Biological phosphorus solubilisation in riparian vegetated buffer strip soils

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....

William Mark Roberts

Statements of Authorship

Please find below a list of published and draft papers included in this thesis with information regarding my contributions to each of the papers. The research leader of these publications has signed to confirm this.

Phosphorus retention and remobilisation in riparian buffer strip soils: a review

I searched and reviewed the literature and wrote this paper.

Student: William Roberts

……………………………..

Research leader: Prof. Phil Haygarth

……………………………..

Microbial biomass phosphorus contributions to phosphorus solubility in riparian vegetated buffer strip soils

I contributed to sample collection, carried out all of the laboratory analysis except for soil total P, performed data management and statistical analysis, designed figures and tables, and wrote the paper.

Student: William Roberts

……………………………..

Research leader: Prof. Phil Haygarth

……………………………..

Retention of phosphorus forms by a narrow vegetated buffer strip

I designed and established the experiment, carried out the entire fieldwork and laboratory analysis, conducted data management and statistical analysis, designed figures and tables, and wrote the paper.

Student: William Roberts

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Research leader: Prof. Phil Haygarth

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Plant root induced phosphorus leaching from riparian buffer strip soils: effects of plant species and soil management

I designed and set up the experiment, carried out the entire greenhouse work and laboratory soil, plant and water total P analysis, performed the data management and statistical analysis, designed figures and tables, and wrote the paper.

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Abstract

Biological phosphorus solubilisation in riparian vegetated buffer strip soils

William Mark Roberts B.Sc. M.Sc.

Appropriate agricultural practices can minimise the contribution that phosphorus (P) transfer from agricultural land makes to surface water eutrophication. Minimising P transfer by establishing riparian 'vegetated buffer strips' is becoming increasingly popular, as they have been shown to reduce total P delivery to streams. However, an uncertainty remains about how buffer strips alter the delivery of dissolved forms of P, which may be highly bioavailable to freshwater algae. The overall aim of this study was to investigate whether biological solubilisation processes operating within buffer strip soils can increase the risk of dissolved P transfer, and in turn, understand how better to manage them in order to minimise this. A soil survey across multiple established buffer strips showed that microbial biomass P contributes to elevated P solubility in buffer strip soils. A plot scale experiment measuring the quantity of P forms in runoff demonstrated that P remobilisation in buffer strip soils could result in increased delivery outputs of dissolved P, given the right rainfall-runoff conditions. A soil column leaching experiment showed that the growth of some common riparian grass species could increase P leaching due to enhanced carbon mobility in the soil. These results are contrary to the perceived role of plants, microorganisms and organic matter solely as sinks for dissolved P in riparian vegetated buffers strips. The acquisition of P during growth of plants and microorganisms and the release of P from biota, may lead to buffer strips increasing dissolved P transfer risk. Management of these biological pools and processes will be necessary if buffer strips are to retain dissolved forms of P. Harvesting and removal of the buffer strip vegetation could provide benefits by tightening the biological retention-remobilisation cycle of P in buffer strip soils.

Acknowledgements

First, I would like to thank Dr. Marc Stutter and Prof. Phil Haygarth for the supervision and many opportunities they have provided over the last 4 years. I would also like to thank Dr. Martin Blackwell, Dr. Tim George, Dr. Ben Surridge and Dr. Nick Chappell for their unofficial supervision, especially when I was away from home. This thesis would have remained a dream had it not been for the support of my parents and partner and for that, I thank them. Many individuals have assisted me in field and laboratory work for which I am extremely grateful and I acknowledge these people individually at the end of each paper.

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1. Introduction

William M. Roberts (1, 2)

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Nutrients in surface waters above natural background levels will stimulate the excessive productivity of primary producers (Elser et al., 2007; Schindler and Hecky, 2009; Vollenweider, 1968). The consequent death and decay of macrophytes and algae causes a reduction in dissolved oxygen concentration especially at night when respiration dominates, and a reduction in water clarity to the point where algae dominate over macrophytes. Within the algal community, there is an increase in dominance of cyanobacteria or 'blue-green algae', which form surface blooms and produce harmful toxins (O'Sullivan, 1995; Wetzel, 2001). The vulnerability of humans to these toxins was highlighted in an extreme case in 1997 when 55 patients died after exposure to cyanobacterial toxins after undergoing routine dialysis treatment in a hospital in Brazil (Jochimsen et al., 1998). There are also secondary impacts such as a reduction in the recreation and biodiversity value of surface waters and water treatment problems associated with removing the toxins and the accompanying tastes and odours. The eutrophication of the Norfolk Broads, UK and Chesapeake Bay, USA are clear examples of how increased nutrients in freshwater and marine water systems can result in these impacts (Boesch et al., 2001; Harper, 1992; Marine Pollution Bulletin, 1977). These impacts have an associated monetary cost. Pretty et al. (2002) estimated that the damage costs, i.e. drinking water treatment costs for nutrient removal, reduced recreational and amenity value of water bodies etc., of these secondary impacts in the UK were £9.3

million per year. This estimate did not include policy response costs, which were estimated at £54.8 million per year. The process of nutrient enrichment and change in ecological structure is termed 'eutrophication' which is now recognized as the one of the main water quality issues in the world and one of Europe's major environmental problems (EEA, 1998 ; OECD, 2001; OECD, 2008; Smith, 2003; Smith and Schindler, 2009). Because of the prevalence and severity of this problem, scientists have made a concerted effort over past decades to improve understanding of causes of eutrophication and to develop rational frameworks for managing and preventing the problem. The following two paragraphs provide a background for the thesis by briefly discussing our current understanding of individual nutrients and forms of nutrients as factors in promoting eutrophication and current legislative approaches to minimising concentrations of these nutrients in surface waters.

Not all nutrients will stimulate algal growth and the exact limiting nutrient in certain surface water typologies (e.g. fresh and marine waters) has been the subject of much research over past decades. This research has struggled to identify the exact nutrient responsible as a vast range of ecological and geochemical factors can influence the nature of nutrient limitation. Despite this, researchers have some made some conclusions, for example, of potassium (K) not being limiting (Wetzel, 2001), of nitrogen (N) being the limiting nutrient in marine waters (Vitousek and Howarth, 1991) and of phosphorus (P) being the limiting nutrient in lakes (Schindler, 1977). More recent works by Elser et al. (2007) involved a meta-analysis of over 2000 nutrient enrichment studies that showed that often there is no one nutrient limiting algal growth with a combination of N and P producing the greatest growth response in both fresh and marine waters. The chemical form of nutrients in surface waters will also influence primary productivity in surface waters, as different forms will vary in their accessibility and availability to algae, and P provides a useful example of this. Waters will contain P attached

to soil particles in both organic and inorganic forms (collectively referred to as particulate P) and P dissolved in solution in inorganic and organic forms (collectively referred to as dissolved P) (Haygarth et al., 1998). The routine analysis of these P forms in river and lake water are operationally defined based on filter pore size and method of analysis and therefore represent fractions rather than exact chemical forms. The operational definition used to distinguish between dissolved P and particulate P is the total amount of P that can pass through a filter, in most studies with a cut-off of 0.45 μm. Some colloidal P will pass through this filter size not and not be truly dissolved in solution (Haygarth and Sharpley, 2000; Haygarth et al., 1997; Heathwaite et al., 2005). The operationally defined distinction between inorganic and organic P is the reactivity with ammonium molybdate as determined by colourimetry. Because some inorganic P forms such as polyphosphates will not react with molybdate, the inorganic fraction is thought to contain mostly orthophosphate, however some organic P will be mineralised during the analysis process (Turner et al., 2003a). The unreactive fraction of P in water will contain P in a range of organic combinations including inositol phosphates, nucleic acids, nucleotides, phospholipids and sugar phosphates as well as condensed inorganic forms including polyphosphates and pyrophosphates (Toor et al., 2003; Turner and Haygarth, 2000). Based on bioassay evidence and depletion studies, the dissolved inorganic P fraction is thought to be almost entirely available for algal growth (Boström et al., 1988). Algae will take up dissolved inorganic P rapidly, leading to a very high, localized concentration of biomass (Dodds and Welch, 2000; Hynes, 1969). The dissolved organic P fraction contains P in organic combinations that are available to aquatic algae that have the ability to release enzymes that hydrolyse the associated phosphate. Whitton et al. (1991) found that of 50 axenic cyanobacterial cultures, nearly all showed phosphomonoesterase and phosphodiesterase activities, and also utilised P monoesters and diesters. Only a few strains of cyanobacteria were capable of utilising inositol phosphates. This data suggests that compounds within the dissolved organic P fraction have a varying

degree of availability to aquatic algae. Particulate P also displays a varying degree of availability with <50 % of river particulate P available depending on watershed (Lee et al., 1980). This availability is thought to be correlated with P sorbed to iron and aluminium oxides (Sharpley et al., 1991). The different measured fractions of P therefore have differing availabilities to aquatic algae over different timescales as do the different forms of P within those fractions. Water quality standards for surface waters and measures for mitigating nutrient inputs to surface waters should therefore focus on minimising the concentrations and loads of the key limiting nutrients and the most available fractions of them.

It is the role of legislation set by governing authorities to ensure the states of water bodies affected by eutrophication are improved and that pristine water bodies do not deteriorate. In Europe, the Water Framework Directive (WFD) (2000/60/EC)(EC, 2000) aims to achieve "good ecological status", and in the USA, the Clean Water Act (1972) aims to "maintain biological integrity". One aspect of meeting such ecological criteria for good water quality involves the setting of chemical standards for P. Setting chemical standards for P is complicated because of the variation in the natural trophic status of water bodies and the need to identify background conditions i.e. before human interference (Dodds and Welch, 2000). Accounting for these complications typically involves investigating the physio-chemical characteristics of pristine water bodies in order to set standards. For example, to establish river background P concentrations for the Water Framework Directive, in 2008 the UK Technical Advisory Group investigated summary statistics of P concentration across thousands of sites considered to be of good biological quality. They selected the mean annual P values achieved by 90 per cent of the sites as the "good" standard. The number of sites also allowed the advisory group to identify two important factors determining the nutrient sensitivity of rivers that in turn affected the standards set: altitude and alkalinity. Low alkalinity, high altitude rivers naturally sensitive to nutrient pressure were set lower

standards for annual mean P concentrations than low alkalinity, low altitude rivers (Table

1.1). Using a modelling approach, Carvalho et al. (2005) estimated that more than 50 % of

UK lakes > 1 ha in size would not achieve good status for P concentrations. Achieving good

status for P is done so in the context of river basin management plans, which describe the

river basin, the pressures acting on it and options for mitigating those pressures, and is

revisited every 6 years. Understanding the contribution of different sources of P to surface

water loadings will allow catchment managers and scientists to incorporate targeted

mitigation options into these plans. The following three paragraphs introduce agriculture as

a source of P to surface waters, the diffuse transfer of P from agriculture to surface waters

and the potential for using riparian vegetated buffer strips to mitigate this transfer.

Table 1.1. Standards for phosphorus in UK rivers for the Water Framework Directive (UKTAG, 2008).

	Status			
	High	Good	Moderate	Poor
Low alkalinity, low altitude	30	50	150	500
Low alkalinity, high altitude	20	40	150	500
High alkalinity, high and low altitude	50	120	250	1000

Low altitude <80 m, high altitude >80 m
Low alkalinity <50 mg l^{-1} annual mean, high alkalinity >50 mg l^{-1} annual mean
Phosphorus concentrations are in μg l^{-1} as dissolved inorganic phosphorus as an annual mean

Sources of P to surface waters that elevate concentrations above background levels can

come from a number of different sources. These may be point sources that have a clearly

identifiable point of entry to the water body, for example, discharges from septic tanks or

waste water treatment works (Palmer-Felgate et al., 2010; Stutter et al., 2010). Sources may

also be diffuse sources that have no identifiable point of entry into the water body, for

example, agricultural runoff. Having no identifiable point of entry to the water body, these

sources are difficult to both identify and mitigate. These difficulties are highlighted by the

fact that, the National Audit Office estimated that 30% of UK surface waters will fail to

achieve 'good status' under the Water Framework Directive (2000/60/EC) (WFD) due to

diffuse pollution and this is despite significant investment into mitigation by government agencies (NAO, 2010). Diffuse transfer of P from agricultural land contributes a large proportion of P loadings to surface waters because excess P fertilizer addition to agricultural soils has increased transfer. For example, in the UK and Denmark, agriculture contributes 29 and 27 % of surface waters P loads respectively. In Ireland and the Netherlands agriculture contributes much more: 73 and 63 % respectively (OECD, 2008). This proportion is thought to be increasing because the relative contribution of point sources to P loads is declining due to effective mitigation (OECD, 2001; White and Hammond, 2009; Withers and Haygarth, 2007). Since the appreciation of this contribution, much research has focussed on understanding diffuse P transfer from agriculture and its mitigation in order to minimise nutrient pressures on surface waters.

