WIC were determined to be a source or sink of P to the water column.

The major findings of this research on seasonal factors affecting P uptake by sediment were:

- There was no significant increase in $EPC_{0}$ by the sediments or decrease in binding energy by sediments upon rewetting, most likely due to the aging of minerals and thus a stabilized strata for P attachment.
- Stream sediments in the OHC and WIC are potentially net immobilisers of P.
Significance of this research

The significant outcomes from the chapters in this thesis that contribute new information to the field of science can be split into two common themes, climate and sediment types which are summarised below:

*Climate and P uptake – differences between perennial and intermittent streams*

This thesis has provided new knowledge about the factors controlling of P retention and release by stream sediments that are exposed to an annual wetting and drying cycle. Unlike sediments in perennial streams (Baldwin *et al.*, 2000), the sediments in intermittent streams are likely to have developed resilience to desiccation. Geochemically, minerals in the sediment have most likely aged, increasing their crystallinity (Baldwin, 1996; McDowell, 2003) such that upon rewetting little difference in P release is seen compared to that of the same sediment that has been wet for a longer period. This is distinctly different to sediment in perennial streams. In a perennial stream scenario, sediment that dries partially or fully, and then is rewet will lead to an increase in P uptake for a short period due to the initial amorphous state of the Fe oxide (De Groot and Van Wijck, 1993; Baldwin and Mitchell, 2000), which ages, causing a large release of P from these sediments (Baldwin *et al.*, 2000; Kerr *et al.*, 2010).

Similarly, biotic communities in the sediment of intermittent streams have most likely shifted towards drought/desiccant resistant communities (Baldwin *et al.*, 2000). Intermittent streams will provide a negligible increase in P in stream water due to biota death. Conversely, should a perennial stream dry out, upon rewetting a large pulse of P will be released (Qiu and McComb, 1994; Watts, 2000) in part due to the death of biota that is not resistant to desiccation.

In terms of biotic control of the retention and release of P in sediment, in perennial streams as particle size increases, controls on P switch from abiotic to biotic (Lottig and Stanley, 2007). This is in part due to the colonisation of algae and other biota on larger gravels (Gainswin *et al.*, 2006b; Lottig and Stanley, 2007). Conditions in perennial streams are conducive to colonization by biota (e.g. continual flow of water). Results from this thesis, identify that in these intermittent streams, this process appears to be reversed. Biotic controls increase in the presence of finer sediment material and diminish in the presence of gravels. Irrespective of stream flow, biota was not the key
driver of P uptake on the south coast of WA, that is, less than 50% of P uptake was attributed to biotic factors. However biota significantly enhanced the capacity of the sediment to retain P and increased the binding efficiency of the sediment.

Sediment Type - mineralogy, particle size and effects on biota

Much of the previous work on sediment P retention and release characteristics have focused on the fine material of sediment, indicating that the <2mm fraction of the sediment may be the most reactive fraction or even the dominant size fraction of those sediments. Conversely, on the south coast of WA, sediment can contain a high proportion of gravel (>2mm). It can be important to account for the gravel fraction when identifying P retention and release characteristics of those sediment, since the gravel may contribute to P retention or dilute P retention capacity. Sediments with a high <2mm fraction (dominated by silt and clay) will have the majority of its affinity for P within the mineralogy of the clay (Stone and English, 1993; Webster et al., 2001; van der Perk et al., 2006; Ryan et al., 2007; Zhuan-xi et al., 2009). In the OHC and WIC, where sand dominates the <2mm fraction, the affinity for P is concentrated in the gravel (>2mm material) due to mineralogy, adsorbing similar quantities of P to the <2mm material under simulated stream conditions. Irrespective of particle size, mineralogy is important in P uptake. Whilst the <2mm fraction in the sediment of these sandy catchments in a Mediterranean climate has less geochemical capacity to retain P, the <2mm fraction is important in maintaining biotic communities in these sediments which enhances the capacity to adsorb and hold onto P.