The transfer of P from agricultural land to surface waters involves several steps which are conceptualised in the 'transfer continuum' model of Haygarth et al. (2005) (Figure 1.1). Briefly, these steps include a 'source' of P and this could be fertilizer applied to the soil or P already held in the soils as part of the natural geological reserves. Phosphorus would then be 'mobilised' from this source or made available for transport by geochemical or biological solubilisation processes or by physical detachment of soil particles containing P, for example, by geochemical desorption of P from soil mineral surfaces into solution or by rain splash impact on the soil surface. To reach surface waters from the point of mobilization, P must be 'delivered'. Delivery is dependent on hydrology as water is the main carrier of P through the environment and may involve belowground pathways such as ground water flow and interflows or aboveground pathways such as overland flow. The mobilisation processes and delivery pathways and factors affecting them will determine the relative proportions of different forms of P delivered. Delivery of P at high concentrations and loads can result in 'impacts' on water quality, these impacts are the symptoms previously mentioned.

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Mitigation options for this P transfer address different aspects of the transfer continuum (Haygarth et al., 2009). Addressing P sources by fertilizer input reduction is considered an optimal mitigation option and the excess P applied to agricultural land is declining as a result of increasing crop yields and P off-takes as well as economic drivers for reductions in P fertilizer use (Defra, 2011; Ulén et al., 2007). Yet, even when soil P inputs are limited it may take decades for soil P status to be reduced to a level whereby P transfer occurs at concentrations and quantities unlikely to have an impact in receiving water bodies (Kronvang et al., 2005; Wall et al., 2013). Therefore, to help buffer this 'lag time', mitigation options must also consider mobilisation and delivery aspects of P transfer.
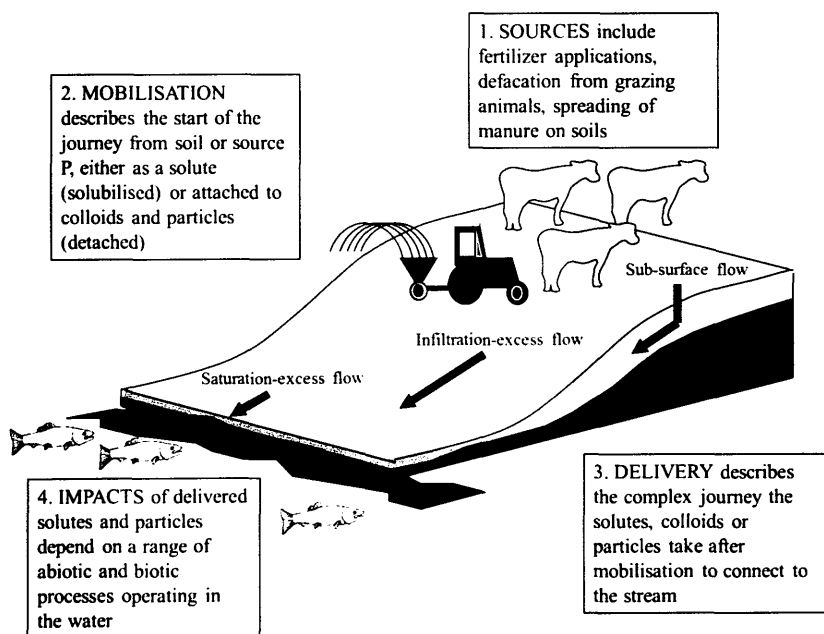
Figure 1.1. The phosphorus transfer continuum (Haygarth et al. 2005).

Riparian vegetated buffer strips are an option for the mitigation of P transfer from agricultural land and specifically address the delivery tier of the continuum. The implementation of buffer strips to provide a water quality benefit involves the cessation of cultivation and fertilizer additions in narrow strips of agricultural fields that border surface

waters and are typically left unmanaged (Figure 1.2). Briefly, the establishment of a continuous vegetation cover brings about changes to the physical properties of the soil, such as increased permeability, which encourages the infiltration of overland flow thereby reducing P loads (Dorioz et al., 2006). Many studies have shown buffers trips to reduce total P delivery and to provide additional benefits such as increased biodiversity and carbon storage (Stutter et al., 2012). These benefits and the ease of legislative provisions validates their popularity (vegetated buffer strips appear in 70% of Europe-wide river basin management plans for the European Union (EU) Water Framework Directive (Royer, 2010)). Legislation such as the General Binding Rules for Agriculture (GBRA, 2008) in Scotland, agri-environment schemes such as Entry Level Stewardship (Defra, 2005) and the aims of charitable organisations such as the Rivers Trusts, currently drive the implementation of buffer strips in the UK. The main future driver is likely to be the Water Framework Directive (WFD) (2000/60/EC)(EC, 2000). Although buffer strips are not compulsory under the directive, for the reasons mentioned earlier, vegetated buffer strips could become a key tool in the effort to achieve this status in years to come and indeed, are already factored into river basin management plans. The final paragraphs in this introduction present the thesis aims and objectives and the rationale behind them.

Figure 1.2. Typical layout and placement of a riparian vegetated buffer strip within the agricultural landscape. In a grazed pasture setting, a fence prevents livestock access to the buffer strips and stream.

Despite incorporation of vegetated buffer strips into agricultural policy and nearly four decades of research into their effectiveness, large uncertainties remain. One of those uncertainties involves how vegetated buffer strips alter the forms of P delivered, as most previous studies have only reported data for total P (Figure 1.3). This is of particular concern especially as dissolved inorganic P would be immediately available for algal uptake and dissolved organic P may also be readily mineralised to phosphate during delivery or by aquatic algae therefore contributing to eutrophication (Boström et al., 1988; Toor et al., 2003; Whitton et al., 1991). In addition, chemical standards for P in surface waters are generally set in terms of dissolved inorganic P. For example, the Water Framework Directive sets a standard of 50 μg L^{-1} DRP in UK low alkalinity rivers (Figure 1.1). Ideally, buffer strips would reduce the delivery of the forms of P that are most accessible and available to aquatic algae.
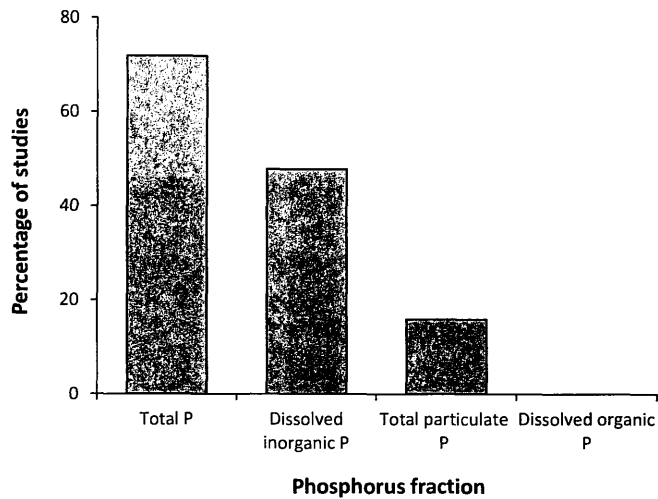
Figure 1.3. Percentage of studies reviewed by Collins et al. (2009) that reported retention of individual phosphorus fractions by vegetated buffer strips.

The first paper in this thesis, 'Phosphorus retention and remobilisation in riparian vegetated buffer strips: a review', presents a literature review focussing on processes that occur within the buffer strip soil that are likely to be important for the retention of dissolved forms of P. The review aimed to develop a conceptual model of vegetated buffer strip functioning in terms of dissolved P, identify key processes within the model that affect DP retention and explore evidence for the controls on these processes. Having drawn on examples from the buffer strip and wider literature, the review brought to light a number of interesting issues. Firstly, the literature shows numerous examples where vegetated buffer strips have increased the delivery of dissolved inorganic P. Secondly, buffer strip soils were found to have a much greater potential for biological solubilisation of P. In the wider P literature, there are also numerous examples where the mobilisation and delivery of dissolved forms of P has been greater from soils with no-tillage compared to ones with tillage (Addiscott and Thomas, 2000; Butler and Haygarth, 2007; McDowell and Sharpley, 2001). These studies attributed this to a build-up of added fertilizer P in the surface of no-tillage soils that leads to the saturation of P sorption sites and therefore increased dissolved P loads. Previous studies

have also suggested that repeated overland flow events and retention of P could saturate P sorption sites in buffer strip soils; however, the literature review found little experimental evidence to support this. Another key feature of a no-tillage soil is the greater quantity of P held in plant and microbial pools, which are often considered as sinks for P in buffer strip soils. However, the processes that plants and microbes use to acquire P and processes associated with the release of P from those pools could also increase soil P solubility therefore posing an increased risk of dissolved P transfer. The literature review also identifies a number of, more specific knowledge gaps related to this:

1. Laboratory scale studies have demonstrated that turnover of microbial biomass phosphorus (P) can increase soil P solubility and leaching therefore increasing the potential for dissolved P transfer to surface waters. However, it is much less clear that the microbial biomass contributes to soil P solubility at larger spatial scales.

2. The majority of studies where buffers strips have reduced loads of dissolved reactive P have attributed retention to the infiltration of overland flow into buffer strip soils. Under soil conditions where little infiltration occurs, buffers strips could increase the transfer of dissolved forms of P due to increased biological P solubilisation in buffer strip soils.

3. It is currently not clear how plant growth and the accompanying acquisition and uptake of P from the soil affect the leaching of dissolved forms of P, or whether this varies between plant species and soil management.

The overall aim of this study was therefore to investigate whether biological solubilisation processes operating in riparian buffer strip soils can increase the risk of dissolved P transfer, and in turn, to understand how better to manage them to minimise this.

The objectives of this study were to:

1. **Determine whether microbial biomass P concentrations influence soil P solubility**

2. **Compare the retention of different P forms by buffer strips during delivery**

3. **Examine the effect of the growth of different plant species in different soils on dissolved P leaching**

These objectives were tailored into specific hypotheses, the testing of which forms the aims of the three experimental papers presented. The first experimental paper in this thesis 'Microbial biomass phosphorus contributions to phosphorus solubility in riparian vegetated buffer strip soils' utilises the variation in organic matter provided by the field-buffer strip situation in an attempt to link organic matter and microbial biomass P concentration to P solubility in buffer strip soils. The second experimental paper 'Retention of phosphorus forms by a narrow vegetated buffer strip' reports measured concentrations and loads of P fractions delivered in runoff from field plots as affected by the presence buffer strips. The third experimental paper 'Plant root induced phosphorus leaching from riparian buffer strip soils: effects of plant species and soil management' presents data from a greenhouse scale experiment that investigated the leaching of P fractions from soil columns packed with two soils of differing management histories sown with three common riparian grass species. The final paper 'Conclusion' returns to the original objectives, presents a conceptual model summarising the findings and discusses the overall scientific and applied implications.

2. Phosphorus retention and remobilisation in riparian vegetated buffer strips: a review

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2.1. Abstract

Diffuse pollution remains a major threat to surface waters, due to eutrophication caused by phosphorus (P) transfer from agricultural land. Riparian vegetated buffer strips are increasingly used to mitigate diffuse P losses from agricultural land, having been shown to reduce total phosphorus (TP) delivery. However, retention of dissolved P (DP) has been lower and in some cases buffer strips have increased delivery to surface waters. The aims of this review were to: 1) develop a conceptual model to enhance the understanding of buffer strip functioning in terms of DP; 2) identify key processes within the model that affect DP retention; and 3) explore evidence for the controls on these processes. We found evidence of a surface layer in buffer strip soils that is enriched in highly soluble P compared to adjacent agricultural land and may be responsible for reported increased DP delivery. Through increased biological activity in buffer strips, plants and microorganisms may assimilate P from particulates retained in the buffer strips and/or native soil P and remobilise this P in a more soluble form. This remobilisation may lead to increased delivery outputs from buffer strips under certain rainfall-runoff conditions. These conclusions are based on a

limited amount of research and a better understanding of biological cycling of P in buffer strip soils is required.

2.2. Introduction

Worldwide, countries must improve water quality to meet increasingly stringent chemical objectives set by governing authorities. Phosphorus (P) remains an important element determining water quality as algal growth in freshwater aquatic systems is partially limited by P (Elser et al., 2007; Vollenweider, 1968). Excess P and subsequent algal growth in surface waters can reduce dissolved oxygen concentrations, increase turbidity and in certain cases produce harmful toxins with secondary effects resulting in water treatment problems and reductions in biodiversity and leisure value of surface waters.

Natural background concentrations of P in soil are insufficient to maintain agricultural production at the current level. To increase agricultural yields, soils are supplemented with P fertilizer often in excess of plant requirements (Holford, 1997). The resulting build-up of P in agricultural soils means that diffuse P transfer from agriculture can contribute large quantities of P to surface water loadings. For example, it was estimated that agriculture contributes 29 and 27 % of surface water P loads in the UK and Denmark respectively (OECD, 2008) . This transfer can be considered in terms of the 'transfer continuum' (Haygarth et al., 2005). This is a four-tier model that incorporates the source, mobilisation, delivery and impact of P transfer to surface waters.

Worldwide catchment scientists are making substantial research efforts into understanding how to reduce P transfer, with a large amount of emphasis on riparian vegetated buffer strips. Buffer strips comprise non-cultivated borders between agricultural lands and surface

waters and provide multiple benefits in terms of water quality protection and biodiversity and are increasingly designed to modify the delivery tier of the phosphorus transfer continuum. Buffer strips retain P as overland flow and shallow subsurface flow passes from the agricultural land and through the buffer strip. Numerous studies have reviewed the literature on retention of P from overland flow by buffer strips (Collins et al., 2009; Dorioz et al., 2006; Hoffmann et al., 2009; Muscutt et al., 1993; Stevens and Quinton, 2009). All of these reviews identified studies where buffer strips increased the delivery of dissolved inorganic P. For example, Hoffmann et al. (2009) recently reviewed monitoring studies of buffer strip retention of P from overland flow. Of the few studies where dissolved inorganic P was measured (n=6), retention of TP ranged from 41 to 95%, whereas retention of dissolved inorganic P ranged from -71 to 95%. The fact that buffer strips in two of the reviewed studies increased the delivery of dissolved inorganic P, suggests that particulate associated P retained in buffer strips and/or native soil P was mobilised within the buffer strip soil and subsequently delivered as dissolved inorganic P. This is a cause for concern as, upon delivery to surface waters, dissolved inorganic P is immediately available for algal uptake. In addition to this water quality objectives for P are set in terms of dissolved inorganic P concentration. For example, the Water Framework Directive sets a standard of 50 μg L^{-1} dissolved inorganic P during base line flow conditions in UK low alkalinity rivers (UKTAG, 2008). If buffer strips are to be considered for large-scale implementation to meet regulatory targets there is a need to improve our understanding of the specific, in-soil, processes that can lead to buffer strips passing on a more bioavailable form of P.

While numerous studies have reviewed the effectiveness of buffer strips in retaining P from overland flow, few have reviewed the studies addressing in-soil processes occurring within the buffer strip soils that are likely to affect dissolved P form retention. Understanding these processes, and how they interact through biogeochemical cycling, will allow the design and

management of buffer strips to enhance dissolved P retention and water quality protection. This review therefore aims to: 1) develop a conceptual model to enhance the understanding of vegetated buffer strip functioning in terms of dissolved P; 2) identify key processes within the model that affect dissolved P retention; and 3) explore evidence for the controls on these processes.

2.3. Conceptual model of vegetated buffer strip functioning

Under normal agricultural management practices P transfer to surface water occurs along a continuum from source, via mobilisation and delivery to impact (Haygarth et al., 2005) (Figure 2.1). 'Source' describes any input of P to soil that creates the potential for an increase in transfer to the wider environment. Before sources of P are delivered, they must be mobilised. 'Mobilisation' describes the initial separation of P molecules from their source via solubilisation or detachment. It operates at the soil profile scale, and involves physical, geochemical and biological processes. 'Delivery' of P from the point of mobilisation to surface waters is complex and dependent on hydrology and may include surface and/or subsurface flow pathways. 'Impacts' relate to an actual change or perturbation in a receiving water body resulting from the P transfers (Haygarth et al., 2005).

Buffer strips function by initially modifying P delivery via retention brought about by physical processes that encourage the infiltration of water containing P and the deposition particulate material containing P (Figure 2.1). 'Retention' is the opposite of mobilisation and therefore also involves physical, geochemical and biological processes. After physical retention, P attached to particles may be retained in biological pools and dissolved may be retained in either geochemical or biological pools by sorption and uptake respectively. Mobilisation of P retained in these pools can then reoccur within the buffer strips soil. This is referred to in the model as 'remobilisation' separating it from mobilisation upslope of the

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buffer strip. Remobilisation may involve geochemical or biological solubilisation processes, for example, P release from plants during senescence. This remobilisation brings about the potential for altered delivery 'outputs' from the buffer strip to surface waters. Thus, rather than being the final sink for P mobilised from field slopes buffer strips actually become a modifying loop in the P transfer continuum, altering the extent, timing and chemical form of P eventually delivered to surface waters. Unless this 'retention – remobilisation loop' is managed, buffers trips will be unable to achieved maximum efficiency with respect to providing a true 'buffer' for P transfers. Therefore, this review explores this set of processes via the following structure (following the layout of Figure 2.1):

i.   Delivery inputs of P to vegetated buffer strips from upslope managed land

ii.   Physical retention of P in vegetated buffer strips

iii. Geochemical retention and remobilisation of P in vegetated buffer strips

iv.   Biological retention and remobilisation of P in vegetated buffer strips

v.   Delivery outputs of P from vegetated buffer strips
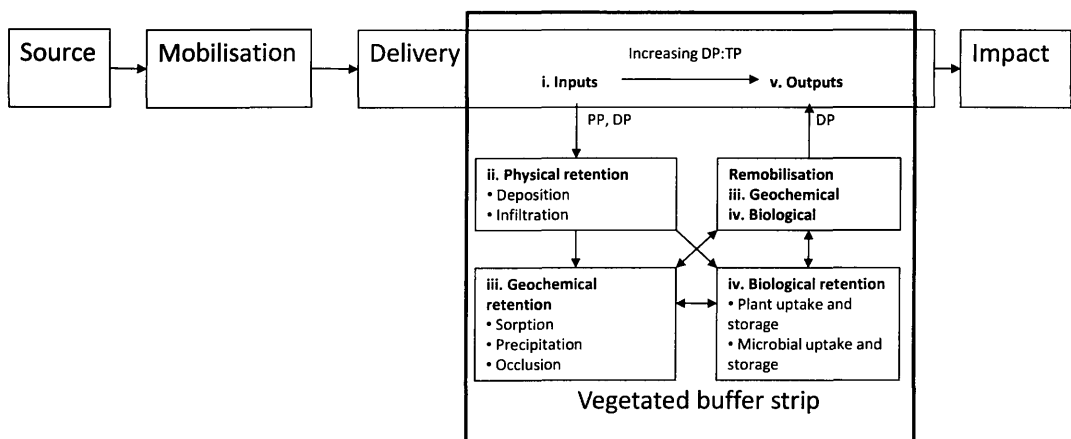
Figure 2.1. Conceptual model of vegetated buffer strip functioning as shown being embedded in the transfer continuum model of Haygarth et al. (2005). Arrows indicate movement of P through the transfer continuum and vegetated buffer strip retention and remobilisation tiers. DP, dissolved phosphorus; PP, particulate phosphorus; TP, total phosphorus.

2.4. Delivery inputs of phosphorus to vegetated buffer strips from upslope managed land

There are many factors affecting P delivery (Beven et al., 2005) and inputs to riparian vegetated buffer strips and we emphasise these here only briefly, concentrating mainly on the forms of P as a key factor in the fate of P entering buffer strips. Phosphorus inputs can be delivered to buffer strips via overland flow or subsurface flows such as interflow, return flow or shallow ground water (Dorioz et al., 2006; Hoffmann et al., 2009; Viaud et al., 2004). However, it is thought that the majority of annual P loss from small catchments occurs during high magnitude rainfall events with overland flow (Haygarth and Jarvis, 1999). We therefore pay particular attention to P inputs via overland flow. Overland flow will contain P attached to soil particles in both organic and inorganic forms (collectively referred to as particulate P or PP) and P dissolved in solution in inorganic and organic forms (collectively referred to as dissolved P, DP) (Haygarth et al., 1998). The operational definition used to distinguish between DP and PP is the total amount of P that can pass through a filter, in most studies with cut-off of 0.45 μm. Some colloidal P will pass through this filter size not and not be truly dissolved in solution (Haygarth and Sharpley, 2000; Haygarth et al., 1997; Heathwaite et al., 2005). The operationally defined distinction between inorganic and organic P is the reactivity with ammonium molybdate as determined by colourimetry. Inorganic forms of P such as inorganic phosphate react with molybdate, however, some inorganic forms such as polyphosphates will not react with molybdate (Turner et al., 2003a). Dissolved reactive P (DRP) is a measure of the minimum amount of P in a sample that is bioavailable and is thought to contain mostly orthophosphate. The dissolved unreactive fraction of P (DUP) in overland flow will contain P in a range of organic combinations including inositol phosphates, nucleic acids, nucleotides, phospholipids and sugar phosphates (Toor et al., 2003; Turner and Haygarth, 2000).

The factors affecting the proportions of these fractions in overland flow may include rainfall intensity, slope, hydrological conditions, fertilizer additions, land use, soil physical characteristics, mobilisation mechanism, and soil P geochemical characteristics (Haygarth and Jarvis, 1999; Kleinman et al., 2002; Nash et al., 2000; Quinton et al., 2001; Uusitalo et al., 2000). This gives rise to a wide variation in the relative proportions of dissolved and particulate and inorganic and organic compounds delivered to buffer strips and will therefore vary spatially and temporally. For example, Hodgkinson and Withers (2007) found that, over a 2 year period, losses of PP in overland flow were lower from grassland (0.16 kg ha^{-1}) compared with arable land (0.22 kg ha^{-1}) within the same catchment. Nash and Murdoch (1997) discovered that DUP in overland flow from grazed pasture with mineral fertilizer application only represented 2-9 % of DP. Whereas, Preedy et al. (2001), found on unfertilized grazed pasture that DUP constituted 29 % of DP in overland flow.

A proportion of PP in overland flow will be inorganic and extractable by methods assumed to extract a 'bioavailable' fraction of P. For example, Uusitalo et al. (2000) measured reactive P extracted by an anion exchange resin from the particulate fraction in 154 overland flow samples. The average amount of reactive extractable P in particulates ranged from 39 to 165 mg kg^{-1} at different sites, depending on soil P status.