These key processes and climatic conditions will determine if the sediments are a source or a sink of P. The simulated stream experiments identified that each component (<2mm, >2mm or whole sediments) of the sediments in the streams were net immobilisers of P, releasing less P than had been retained. This idea that stream sediment in sandy agricultural catchments in a Mediterranean climate are net immobilisers of P was reinforced through the relationships of median stream FRP$_H$ and the EPC$_0$ of each sediment studied. All the sediments had a lower EPC$_0$ than the median FRP$_H$ values in stream water consistent with modelling outcomes by Keipert et al., (2008) and Rivers et al., (2011) conducted on sandy catchments in southwest WA.
**Differences and similarities**

The results of this research have provided a distinction between different climates, mineralogy, sediment material and their associated stream flow. Whilst fundamental processes such as biotic uptake of P and Fe oxide controls on P adsorption by sediment do not differ between stream types (i.e. intermittent, perennial), this thesis has identified that it is pertinent to consider the aforementioned variable factors (e.g. sediment material) when determining the capacity of stream sediments to retain or release P.

**Gravel. A case in point**

This thesis identified that the gravel fraction is an important component of the stream sediment. On the south coast of WA, this importance is amplified, as the gravels are often lateritic and the <2mm fraction is dominated by sand. The results suggest that the gravel fraction will provide a long-term store of P due to its mineralogy. Significantly, the comparison of gravel fractions with the sand fractions in this study indicates that mineralogy can be more important than particle size.

Identification that the gravel fraction is important for P retention and release by stream sediment has implications for measuring stream sediment P retention and release characteristics. Traditionally the <2mm fraction alone is used in measuring P sorption characteristics. For sediments on the south coast of WA, the exclusion of gravel when measuring the P sorption characteristics may underestimate the sediments capacity to adsorb P. Similarly, in streams where gravels are inert to P uptake but are a large fraction of the sediment, examining the <2mm fraction alone without accounting for the diluent effect of the gravel fraction may lead to overestimation of the streams capacity to adsorb P.

**Implications of this research**

Importantly, the findings of this thesis clearly reveal that in sandy catchments on the south coast of WA, stream sediments are an important component in the removal of P from stream water. This has implications for both modelling of P loss in catchments and also measurements of the efficacy of where BMPs are implemented in catchments.

**Modelling P loss in agricultural catchments**

The stream component of P loss catchment models has been considered the weakest link (Haggard and Sharpley, 2007). In Australia, specifically no information has been
available on P retention and release by stream sediments, the models have tended to use a suggested stream loss rate or develop an algorithm based on stream length and depth, catchment area and slope based on the Bransby-Williams formula (Weaver et al., 2004). The findings of this thesis provides understanding of the factors to be considered for catchment P loss models for the OHC and WIC as well as catchments with similar sediment, land use and climate. At a broader scale, the new understanding of P controls of sediments provides some insights for consideration in other catchments that may strengthen the stream component of models.

**Understanding efficacy of BMPs**

Best management practices for minimising nutrient loss can occur on the landscape (fertiliser management, pasture species and management, soil amendment, tillage practices), adjacent to streams (fencing, riparian buffers), or within streams (riffles, pools, wetlands).

Given that streams can retain or release P, determining the efficacy of BMPs would appear more complex than simply measuring water quality (WQ) change and linking that directly to the implemented BMP. As identified in this thesis, stream sediments modify the amount of P in the stream water. In some instances, P is stored in the sediment (instream legacy P) and can eventually be remobilised from storage through various mechanisms and pathways (Jarvie et al., 2013a; Sharpley et al., 2013), such as turbulent flow in streams.

The problem of legacy P has become important in nutrient management in agriculture due to the identification that legacy P, in this case, instream, in agricultural areas may mask or buffer the efforts of conservation within a catchment (Sharpley et al., 2013). Implementation and subsidisation of BMPs such as fencing for livestock exclusion from streams and riparian revegetation, requires investment of both time and funds. These investments must be based on sound science, as well as providing cost-effective solutions. Hence, BMP effectiveness needs to be determined in the absence of influences of retention and release of P by stream sediments.

To better determine the efficacy of BMPs, the influence of streams on P needs to be separated from the effect of the BMP itself. This is because measurements of the effectiveness of BMPs most often occur in the presence of a stream. That is, BMP experiments are conducted in a catchment that includes a stream, and these often occur
as paired catchment studies or before and after ‘BMP implementation’ experiments. Experimentally, it is necessary to vary only the factor you are testing whilst maintaining every other factor constant in order to determine the effectiveness of your varied factor (BMP) in reducing P export. However, it is clear from the experimental results in this thesis that stream materials including gravel can retain significant amounts of P, and that retention and release characteristics can change over time as sedimentary materials become increasingly saturated with P. Implementing a BMP on the landscape that changes the concentration of P delivered to a stream will therefore alter how the stream sediment responds as an immobiliser or source of P, and to what extent.