2.5. Physical retention of phosphorus in vegetated buffer strips

The physical processes of retention are some of the most thoroughly researched in buffer strip studies. Again, we provide a brief overview. Physical retention is the initial step in the 'retention-remobilisation loop' (Figure 2.1) and will generally be confined to P in overland flow as the surface soil is where these processes occur. Two characteristic features aid physical retention in buffer strips: dense above ground vegetation and a dense root system with increased number of fine roots. Dense above ground vegetation in the buffer strip

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increases hydraulic roughness, decreasing overland flow velocity and the energy available to transport particulates. The combination of these soil and runoff changes leads to the deposition of PP (Dillaha and Inamdar, 1997; Uusi- Kämppä, 1997). Even so, P associated with clay and colloidal sized fractions may not be deposited (Owens et al., 2007; Syversen and Borch, 2005). Denser root systems in buffer strips encourage infiltration during infiltration excess overland flow by increasing the permeability and porosity of the soil (Cooper et al., 1995; Räty et al., 2010b; Zaimes et al., 2008). Infiltration, encouraged by the reduction in flow velocity and the increased soil permeability and porosity mentioned above, increases contact time of DP with soil surfaces and the rhizosphere. Dorioz et al. (2006) suggests that the combination of these processes results in a partial decoupling and separate storage of DP and PP. However, during certain rainfall-runoff conditions, for example, during saturation excess overland flow, no infiltration of DP may occur within the buffer strip.

Karr and Schlosser (1978) quickly identified factors affecting the physical retention of P in buffer strips as width and slope, both prior to water reaching the vegetated area and of the vegetated area and vegetation characteristics. In a recent review paper, Zhang et al. (2010) gave a very detailed account of the effect of these factors on P retention and found that buffer strip width had the greatest impact on retention of P from overland flow. Many studies investigating the factors affecting the physical retention of P in buffers strips have been short-term 'event based' studies that focus on P retention from natural or simulated overland flow at the plot scale with results expressed as a percentage of P retained from overland flow. Physical retention of P generally increases as the width of the buffer strip increases (see examples in Table 2.1), and Collins et al. (2009) provides a more comprehensive review of this. Physical retention of P decreases with increased slopes and resulting flow velocity. Dillaha et al. (1988) used a plot experiment with simulated rainfall events to test the effect of slope (11% and 16%). For all of the experiments the buffer strips

on the 11% and 16% slopes retained 63% and 52% of TP respectively and -20% and -108% of DRP respectively. Physical retention of P also varies depending on vegetation type in the buffer strip (Table 2.2). From the studies reviewed it is not clear which particular plant species enhances physical retention or whether single species or multispecies buffer strips retain more P. Lee et al. (1998) concluded that the single species buffer strip retained more P due to a more uniform distribution of stems. This was contrary to the results of Young et al. (1980) who found that multispecies buffer strips retained more P (Table 2.2.). There is still a need to identify the exact plant traits that allow physical retention processes to be maximised.

In summary, the evidence shows that physical retention mechanisms in buffer strips effectively reduce TP delivery during individual studied events. This is likely to be due to retention of PP, as retention of DP is much lower than for TP in previous studies. The situation for DRP and DUP is uncertain; being considerably less well documented compared to TP. While altering the physical properties of the buffer strip will likely effect DP retention, buffer strips probably remain less effective for DP than PP retention. In some cases, DP delivery has been increased during buffer strip passing, suggesting that processes other than physical ones are likely to be of greater influence on DP.

Table 2.1. Short-term studies investigating phosphorus retention from overland flow by buffer strips of varying widths.

Author	Location	Duration	Buffer strip width	Retention †	
				TP	DRP
			m	%	%
Dillaha et al., 1988	USA	2 days	4.6	57.5	-64
Dillaha et al., 1988	USA	2 days	9.1	68.5	-10.5
Lee et al., 1999	USA	2 hours	3	37.4	34
Lee et al., 1999	USA	2 hours	6	52.3	42.7
Abu-Zreig et al., 2003	Canada	54-101 mins	2	32	-
Abu-Zreig et al., 2003	Canada	54-101 mins	5	54	-
Abu-Zreig et al., 2003	Canada	54-101 mins	10	67	-
Abu-Zreig et al., 2003	Canada	54-101 mins	15	79	-
Syversen, 2005	Norway	2 days	5	78	-
Syversen, 2005	Norway	2 days	10	85.4	-

† DRP, dissolved reactive phosphorus; TP, total phosphorus

Table 2.2. Short-term studies investigating phosphorus retention from overland flow by vegetated buffer strips with varying species composition.

Author	Location	Duration	Vegetation		Retention †	
			Common name	Latin name	TP	DRP
					%	%
Young et al., 1980	USA	1 days	Orchard grass	*Dactylis glomerata*	66	-
Young et al., 1980	USA	1 days	Sorghum and sudan grass	*Sorghum Sp.* and *Sorghum bicolor*	88	-
Lee et al., 1999	USA	2 hours	Switch grass	*Panicum virgatum*	47	42
Lee et al., 1999	USA	2 hours	Bromegrass, timothy and fescue	*Bromus Sp., Phleum pratense* and *Fescuta Sp.*	42	35
Syversen, 2005	Norway	2 days	Unknown	Unknown	84	-
Syversen, 2005	Norway	2 days	Aspen	*Populus tremuloides*	77	-
Syversen, 2005	Norway	2 days	Aspen, mountain ash and birch	*Populus tremuloides, Fraxinus texensis* and *Betula Sp.*	98	-
Abu-Zreig et al., 2003	Canada	54-101 mins	Perennial ryegrass	*Lolium perenne*	65	-
Abu-Zreig et al., 2003	Canada	54-101 mins	Red fescue and birdsfoot trefoil	*Festuca rubra* and *Lotus corniculatus*	54	-
Abu-Zreig et al., 2003	Canada	54-101 mins	Native riparian vegetation	Unkown	68	-

† DRP, dissolved reactive phosphorus; TP, total phosphorus

2.6. Geochemical retention and remobilisation of phosphorus in vegetated buffer strips

The geochemical retention of P in buffer strip soils is probably confined to DP as PP is already sorbed to sediments or held in high molecular weight organic combinations that are deposited on the soil surface. After infiltration during infiltration excess overland flow, DP percolates down through the soil profile where it may be sorbed to soil constituents (Figure 2.1). Hoffmann et al. (2009) describe in detail the sorption/desorption and

precipitation/dissolution processes that are relevant to geochemical retention of P in buffer strip soils. Here we are mainly concerned with the different fractions of P in buffer strip soils, the equilibrium dynamics that govern sorption and desorption reactions and the remobilisation of P from these fractions.

Concentrations of TP in the surface soils of buffer strips are generally lower than concentrations in adjacent agricultural land (Aye et al., 2006; Owens et al., 2007; Zaimes et al., 2008). Owens et al. (2007) suggested that this is because buffer strips trap coarse particulates that have a lower TP concentration than the bulk agricultural soil from which they were derived. The determination of labile P fractions in buffer strip soils tends to be carried out by extraction with $NaHCO_3$ (Olsen P), although other extractants are also used (Table 2.3). The results of these extractions seem to indicate very variable differences in labile P between buffer strips and neighbouring agricultural surface soils (Table 2.3) and it is difficult to draw any conclusions from this (Abu-Zreig et al., 2003; Stutter et al., 2009; Young-Mathews et al., 2010).

The highly soluble P fraction in soil is typically extracted with deionised water or with a weak salt ($CaCl_2$ or NaCl) solution. The majority of studies reviewed found that highly soluble P mean concentration was higher in buffer strip surface soils relative to adjacent agricultural soils (Table 2.4). Stutter et al. (2009) showed highly soluble P concentrations to be significantly ($p < 0.05$) higher in buffer strip soils relative to upslope arable soils. Aye et al. (2006) found that highly soluble P declined rapidly with depth from 0.17 mg L^{-1} at 0-2.5 cm to 0.04 and 0.03 mg L^{-1} at depths of 2.5-7.5 and 7.5-15 cm respectively, suggesting the increased risk of DP leaching is confined to surface soil horizons. Increased highly soluble P in buffer strip surface soils suggests that buffer strips present a higher risk of DP leaching than adjacent agricultural land as this fraction has been shown to be strongly correlated to P

concentration in overland and subsurface flow (McDowell and Sharpley, 2001; Pote et al., 1996).

Table 2.3. Labile phosphorus concentrations extracted from vegetated buffer strip and adjacent agricultural soils.

Author	Location	Buffer strip age	Sample depth	Method	Units †	Buffer strip soil P	Field soil P
Aye et al., 2006	New Zealand	4-5 yr	0-15 cm	Olsen P	mg kg^{-1}	36	48
Aye et al., 2006	New Zealand	4-5 yr	0-15 cm	Olsen P	mg kg^{-1}	58	48
Aye et al., 2006	New Zealand	4-5 yr	0-15 cm	Olsen P	mg kg^{-1}	51	76
Cooper et al., 1995	New Zealand	15 yr	0-5 cm	Olsen P	mg kg^{-1}	49.2	16
Schroeder and Kovar, 2008	USA	13 yr	0-5 cm	Bray P-1	mg kg^{-1}	45.9	81.2
Stutter et al., 2009	UK	3 and 8 yr	0-6 cm	Olsen P	mg kg^{-1}	27.5	27.9
Stutter et al., 2009	UK	3 and 8 yr	0-6 cm	Fe hydroxide impregnated paper strip P	mg kg^{-1}	34.3	17
Uusi-kämppä., 2005	Finland	8 yr	0-2 cm	Olsen P	mg l^{-1}	51	40
Uusi-kämppä., 2005	Finland	8 yr	0-2 cm	Acetate and acetic acid extractable P	mg kg^{-1}	14	7.5
Young-Matthews et al., 2010	USA	Unknown	0-15 cm	Olsen P	mg kg^{-1}	22.3	14.6

† Units: mg l^{-1} of extractant or mg kg^{-1} of soil

Table 2.4. Highly soluble reactive phosphorus concentrations extracted from vegetated buffer strip and adjacent agricultural soils.

Author	Location	Buffer strip age	Sample depth	Method	Soil: solution	Units †	Buffer strip soil P	Field soil P
Aye et al., 2006	New Zealand	4-5 yr	0-15 cm	0.01 M CaCl$_2$	1: 5	mg l^{-1}	0.19	0.14
Aye et al., 2006	New Zealand	4-5 yr	0-15 cm	0.01 M CaCl$_2$	1: 5	mg l^{-1}	0.19	0.12
Aye et al., 2006	New Zealand	4-5 yr	0-15 cm	0.01 M CaCl$_2$	1: 5	mg l^{-1}	0.14	0.16
Cooper et al., 1995	New Zealand	15 yr	0-5 cm	Deionised water	1:10	mg kg^{-1}	2.09	1.27
Stutter et al., 2009	UK	3 and 8 yr	0-6 cm	0.01 M CaCl$_2$	1: 3	mg l^{-1}	0.21	0.07

† Units: mg l^{-1} of extractant or mg kg^{-1} of soil

Sorption/desorption processes are governed by the concentration of P in solution which controls the amounts of sorbed P. The point where sorption equals desorption is known as the equilibrium phosphate concentration (EPC_0). A number of studies have found the EPC_0 in buffer strip surface soils to be increased relative to agricultural arable land (Aye et al., 2006; Cooper et al., 1995; Schroeder and Kovar, 2008; Stutter et al., 2009). Schroeder and Kovar (2008) found that EPC_0 declined rapidly from 0.5 mg kg^{-1} at 0-5 cm to 0.13 to 0.1 mg kg^{-1} at depths of 5-10 and 10-15 cm, respectively. This suggests that a change in soil conditions or an increase in the contents of soil constituents that compete with P for sorption sites has led to altered sorption of P in buffer strip surface soils. Stutter et al. (2009) found that NaCl extractable organic carbon (C) was higher in buffer strip than arable surface soils and, indeed, such fulvic acids may compete with P for similar sorption sites (Guppy et al., 2005a; Guppy et al., 2005b). This increase in EPC_0 is likely to be a key indicator of sorption processes affecting solution P concentration at the soil surface.

Vidon et al. (2010) suggested that direct desorption of P from sediments deposited in the buffer strip could be a significant source or 'hot spot' for DP leaching. However, Stutter et al. (2009) mixed sediments with their parent field soils in different proportions and found that the EPC_0 of the resulting mixtures decreased with an increasing percentage of sediment. They concluded that PP entering buffer strips was strongly sorbed and unlikely to be leached without further biological processing.

After infiltration, sorption and retention in geochemical pools, there is also potential for remobilisation of DP. Because Fe is so important for P sorption and geochemical retention in buffer strips, reductive dissolution of Fe(III) following a shift to an anaerobic metabolism could be an important remobilisation mechanism given the right environmental conditions and hydrological setting of the buffer strip. Young and Briggs (2008) found a weak negative

correlation between the depth of the water table from the soil surface and DRP concentration in buffer strip soil solutions at 50 cm depth ($r=-0.47$, $p=0.06$) suggesting remobilisation of P in the lower soil horizons by reductive dissolution of Fe(III).

It has been suggested that, after repeated overland flow events and DP retention in buffer strips, soil sorption sites could become saturated with P resulting in conditions favourable for the release of DRP. In such a case, saturation of the soil with DRP retained from overland and subsequent remobilisation would reduce the apparent effectiveness of buffer strips at retaining DRP rather than resulting in an overall increase in delivery over the long-term. Young and Briggs (2008) studied some chemical properties of field and buffer strip soils at 16 locations spread between 2 different sites. They found that the percentage saturation of poorly crystalline Fe and Al oxides by P was lower in the buffer strip soils than in the neighbouring arable soils at most locations ($n=13$). This is further confirmed by the work of Stutter et al. (2009) who found little difference in saturation of poorly crystalline Fe and Al oxides by P between buffer strip soils and upslope agricultural land. This suggests that, in these cases, the functioning of buffer strips as a sink for P from overland flow has not led to saturation of the soil with P.

In summary, buffer strip soils do not seem to become saturated with P but still show elevated P solubility and EPC_0 values in surface soils. The increased highly soluble P represents an increased risk of DP leaching from the surface layer, delivered via overland flow passing through buffer strips during saturated conditions. Any DP percolating vertically down the soil profile during infiltration of excess overland flow is more likely to be sorbed to soil surfaces in subsoil with increased sorption (manifested in lower EPC_0). Here, there is potential for remobilisation by Fe(III) reduction which will reduce the effectiveness of the buffer strip at retaining P in geochemical pools. However, this mechanism is unlikely to

contribute to increases in DP delivery and the reported highly soluble P concentrations that are elevated solely in the surface layer.

2.7. Biological retention and remobilisation of phosphorus in vegetated buffer strips

Phosphorus is an essential macronutrient for both plants and microorganisms and is necessary for an array of different functions e.g. as a structural element in nucleic acids and phospholipids (Cole et al., 1977; Schachtman et al., 1998; Turner et al., 2001). Plants and microorganisms will therefore represent important pools for the retention of P in buffer strips (Figure 2.1). Here, we refer to retention as the uptake and storage of P within plants and microorganisms and remobilisation as the release of P during death.

Despite the abundance of P forms in most soils, plants and microorganisms almost exclusively derive their P requirement from phosphate anions contained within the soil solution (Richardson, 2001). Because soil solution P concentrations are often low due to sorption, plants and microorganisms may also release exudates to solubilise P from soil surfaces and enzymes to liberate P anions from the soil organic P stock (Richardson et al., 2005; Rodríguez and Fraga, 1999). Both inorganic and organic forms of native soil P, retained DP and PP and P delivered to the buffer strip via shallow subsurface flow will all constitute sources of P to plants and microbes (Figure 2.1). The acquisition from these sources by exudates and enzymes could represent a remobilisation of P with consequences for P leaching, yet, it is often assumed that the accompanying uptake would reduce the leaching of P from the rhizosphere.

4.7.1. Phosphorus retention in and remobilisation from plant pools

Dosskey et al. (2010) reviewed the role of plants in buffer strips and noted that plant stand age, plant species, P inputs and season will all influence P retention. In general, nutrient incorporation into biomass will increase rapidly in early succession, will reach a maximum, and then slowly decline to zero as a steady state community is approached (Vitousek and Reiners, 1975). Different plant species will accumulate P at different rates and in different amounts. Kelly et al. (2007) found that switchgrass (*Panicum virgatum*) and alfalfa (*Medicago sativa*) stands reached this steady state after 4 years growth and ceased to accumulate P, whereas cotton-tree (*Hibiscus tiliaceus*) continued to accumulate P. For some common herbaceous buffer strip species, TP concentrations in tissue increase in the order: timothy (*Phleum pratense*), common bent (*Agrostis castellana*), meadow fescue (*Festuca pratensis*), white clover (*Trifolium*), milfoil (*Achillea millefolium*) and dandelion (*Taraxacum officinale*) (Räty et al., 2010a). Soil P status in the buffer strip will also affect the magnitude of P retention by plants. Fortier et al. (2010) found that plant TP in poplar (*Populus Sp.*) aboveground biomass was positively correlated with P supply rate to roots ($R^2=0.21$, $p<0.001$). Of the above ground plant parts, this relationship was strongest for TP concentration in leaves ($R^2=0.22$, $p<0.001$). On a seasonal basis, uptake and plant TP concentration will be highest during the growing season and lowest when plants are dormant during winter. Kelly et al. (2007) showed how plant TP in buffer strips sown with smooth bromegrass (*Bromus inermis*) increased from 1.7 g m^{-2} in May to 4.1 g m^{-2} in August and then declined to 2.6 g m^{-2} in September with 1.5 g m^{-2} therefore lost during autumn.

This loss of P from plants during autumn occurs because light conditions no longer favour photosynthesis. Whole plants, roots or leafs die off or 'senesce' and release a proportion of the total P either as immediately soluble DP or as more stable forms contained within decaying leaf and root tissues (Dosskey et al., 2010). A number of factors affect the

proportion of P in senescing plant material released as DP. Plants species that display greater total P concentrations will release more DP (McDowell et al., 2011). Plants subject to higher soil P levels and exhibit higher tissue P concentrations therefore have the potential to release more DP during senescence. Kröger et al. (2007) found that rice cutgrass (*Leersia oryzoides*) subjected to high P supply had significantly higher plant TP concentration and remobilised more DRP during senescence than those subject to low P supply ($p<0.001$). The amount of DP released is also increased by freezing and thawing, drying and rewetting cycles (Roberson et al., 2007). The senesced plant material containing P in more stable forms will become part of the native soil P and will require decomposition by microbes before remobilisation or further retention.

The seasonal aspect of retention in and remobilisation from plant pools has been attributed to seasonal variation in DRP retention in buffer strips. Uusi-Kämppä (2005) monitored DRP retention in an unmanaged grass buffer strip over a ten year period. Over the course of the experiment, the mean concentration was higher in spring in the unmanaged buffer strip plots (0.12-0.28 mg l^{-1}) compared to the plots without a buffer strip (0.06-0.14 mg l^{-1}). She attributed this to freezing of senesced vegetation over winter and release of DRP during spring snowmelt. Such a situation is a clear example of how biological solubilisation processes in buffer strips can alter the timing, extent and forms of P delivered.

Plant communities play an important role in the retention of P in buffer strips. Even in mature communities where net uptake is near zero, plants do still provide a sink for P by storage in plant tissues. Plants can also provide additional P storage when P inputs to the buffer strip are high but this is also likely to result in increased remobilisation during whole plant, root or leaf senescence. Because of a combination of P solubilising exudates and remobilisation during senescence, plants may play a role in converting PP to more soluble

forms, which may be released during spring and autumn and contribute to increased soluble P levels in buffer strip soils.

4.7.2. Phosphorus retention in and remobilisation from microbial pools

The soil microbial biomass can represent significant pools of P in grassland ecosystems (Cole et al., 1977; Halm et al., 1972) and also regulate the turnover of organic P in soils (Oberson and Joner, 2005). Despite this, studies have paid very little attention to the microbial biomass in regarding P retention, mobilisation and cycling in buffer strip soils. In a similar way to plants, retention in and remobilisation from the microbial biomass will exhibit changes caused by succession and seasonal variation in environmental conditions.

Organic matter and organic C provide energy for microbial growth and C for the formation of cell structures and are therefore essential soil constituents for the microbial biomass (Coyne, 1999). Carbon, which is often low in arable soils due to tillage, often limits the soil microbial biomass in arable systems. Organic matter and organic C accumulate in the surface soil as tillage ceases and downslope arable land becomes buffer strips (Marquez et al., 1998; Potthoff et al., 2005). As a result total fungi, total bacteria, microbial biomass C, microbial biomass phosphorus (MBP), soil respiration and phosphomonoesterase enzyme activity have all been shown to be greater in buffer strip soils compared to adjacent agricultural land (Cooper et al., 1995; Krutz et al., 2006; Marquez et al., 1998; Staddon et al., 2001; Stutter et al., 2009; Tufekcioglu et al., 1998; Tufekcioglu et al., 2001). Cooper et al. (1995) measured microbial biomass C and found it to be greater in buffer strip soils (1900 mg kg^{-1}) compared to adjacent agricultural soils (1081 mg kg^{-1}). As C:P ratios in the microbial biomass are relatively constrained (Cleveland and Liptzin, 2007; Turner et al., 2001), it is likely that MBP was also greater. Stutter et al., (2009) measured MBP directly and found it was greater in the surface soil of an 8 year old buffer strip (108 µg g^{-1}) than in a 3 year old buffer strip (43 µg g^{-1})

and upslope arable land (33 µg g^{-1}). These were greater concentrations than those of Olsen P (extracted on dry soil) measured in the same study. This suggests that the microbial biomass is an important pool for P retention and may increase with organic matter and C as buffer strips are established on agricultural soils.

Similarly to plants, this retained P will also be remobilised. Microbial turnover of P creates fractions of soil solution P due to microbial death and release of P. Microbial activity determines the turnover of P through the microbial biomass at stable respiration rates and the size of the associated fractions of organic and inorganic P in solution (Lee et al., 1990; Seeling and Zasoski, 1993). Studies have inferred microbial activities in buffer strip soils from measurements of soil respiration (Tufekcioglu et al., 1998; Tufekcioglu et al., 2001). Tufekcioglu et al. (1998) found that soils under buffer strips had significantly greater ($p<0.05$) respiration rates than under adjacent arable land. Greater microbial P and microbial activity in buffer strip soils suggests that the soil solution pools of P associated with microbial turnover are greater. Yet, it is still not clear whether the microbial biomass contributes to P solubility at spatial scales beyond the laboratory and under natural field conditions.

Seasonal fluctuations in the size of the microbial biomass in grassland soils are positively related to soil moisture (Chen et al., 2003). An increase in the size of the microbial biomass suggests retention of P and a reduction in size suggests remobilisation of P. Remobilisation from microbial pools in buffer strips will increase during drier months and retention will increase during wetter months giving a seasonal aspect. Shorter-term fluctuations in soil moisture and MBP due to rapid drying and wetting cycles also enhance microbial turnover and release of DP. Rapid soil drying leads to microbial death and the following rewetting leads to cell lysis and release of intracellular P (Bottner, 1985; Turner et al., 2003c). The greater the initial MBP the greater the amount of P that will be released during drying and

rewetting cycles (R^2=0.58) (Turner and Haygarth, 2001). As the microbial biomass and the P held within it is greater in buffer strip soils relative to adjacent agricultural soils, more P is expected to be released in buffer strip soils because of seasonal and shorter-term changes in soil moisture. Other factors such as the rate of rewetting will also influence the amount of P released (Blackwell et al., 2009) as will soil freezing and thawing (Blackwell et al., 2010).

In summary, the microbial biomass holds large quantities of P in buffer strip soils that they acquire from a range of sources. The extent of this retention will vary seasonally and may increase as C increases in buffer strip soils due to no tillage. Phosphorus also has the potential to be remobilised from this pool. The extent of remobilisation will depend on soil C contents, and seasonal and short-term fluctuations in soil moisture. The magnitude of this remobilisation will potentially be greater in buffer strips than in adjacent agricultural soils, as MBP has been found to be greater in buffer strip soils. Whilst microbial activity may benefit pesticide degradation and denitrification processes in buffer strips, the effect on P retention may be negative due to increased turnover and subsequent remobilisation of P during microbial death. More research is needed to determine whether microbial turnover is responsible for elevated highly soluble P concentrations in buffer strip surface soils.