For example in a *status quo* situation where no management is implemented (control catchment), stream sediment will most likely retain P (landscape P concentration > sediment EPC<sub>0</sub>), and the measured values in the stream will most likely lead to an underestimation of P loss from the landscape (Figure 31). A landscape BMP such as fertiliser management (managed catchment) (Table 12) is implemented and a large reduction in P loss from the landscape occurs (Figure 31), then the effectiveness of the BMP may be underestimated due to the release of legacy P from stream sediment (landscape P concentration < sediment EPC<sub>0</sub>) (Figure 31).

![Figure 31](image-url) Conceptual model of how retention and release of P by stream sediments can affect interpretation of management interventions in agricultural landscapes. The bar chart of the stream indicates whether the stream will release or retain P under management conditions. The amount of P lost from the landscape and P entering the stream is represented by the grey rectangles. For simplicity, landscape P loss is the P lost from the landscape prior to entering the stream network. The catchment P loss is the measured P loss (generally from WQ samples).
To better understand the situation, a ‘paddock’ may lose 100 units of P, however stream water samples collected to measure water quality may only identify 70 units of P lost. Therefore a monitoring program may underestimate the actual loss of P from agriculture due to the removal of P by the stream sediment (Figure 31). In this case the stream is providing a “free kick” to WQ. Similarly, the inclusion of a best management practice somewhere in the catchment may reduce the P lost from the landscape from 100 units to 25 units of P (Figure 31). Due to legacy P stores in streams and a reduction in the P concentration entering the stream upon implementation of a BMP, the sediment will release P into the water column, therefore masking the effectiveness or ineffectiveness of the implemented BMP (Figure 31) and possibly providing a similar or less effective result than the status quo (Figure 31). A case study of such a scenario is in a report undertaken by URS (2010) assessing Alkaloam® (a bauxite residue derived soil amendment) spread on a sandy catchment on the southwest coast of WA. The Alkaloam® was spread only on the agricultural landscape at a paddock scale and not in the stream network (Summers et al., 2001). The P concentration seen in the measured P loss in this catchment seen took 12 years to equilibrate, suggesting that legacy P from the stream was contributing to the measured P loss. The results of another study in the same region within the same report (URS, 2010) where Alkaloam® was spread across the entire catchment on both the agricultural landscape and the stream network showed an immediate and sustained drop in the measured P concentration in the WQ. The gradual decline in P concentration in areas where the stream sediment was not amended with Alkaloam® suggests that stream sediment was counteracting the effectiveness of the Alkaloam® by releasing P from legacy P stores in stream sediments.

Without being able to separate these effects, it is difficult to determine how effective BMPs are since the stream may retain P, or release P. It may be suggested that paired catchment experiments could resolve this problem, however the stream sediment in a managed catchment will interact with P differently from that of a control catchment, and hence factors that need to remain constant experimentally will unfortunately vary depending on how effective a BMP is.