2.8. Delivery outputs of phosphorus from vegetated buffer strips

Due to retention and remobilisation, vegetated buffer strips have the potential to alter the forms of P that are delivered to surface waters and therefore act as a delivery modifier. In all monitoring studies reviewed, buffer strips reduced TP delivery to surface waters. This reduction is attributed to the retention of PP by physical retention processes. In the majority of cases buffer strips also reduced DP delivery but to a lesser extent (Hoffmann et al., 2009). Therefore, the ratio of DP to TP in delivery inputs to buffer strips is lower than delivery

outputs from buffer strips. We identified several additional cases in the literature where buffer strips increased DP delivery by overland flow over the medium-term (Daniels and Gilliam, 1996; Hodgkinson and Withers, 2007; Newbold et al., 2010; Nieminen et al., 2005). In these cases, this ratio is likely to be even more marked. Most of the monitoring studies reviewed were conducted at the plot scale. McKergow et al. (2003) studied stream water P concentrations in a small catchment 6 years before and 4 years after buffer strip implementation. After implementation, the ratio of DRP to TP in stream water changed from 0.5 to 0.75. In addition, the median DRP as a mean concentration during events increased by 60% and the raw median concentration increased from 0.18 to 0.35 mg l^{-1}. In this example, P delivery was clearly modified due to buffer strip implementation and completion of the retention-remobilisation loop with a subsequent impact on the forms of P in surface water. Because of a lack of information on organic P retention in buffer strips, it is not clear how they modify the delivery of organic DUP forms.

2.9. Discussion

Retention of DP from overland flow by buffer strips is generally lower than retention of PP. There are also numerous examples in the literature where the implementation of buffer strips has led to increased DRP delivery. Even when the physical properties of the buffer strips are altered to increase physical retention, they can still increase DRP delivery and therefore other factors must influence retention. Geochemical remobilisation of DP retained in buffer strips by soil saturation and Fe(III) reduction has the potential to reduce apparent buffer strip effectiveness. However, to increase DRP delivery, P other than retained DP must be remobilised within the buffer strips. Remobilisation of P from particulates retained in the buffer strip and/or native soil P (accumulated in the soil through fertilizer addition prior to buffer strip establishment) could be responsible for reported increases in DP delivery. The

latter may also be highly relevant, as some studies have found an increase in DP leaching following conversion of arable land to grassland (Meissner et al., 1998; Ylaranta et al., 1996).

In the studies by Stutter et al. (2009) and Zaimes et al. (2008) MBP and soil TP concentrations were around 0.1 mg kg^{-1} and 0.5 mg kg^{-1} respectively in buffer strip soils. If we assume a soil bulk density of 1 g cm^{-3} then for a 5 cm soil layer these pools are 5 g m^{-2} for MBP and 25 g m^{-2} for TP. Kelly et al. (2007) found that plant TP in smooth bromegrass was around 4 g m^{-2}. Because microbial P is extracted and measured as part of total P, MBP and plant TP together could constitute up to an equivalent of 45% of buffer strip P. This highlights the importance of biological pools in retention and remobilisation especially when a considerable amount of total soil P may be refractory or immobile. Plants and microorganisms have the potential to assimilate P from particulates that have been retained by physical processes and native soil P that was otherwise refractory or immobile. Remobilisation of this P during microbial and plant death has the potential to increase soil P solubility resulting in reported increases in surface soil soluble P concentrations in buffer strips. Still, these observations are made on a limited amount of evidence and more research is required into the role of different remobilisation mechanisms in enhancing soil solution P concentrations.

Vegetated buffer strips that possess a surface soil layer enriched in soil solution P pose an increased risk of DP leaching and are likely to be responsible for reported increases in DP delivery. How this remobilised P is delivered to surface waters would depend on the hydrological conditions of the buffer strip. During saturation excess overland flow or return flow within the buffer strip, when little infiltration exists, considerable amounts of remobilised P could be delivered by overland flow. During infiltration excess overland flow in upslope managed land, infiltration within the buffer strip may be great with remobilised P percolating vertically down the soil profile. Infiltrated DP is more likely to be sorbed to soil

surfaces in subsoil with increased sorption (manifested in lower EPC_0). Here, there is potential for remobilisation by Fe(III) reduction with subsequent delivery via interflows or shallow groundwater. It is possible that studies measuring only P retention from overland flow could have overlooked this delivery pathway.

The majority of studies focussing on the retention of P in buffer strips from overland flow only measure TP. As a result there is a lack of information on the retention of DRP and even more so, on the retention of DUP. This is important because phosphatase enzymes can be transported with dissolved organic P in overland and subsurface flow with the potential to liberate the associated phosphate anions (Toor et al., 2003)). Recent studies have shown that aquatic algae also possess these enzymes (Cotner and Wetzel, 1992). In addition, most studies have been short to medium-term and have been compiled into reviews that may not give a true picture of the long-term P retention. A combination of a lack of long-term studies and information on the retention of different P forms confound any attempt to identify seasonal patterns caused by retention and subsequent remobilisation.

Riparian vegetated buffer strips represent a unique situation where P is transferred from an agricultural system of relatively low biological activity to a system of high biological activity. Mobilisation processes will differ between these systems with mobilisation in agricultural land dominated by physical processes such as particle entrainment in overland flow and remobilisation in buffer strips dominated by biological and geochemical solubility processes. The difference in mobilisation mechanisms between the systems can, in certain situations, result in increased DP delivery outputs. Therefore, rather than being the final sink for P mobilised from field slopes buffer strips actually become a modifying loop in the P transfer continuum, altering the extent, timing and chemical form of P eventually delivered. Given

the multiple benefits that buffer strips provide this review is not intended as a case against implementation but as a case for management.

In order to improve understanding of buffer strip functioning in terms of DP retention, research should be carried out in the following areas:

- The role of plant growth and the accompanying P acquisition in promoting or reducing P leaching
- Microbial contributions to P solubility at spatial scales beyond the laboratory
- The effectiveness of buffer strips at retaining multiple P forms during saturated soil conditions
- The long-term retention of DP forms in buffer strips therefore capturing changes in soil properties that occur over larger timescales e.g. organic matter build up
- Catchment scale impacts of buffer strips on P forms in surface waters

A greater understanding in these areas will facilitate the development of management techniques that enhance DP retention and water quality protection by tightening the 'retention-remobilisation loop'.

2.10. Acknowledgements

3. Microbial biomass phosphorus contributions to phosphorus solubility in riparian vegetated buffer strip soils

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3.1. Abstract

This study tests the hypothesis that microbial biomass phosphorus (P) contributes to P solubility in riparian buffer strip soils. In thirty-six soils collected from buffer strips within three UK soil Associations, water extractable inorganic P solubility was most strongly related to $NaHCO_3$ extractable inorganic P. However, within individual soil Associations where soil pedological properties and management were similar, water extractable inorganic P was most strongly related to microbial biomass P. These results highlight the difficulty in predicting dissolved P leaching risk based on agronomic soil P tests alone and the dissolved P leaching risk presented by having soils high in organic matter and microbial biomass P in close proximity to surface waters.

3.2. Introduction

Phosphorus (P) transfer from agricultural land contributes to the eutrophication of surface waters. Much research emphasis has been placed on the role of geochemical desorption of P in increasing the risk of dissolved P transfer. However, laboratory scale studies have demonstrated that turnover of microbial biomass P can increase soil P solubility and leaching therefore increasing the potential for dissolved P transfer to surface waters (Blackwell et al., 2013; Seeling and Zasoski, 1993). It is much less clear that the microbial biomass contributes to soil P solubility at larger spatial scales because under natural field conditions many additional factors affect P solubility, for example geochemical solubility controls. Riparian vegetated buffer strips present an opportunity to study P solubility in soils of increased organic matter contents but otherwise similar pedological properties compared with adjacent upslope arable field soils. Because microbial concentrations of P have been shown to be strongly correlated with soil organic matter (Joergensen et al., 1995), studying otherwise similar soils but with varying concentrations of organic matter may give insight into the contribution of microbial biomass P to P solubility. The aim of this study was to test the hypothesis that microbial biomass P contributes to P solubility in riparian buffer strip soils.

3.3. Material and methods

Soil samples were collected from existing buffer strips established on three UK soil Associations of differing characteristics within the national Demonstration Test Catchments (Figure 3.1). The buffer strips were established on arable land under either Countryside Stewardship or Environmental Stewardship agri-environment schemes (Table 3.1). Appendix 1 provides additional details on site location and characteristics. At four buffer strips on each soil, 5 soil cores (0-7 cm depth) were collected and bulked from positions within the upslope

arable field and 2 m and 4 m within the buffer strip from the upslope edge during January

2011 (Figure 3.2).
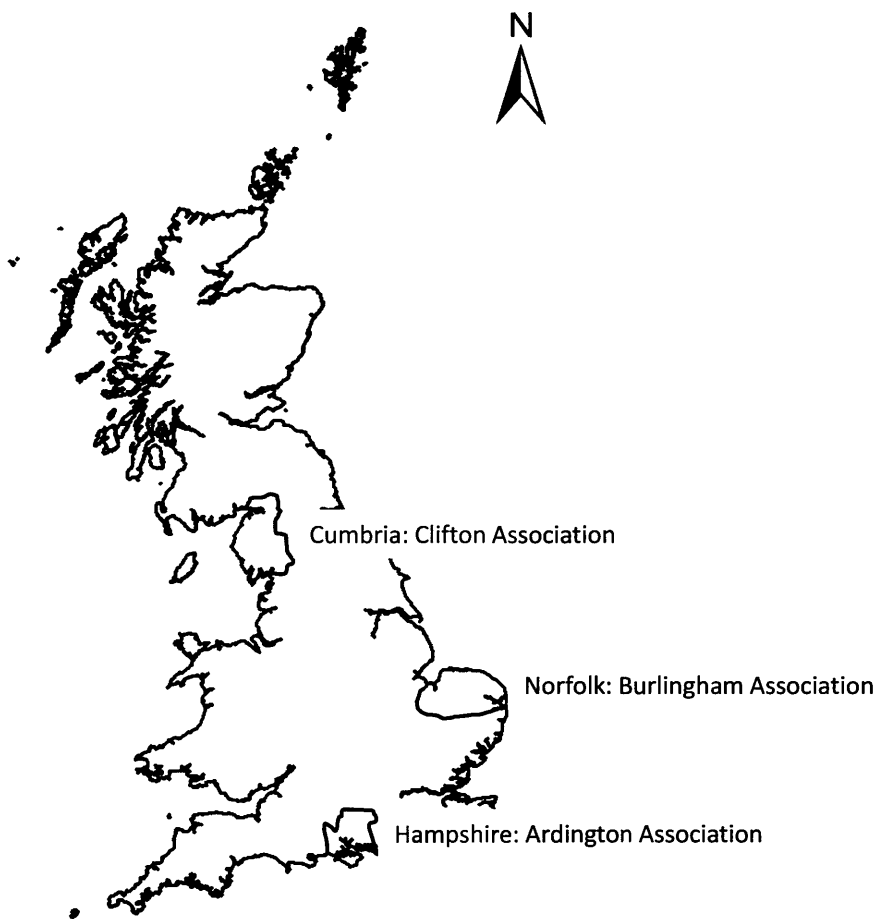
Figure 3.1. Location of the three soil Associations within England, Scotland and Wales.
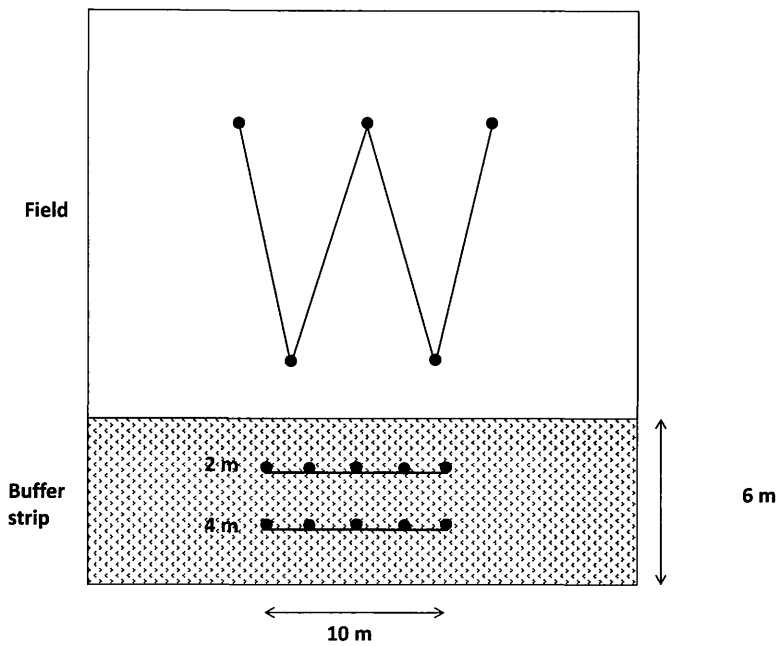
Figure 3.2. Soil collection protocol at each of the four buffer strip sites within each soil association. Black dots indicate points for collection of soil cores, which were then bulked.

With the exception of soil total P, sample analyses were carried out in triplicate on field moist soils that were sieved to <2 mm. Soil samples were assayed for basal soil respiration to infer microbial activity and glucose substrate induced soil respiration to approximate microbial biomass size (Campbell et al., 2003). Microbial biomass P was determined by a chloroform fumigation and extraction method to quantify concentrations of P held within the soil microbial biomass (Brookes et al., 1982). Total soil P was measured using an Accuris inductively coupled plasma optical emission spectrometer (ARL/Fisons, Eclubens, Switzerland) after aqua regia acid digestion of air dried soils that were sieved to <2 mm. An agronomic soil test, NaHCO$_3$ extractable inorganic P, originally designed to estimate plant available P but commonly used for determining P leaching risk, was conducted on samples according to the methods of Olsen and Sommers (1982). Phosphorus solubility was determined by extracting 5 g (dry weight equivalent) of soil with 25 ml of deionised water and shaking end-over-end for 1 hour before filtration through a 0.45 μm membrane. The concentrations of total P in potassium persulphate digested filtrates (Rowland and Haygarth,

1997) and the concentrations of inorganic P in undigested filtrates were determined by ammonium molybdate colourimetry (Murphy and Riley, 1962). Organic P concentrations in the water extracts were calculated as the difference between inorganic P and total P concentration.

The variance of transformed data was analysed by linear modelling to determine significant differences between group means and significant relationships between P solubility and independent variables individually or in combination (R statistical software version 2.14.1). Sample populations were analysed on the basis of a 'position' factor indicating whether samples were from the arable field or positions within the buffer strip and a 'soil' factor indicating significance between different soil Associations.

3.4. Results

Table 3.2 presents mean concentrations of determinants within groups and significant differences in between them. Organic matter and microbial biomass P concentrations were related (R^2=0.80, $p \leq 0.001$) and means were higher ($p<0.05$) in the 2 m and 4 m position groups compared with the field group (Table 3.2). Mean concentration of water extractable inorganic P was significantly ($p<0.05$) higher in the 2 m position group compared to the field group and was increased in the 4 m group (Table 3.2). In the data as a whole, incorporating variation in soil pedological properties and management caused by the soil factor, water extractable inorganic P concentration was most strongly related to $NaHCO_3$ extractable inorganic P (R^2=0.58, $p \leq 0.001$). Within individual position groups, the slopes of this relationship were greater in the two buffer strip position groups compared to the field group (Figure 3.3) which confirmed that other factors were contributing to P solubility within the buffer strip soils. Inclusion of microbial biomass P and water extractable organic P in the statistical model increased R^2 to 0.65. The variation caused by the soil factor was removed by

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investigating relationships within individual soil groups where water extractable inorganic P was found to be most strongly related to microbial biomass P (Figure 3.3). Therefore, by incorporating soil as a factor in the statistical model for the data as a whole, microbial biomass P was a significant (p=0.01) factor determining variation in water extractable inorganic P.

Table 3.1. Description of the location, local climate, underlying geology and vegetation of the three study soils (Collins et al., 2012; Soil survey of England and Wales, 1983).

Soil Association	County, river catchment	Average annual rainfall (mm)	Geology	Soil Description	Percentage sand, silt and clay	Field crop	Riparian vegetation characteristics
Ardington	Hampshire, Avon	749 (Boscombe down)	Cretaceous; glauconitic sand, loam & clay.	Deep, well drained, sandy silt loamy glauconitic soils	32, 57, 11	Wheat, fodder beans, winter barley and oats	Tall vegetation with moderate % cover of perennial forbs, low perennial flower numbers and low grass cover
Clifton	Cumbria, Eden	947 (Penrith)	Reddish till	Slowly permeable, seasonally waterlogged, reddish sandy silt loamy soils	25, 58, 17	Oats, spring barley, oil seed rape and wheat	Species rich, dense vegetation with high % cover of perennial forbs and high perennial flower numbers and moderate grass cover
Burlingham	Norfolk, Wensum	653 (Marham)	Chalky till and glaciofluvial drift	Deep, slowly permeable, seasonally slightly waterlogged, sandy silt loamy soils	28, 58, 14	Spring barley, oil seed rape and wheat	Short vegetation with moderate % cover of perennial forbs, moderate perennial flower numbers and moderate grass cover

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Table 3.2. Means and standard errors of determinants measured within soil and position factor groups with overall factor significance.

	Soil			Position			Overall significance	
	Ardington (n=12)	Clifton (n=12)	Burlingham (n=12)	Field (n=12)	2 m (n=12)	4 m (n=12)	Soil	Position
pH	5.97^a	5.89^{ab}	5.46^a	5.88	5.7	5.61	p=0.009	p=0.759
Soil moisture (g kg^{-1})	308 ± 14^a	278 ± 16^{ab}	238 ± 30^b	230 ± 18^a	289 ± 24^{ab}	304 ± 20^b	p=0.011	p=0.019
Organic matter (g kg^{-1})	55 ± 4	66 ± 5	67 ± 15	41 ± 4^a	73 ± 10^b	75 ± 9^b	p=0.338	p≤0.001
Basal soil respiration (µg C g^{-1} hour^{-1})	0.32 ± 0.05	0.27 ± 0.03	0.40 ± 0.07	0.20 ± 0.03^a	0.35 ± 0.06^b	0.43 ± 0.05^b	p=0.199	p=0.002
Glucose SIR† (µg C g^{-1} hour^{-1})	1.55 ± 0.36	1.53 ± 0.34	1.27 ± 0.35	0.27 ± 0.09^a	1.35 ± 0.21^b	2.73 ± 0.21^c	p=0.174	p≤0.001
Microbial biomass P (mg P kg^{-1})	50.6 ± 7.8	51.4 ± 7.9	64.2 ± 20.0	23.6 ± 2.4^a	73.8 ± 16.1^b	68.7 ± 11.5^b	p=0.857	p≤0.001
Total P (mg P kg^{-1})	683 ± 83^{ab}	806 ± 89^a	550 ± 31^b	559 ± 73	730 ± 77	751 ± 74	p=0.048	p=0.119
NaHCO$_3$ extractable inorganic P (mg P kg^{-1})	54.4 ± 10.7^a	24.8 ± 2.6^b	22.5 ± 3.6^b	23.1 ± 3.1	36.0 ± 8.0	42.7 ± 10.0	p=0.002	p=0.111
Water extractable total P (mg P kg^{-1})	4.47 ± 0.65^a	1.07 ± 0.16^b	1.14 ± 0.32^b	1.18 ± 0.27^a	2.87 ± 0.63^b	2.64 ± 0.78^{ab}	p≤0.001	p=0.008
Water extractable inorganic P (mg P kg^{-1})	3.41 ± 0.54^a	0.57 ± 0.08^b	0.57 ± 0.15^b	0.84 ± 0.23^a	1.89 ± 0.57^b	1.82 ± 0.62^{ab}	p≤0.001	p=0.022
Water extractable organic P (mg P kg^{-1})	1.01 ± 0.28	0.58 ± 0.09	0.58 ± 0.17	0.38 ± 0.10^a	0.97 ± 0.20^b	0.81 ± 0.25^{ab}	p=0.426	p=0.026

† SIR, substrate induced respiration.
Different letters between groups within factors denote groups are significantly different at the $p≤0.05$ significance level as determined by linear modelling

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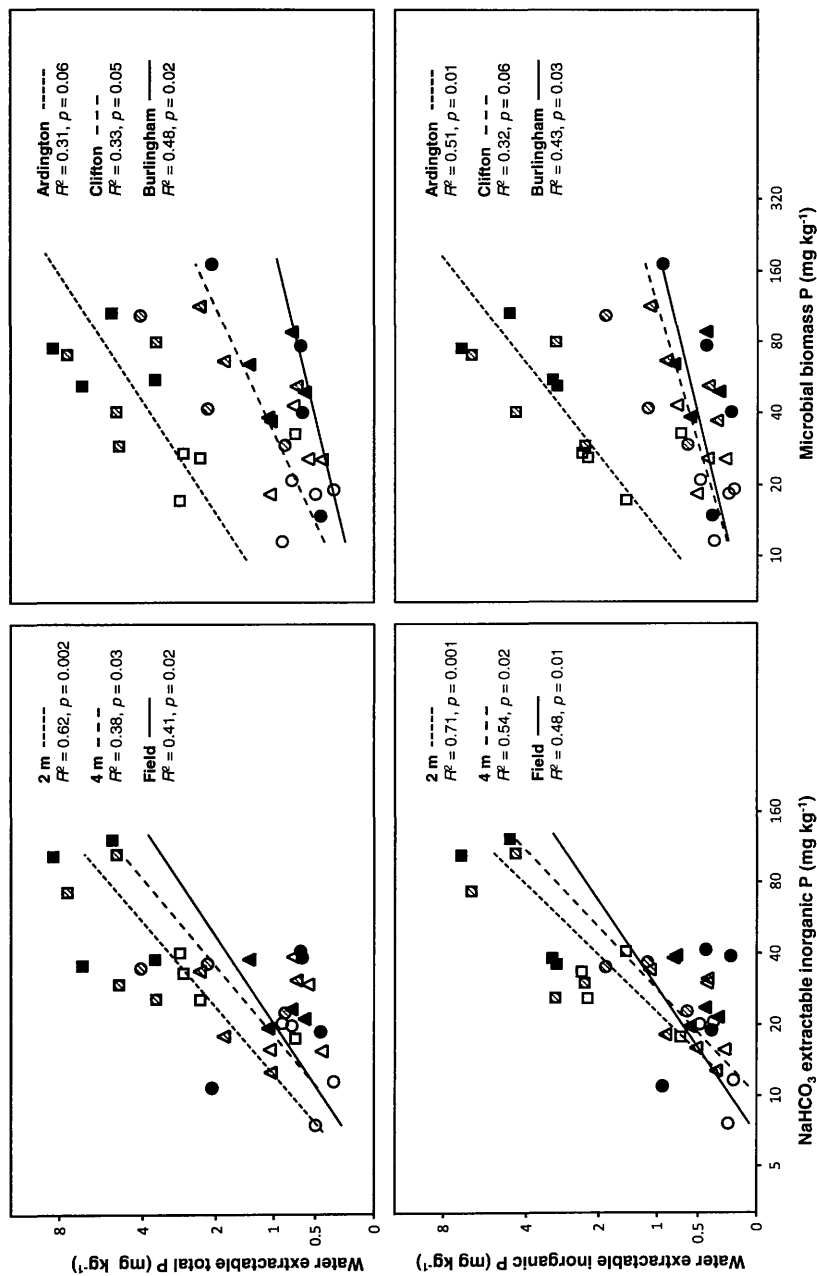
Figure 3.3. Relationships between water extractable phosphorus fractions and NaHCO$_3$ extractable inorganic phosphorus within individual position groups and relationships between water extractable phosphorus fractions and microbial biomass phosphorus within individual soil groups. Shapes indicate that groups are from within the soil factor where squares, circles and triangles denote samples from the Ardington, Burlingham and Clifton soil association groups respectively. Shading within shapes indicates that groups are from within the position factor where transparency, hatching and opacity denote samples from field, 2 m and 4 m position groups respectively.