The significant impact of stream sediment on the retention and release of P raises two questions, 1) what are the amounts of P actually being lost from the landscape? and 2) are the current methods for measuring BMP efficacy (i.e. WQ samples) providing an accurate assessment of the impact of the BMP on P loss from the landscape?
As well as identifying the potential to underestimate P lost from the landscape and the efficacy of BMPs due to the interaction of P with sediment, Table 12 also brings into question whether the effectiveness of BMPs may be determined from short term monitoring programs (~1 year), when long term monitoring (~10 years or more) may be required for stream sediment to reach equilibrium with managed P concentrations from the landscape irrespective of BMP implementation. The length of time of WQ monitoring can affect the capacity of a monitoring program to determine if significant trends are occurring. For example, on the west coast of WA, Alkaloam® had been applied to a catchment and WQ monitored for 12 years (URS, 2010). Whilst there was an overall downward trend in P concentrations, the two years immediately following initial application showed a decrease, indicating a positive effect of this BMP. However, the following three years showed increased P concentrations similar to those pre-implementation of the BMP. However, by the twelfth year of monitoring, a noticeable reduction in P concentration in streamwater had been achieved. To restate, if short term monitoring is undertaken, there may be an underestimation of the impact of the BMP on the reduction of P lost from the landscape (Figure 32), whereas longer term monitoring may identify a more accurate response of the implemented BMP as noted by a difference in reduction of P lost from the catchment in the short term and long term monitoring periods (Figure 32). As the P lost from a landscape prior to entering a stream is very difficult to measure, current methods will continue to be used. Thus, the length of time that WQ is monitored may have an effect on identifying the potential maximum efficacy of a BMP in reducing landscape P loss. Table 12 shows conceptual models of whether short or long term monitoring will possibly provide an overestimation or underestimation of the efficacy of the implemented BMP on varying soil and sediment types. For example, for the implementation of fertiliser management on a sandy soil, short term monitoring will likely lead to an underestimation of the efficacy of fertiliser management and that longer term monitoring should improve the estimation.
Figure 32. Conceptual model of the impact of monitoring program length on testing the BMP efficacy post implementation, on catchment P loss. The dotted line loss is the measured P value after a short period (e.g. 1 yr), and the solid line is the measured P value after a long period of monitoring.
Table 12. Potential influence of streams on the measured response of landscape on catchment P loss to the implementation of some BMP’s.

<table>
<thead>
<tr>
<th>Sediment¹</th>
<th>Sediment sub-descriptor²</th>
<th>BMP³</th>
<th>Landscape loss⁴</th>
<th>Catchment loss⁵</th>
<th>Influence of stream</th>
<th>Measure efficacy of BMP⁶</th>
</tr>
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<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Retention</td>
<td>Short term</td>
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<td></td>
<td></td>
<td></td>
<td>n/a</td>
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<tr>
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<td>Release</td>
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<td>Underestimation</td>
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</tr>
<tr>
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<td>Riparian Vegetation</td>
<td></td>
<td></td>
<td>Retention</td>
<td></td>
<td>Overestimation</td>
</tr>
<tr>
<td>Clay</td>
<td>Riparian Vegetation</td>
<td></td>
<td></td>
<td>Retention</td>
<td></td>
<td>Overestimation</td>
</tr>
</tbody>
</table>

¹ Sediment – is the dominant material for this scenario.
² Sediment sub-descriptor – secondary information relating to sediment type that may affect P retention and release.
³ BMP – the best management practice implemented to reduce P loss from the landscape.
⁴ Landscape loss – P lost from the landscape prior to entering the stream. The y-axis on for landscape P loss represents the P “entering the stream” and the x-axis represents time (conceptual).
⁵ Catchment loss – P loss measured including cycling of P instream. The y-axis on charts for catchment loss represents the amount of P measured in WQ samples and the x-axis represents time.
⁶ Measured efficacy of BMP, in relation to time periods, providing an estimation to whether a more accurate measure of BMP efficacy will likely occur short or long term, this is conceptual.
When determining the effect of stream sediment P retention and release on BMP efficacy, such as the scenarios in Table 12, it is assumed that the system has been exposed to current management practices in mature agricultural systems (approximately 50-70 years of annual fertilisation). This will suggest that there is excess P in some soil types and that P loss from the landscape will occur.

Unlike Alkaloam®, riparian vegetation on sandy soils can cause minimal reductions to the landscape P loss. The losses of P can be similar to that of a sandy landscape without riparian vegetation (McKergow et al., 2003) (Table 12). The catchment P loss could indicate a reduction in the P lost from the landscape. This could be misinterpreted to be the result of the introduction of riparian vegetation if no consideration is given to the retention of P by stream sediment. Thus, efforts could be misplaced on replanting riparian vegetation as a BMP for removal of P in sandy landscapes prior to entering streams. Thus, when querying the efficacy of a BMP, consideration should be given to soil and sediment type of the catchment.

The effect of stream sediment retention and release of P affecting the landscape P loss could have a significant affect on the uptake of BMPs by landowners. The perceived ineffectiveness of BMPs, due to no change in water quality in the catchments, may leave landowners wary of further participation in future opportunities to implement new BMPs when they arise. The overestimation of the efficacy of a BMP to reduce the P loss from the landscape may use large amounts of private and public funding at the expense of the implementation of other BMPs that may be more effective in reducing P loss from the landscape.

Therefore, extended research into methodology and analysis of P loss from catchments with and without BMP’s implemented to separate the catchment P source from the stream P source to identify the efficacy of BMP’s is required. As discussed, a paired catchment experiment may prove difficult due to the dynamics of the stream sediments ability to retain and release P under management and no management. Similarly, a before and after experiment (pre- and post-BMP implementation) would not be able to separate the stream P source from the catchment P source as the potential for a stream to become a net immobiliser or source of P once BMP’s are in place (Figure 31). Ideally but highly impractical would be to separate the landscape hydrology and movement of P from the stream hydrology to determine how effective the BMP’s implemented were in reducing P loss.
This option however is complicated by the potential for a stream to become a net immobiliser or source of P once BMP’s are in place (Figure 31).

**Critical assessment of approach**

This study gave clarity to factors affecting the uptake and release of P by stream sediment on the south coast of WA and what is similar or different to other regions of the world where research on sediments have been undertaken. However there is always opportunity to maximise the research presented through improved experimental design. It would be beneficial to identify the variability in results using different sediment:solution ratios in batch experiments. Fluvarium base experiments in essence (by design of the infrastructure) have a set soil:solution ratio but batch experiments can vary in their ratios. Experiments calculating EPC₀ in the literature used sediment:solution ratios ranging from 1:4 through to 1:400. This is very pertinent to EPC₀ calculations as the EPC₀ is used as a proxy to identify whether a stream acts as an immobiliser or releaser of P. Furthermore, the inclusion of temporal factor in experiments for EPC₀, that is, how does it change over time with the addition or removal of P from stream water, as this research identified that continually application of P diminishes the sediments capacity to uptake P. This assessment of experimental design provides opportunity for future work to better understand the dynamics of P regulation by stream sediments.
Recommendation for future work

This thesis examined the role of streams in P retention and release in agricultural catchments with both a Mediterranean climate and sand dominated soils. This has led to an improved understanding of some factors affecting P retention and release by stream sediment such as sediment particle size and mineralogy.

There is a requirement for experimental work that considers how to best separate catchment P signals into those arising from stream sediment and those arising from the landscape. This separation should lead to improved understanding of the effectiveness of BMP’s designed to reduce P losses as well as better estimates of P loss from the landscape pre-BMP implementation. This could be achieved by through the use of infrastructure that separates the hydrology of the landscape from that of the stream, allowing separate measurements of both. Additionally, clever use of tracers, such as bromide, fluoride or chloride could lead to a better understanding of P retention and release in various transport pathways from the landscape to the stream, and within the stream itself.

The EPC\(_0\) of sediment is one of the major controls on P in the streamwater and therefore further work to understand factors that affect EPC\(_0\) is warranted. Tracking the dynamics of sediment EPC\(_0\) over time as stream P concentrations vary would be beneficial. This could include sampling EPC\(_0\) of sediment over a time period on sediments that were in a fully managed (BMP implemented) and unmanaged catchments and with catchments with varying degrees of management as well as catchments which have had the landscape P sources completely turned off. These experiments would assist to characterise the longevity of sediment to retain or release P, and provide evidentiary basis to the implied influence of streams on the efficacy of BMP’s (Table 13).

It would be beneficial to undertake further fluvarium experiments with various P concentrations, above, below and close to the EPC\(_0\) of the sediment to identify how the sediment reacts at different P concentrations. Experiments that included measurements of EPC\(_0\) after build or release phases, and setting starting P concentrations according to the EPC\(_0\) measurements would provide improved understanding of the effects of EPC\(_0\) dynamics on the P concentrations in streams. P release experiments could also be undertaken to study the dynamics of EPC\(_0\) after P has been released. Similarly, as the EPC\(_0\) of the sediment could be measured between build or release phases, a starting P concentration equal to the EPC\(_0\) could be used to confirm that neither uptake or release
would occur. This would add further understanding to EPC$_0$ dynamics, and its relationship to the efficacy of BMP’s.

To further enhance the capacity of a stream to retain P, this thesis identified that some gravels retain P. There is opportunity to modify abiotic processes in stream through the addition of P sorptive gravel material (i.e. lateritic gravel) on streambeds as a management tool for mitigating P loss from agricultural catchments. However, it would require the identification of gravel material that will not lose its capacity to retain P in a short period of time (Summers et al., 2014).
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