3.5. Discussion

The relationships between NaHCO$_3$ extractable inorganic P and water extractable inorganic P concur with the findings of previous studies on the relationship between such agronomic soil P tests and P concentrations in more soluble fractions (Pote et al., 1996) and suggests saturation and subsequent desorption of P. However, the combination of NaHCO$_3$ extractable inorganic P, microbial biomass P and water extractable organic P explained a greater amount of variation in inorganic P solubility. As well as desorption, inorganic P released from the microbial biomass and mineralisation of soluble organic P both contribute to the soluble inorganic P fraction. The relationships between water extractable inorganic P and microbial biomass P within the soil groups shows how, when soil pedological properties and management are held relatively constant, variations in microbial biomass P concentrations can be directly responsible for significant variations in soil P solubility. Both of these findings suggest that the soluble inorganic P fraction is partially independent of soil P determined by agronomic soil P tests which may not be sensitive to small but environmentally significant changes in P solubility. Mobilisation of P from the microbial biomass could, therefore, be responsible for previously reported variations in P solubility and leaching from soils with similar agronomic soil P concentrations but different concentrations of organic matter (McDowell and Sharpley, 2001; Stutter et al., 2009). Elucidating the exact mobilisation mechanisms by which microbial biomass P contributes to P solubility will require targeted approaches and the novel experimental design will guide these future studies. Given the stable temperatures and soil moisture conditions during the period of sampling, the increased solubility is most likely to be due to microbial turnover of P during basal mineralisation at stable respiration rates. Under stable soil conditions, the soluble organic and inorganic P fractions would be constantly maintained by microbial turnover as a consequence of microbial death and P mobilisation coupled with simultaneous multiplication and P immobilisation (Oberson and Joner, 2005). Subsequent biological or biochemical

mineralisation of soluble organic P would also contribute to the soluble inorganic P fraction. Phosphorus turnover would also be enhanced during unstable soil conditions such as soil drying or freezing where large quantities of P could be mobilised in riparian buffer strip soils, due to microbial cell lysis and subsequent release of P (Blackwell et al., 2010).

3.6. Conclusion

Microbial biomass P contributed to variation in water extractable P within the data as a whole and within data for the individual soil Associations tested. Phosphorus solubility is therefore partially independent of agronomic soil P concentrations and depends on a range of processes, which suggests that agronomic soil P testing alone will not accurately predict dissolved P leaching risk. Combining these soil tests with simple analyses for example, organic matter, clay mineral contents and water extractable P, would greatly aid the prediction of P leaching risk at appropriate catchment management scales. While the variation in organic matter provided by the experimental system served well to study the microbial driver of P solubility, this variation also has implications for P transfer to surface waters. Riparian buffer strip and other riparian agricultural soils showing increased organic matter and microbial turnover of P may bring a dissolved P leaching risk at a critical landscape location due to increased soil P solubility. In order to reduce this risk, management of P mobilisation may be required and in the case of riparian vegetated buffer strips, occasional vegetation removal and/or tillage could help to slow organic matter build up. A better understanding of these processes and their contribution to P transfer at larger spatial scales will facilitate the development of these management strategies.

3.6. Acknowledgements

4. Retention of phosphorus forms by a narrow vegetated buffer strip

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4.1. Abstract

The establishment of riparian vegetated buffer strips is becoming an increasingly popular option for the mitigation of phosphorus (P) transfer from agricultural land to surface waters. However, there is still an uncertainty about how they influence the different forms of P that are delivered across or through the field slope, which is important as P form potentially affects its accessibility and bioavailability to downstream algal communities. Riparian buffer strips may reduce particulate P loads delivered to surface waters by overland flow due to soil particle trapping processes but also have the potential to increase the loads of dissolved forms of P due to biological solubilisation within buffer strip soils. The aim of this study was to investigate the hypotheses that: a) vegetated buffer strips would reduce loads of particulate P forms compared to inputs and that, b) vegetated buffer strips would increase loads of dissolved P forms compared to inputs. To test this, a field plot experiment in a randomized block design was established. Runoff samples were collected from plots with and without downslope buffer strips and analysed for a range of P fractions during a winter hydrological season. Plots with buffer strips produced lower total loads of total particulate P (0.64 ± 0.18 kg ha^{-1}) fractions than plots with no buffer strips (1.17 ± 0.57 kg ha^{-1}). Buffer

strips had no effect on dissolved reactive P loads but produced dissolved unreactive P loads that were 47 % higher than from plots with no buffer strips. The buffer strips were therefore most effective where the dominant mobilisation process in the upslope-managed land was soil particle detachment with P delivery inputs dominated by particulate forms.

4.2. Introduction

Phosphorus (P) transfer from agricultural land contributes to the eutrophication of surface waters worldwide (Carpenter et al., 1998). The mitigation of this P transfer is necessary in order to negate the environmental, social and economic impacts of eutrophication and to meet current water quality targets. The 'transfer continuum' model of Haygarth et al. (2005) outlines the steps involved in P transfer: P in a 'source' such as the soil itself or added fertilizer is 'mobilised' from the soil as a solute or a solid which is then 'delivered' in hydrological flows with a subsequent 'impact' on the surface water. Phosphorus transfer mitigation options address the different steps in the model (Haygarth et al., 2009) and one option for mitigation of P transfer during delivery involves the establishment of 'vegetated buffer strips' that are uncultivated riparian borders often left absent of management including harvesting, tillage, grazing and/or fertilizer additions.

Riparian vegetated buffer strips are becoming an increasingly popular option, having been shown in plot scale studies to reduce total P concentrations and loads during overland flow. The majority of these studies have only reported data for total P, which leaves an uncertainty about how effectively buffer strips retain different forms of P. For example, Collins et al. (2009) recently reviewed 25 studies of P retention by buffer strips. Within this review, 72% of the studies reported data for total P, 48% reported data for dissolved molybdate reactive P, 16% reported total particulate P data, no molybdate unreactive P

fractions were reported and only 40% of the studies measured more than one P fraction. The form in which P is delivered to the surface waters, as affected by the buffer strips, will potentially affect its accessibility and bioavailability to downstream algal communities. For example, phosphates occluded within the mineral lattice structure of soil particles in runoff water will be less accessible to aquatic algae than phosphates dissolved in solution. Dissolved forms of P are of particular importance to water quality as phosphate would be immediately available for algal uptake and organically complexed phosphate may also be readily mineralised to phosphate during delivery or by aquatic algae therefore contributing to eutrophication (Boström et al., 1988; Toor et al., 2003; Whitton et al., 1991). Ideally, buffer strips would reduce the delivery of the forms of P that are most accessible and available to aquatic algae but because different processes may be responsible for the retention of different forms of P, this may not be realistic under varying soil, rainfall and overland flow conditions.

Establishment of vegetated buffer strips involves the conversion of downslope arable land adjacent to watercourses to a no-tillage system. This promotes the proliferation of natural or introduced plant species with accompanying changes to the physical properties of the soil. An increase in plant root density and turnover may increase soil permeability and porosity which encourages infiltration of overland flow therefore reducing P loads (Collins et al., 2009; Zhang et al., 2010). Infiltration of overland flow within buffer strip soils is the main reason that they have been shown to consistently retain P and empirical relationships between overland flow and P load reduction are commonly reported (Al-wadaey et al., 2012; Borin et al., 2005; Dosskey et al., 2007; Wanyama et al., 2012). Where little infiltration occurs, buffer strips must reduce P concentration in-order to reduce P load. To reduce concentrations and therefore loads of particulate P, buffer strips promote an increase in plant shoot density that may increase soil surface roughness, consequently slow overland

flow, and result in the deposition of soil particles and associated P. Buffer strip plants may also affect the biogeochemical properties of the soil which could promote P mobilisation potentially increasing the concentration of dissolved forms of P in overland and shallow subsurface flow (Stutter et al., 2009). In Spring, during growth, plants may exude organic compounds to solubilise soil P, for example, citric acid exudation chelates base cations with the subsequent release of the associated P (Jones, 1998; Richardson et al., 2009a). Plants also input large quantities of fresh organic matter to the soil as root exudates during growth and as senesced plant material during Autumn, which could stimulate microbial turnover of P thereby increasing solubility. Build-up of stabilised organic matter over several years of inputs may also increase microbial turnover of P during basal mineralisation at stable respiration rates (Roberts *et al.*, 2013). Growing plants also make large contributions to dissolved reactive P concentrations in overland flow due to leaching of P from leaves (McDowell et al., 2007; Sharpley, 1981). These biological processes could lead to buffer strips increasing the concentrations and therefore loads of dissolved P forms delivered to surface waters by overland flow; especially where overland flow is not reduced due to infiltration, for example during saturation excess overland flow.

Retention of different P forms by buffer strips would therefore not only be dependent on seasonal and longer-term changes in soil physical and biochemical conditions but also on differences in rainfall-overland flow conditions from one event to another. This would give rise to variations between P forms and temporal variations that may have been overlooked by previous studies that have measured only total P or that utilised very short-term rainfall or overland flow simulations (Abu-Zreig et al., 2003; Dillaha et al., 1988; Syversen, 2005). To investigate the nature of the retention of different P forms in narrow vegetated buffer strips, we utilised a plot scale study that captured multiple natural runoff events. The aim of the study was to investigate the hypotheses that: a) vegetated buffer strips would reduce loads

of particulate P forms compared to inputs and that, b) vegetated buffer strips would increase loads of dissolved P forms compared to inputs.

4.3. Material and Methods

4.3.1. Site description and experimental design

The study site was at Newton Rigg Agricultural College within the River Eden Demonstration Test Catchment (EdenDTC - www.edendtc.org.uk), Cumbria, UK (54.4°N, 2.5°W, 174 m a.s.l) (Figure 4.1). Newton Rigg has a maritime climate and receives an annual rainfall of 947 mm with mean minimum temperatures of 4.9 and mean maximum temperatures of 12.4 °C (Met Office 1981 to 2010 average). The soil at Newton Rigg forms part of the Clifton soil Association, soils of which are characterised as slowly permeable, seasonally waterlogged, reddish sandy silt loamy soils (25 % sand, 58 % silt and 17% clay) (Collins et al., 2012; Soil survey of England and Wales, 1983). An erosive field slope (4 % slope and in winter barley) at the site served as the experimental area having been identified as an area of potential saturation excess overland flow. Twenty four soil samples (0-7 cm depth) collected in a stratified design from within in the experimental area had a mean pH of 5.89, mean bulk density of 1.04 g cm^3 (percentage coefficient of variance (% CV): 11.9), mean organic matter of 24.35 g kg^{-1} (% CV: 66.3) and mean Olsen P of 67.58 g kg^{-1} (%CV: 30.0). The mean concentration of 0.01 M CaCl$_2$ (1:10 soil to solution ratio) extractable reactive P was 5.89 g kg^{-1} (% CV: 64.5) and mean percentage P saturation of Al and Fe mineral phases (molar ratio) as determined by 0.2 M ammonium oxalate extraction was 17.47 (% CV: 16.3). In early-Summer 2011 the barley (*Hordeum vulgare* L.) was harvested from the experimental area and a 1 metre wide buffer strip sown across the mid-slope unit with a 50:50 by weight seed mixture of red fescue (*Festuca rubra* L.) and perennial ryegrass (*Lolium perenne* L.). Collins et al. (2012) found in a recent study that 48 % of buffer strips established under Countryside

and Environmental Stewardship Schemes in the UK were done so by sowing a low diversity grass seed mix with red fescue and perennial ryegrass two of the most common grass species found in buffer strips. Runoff plots arranged in a randomised block design across the slope, avoided compacted features such as tramlines and incorporated three treatments and three replicates of each treatment. Treatments comprised control plots with no buffer strips, plots with buffer strips and plots with buffer strips where vegetation was topped once in August 2011 in accordance with Entry Level Stewardship scheme guidelines for buffer strip management (Defra, 2005). For the no buffer strip treatment, plots measured 0.5 m (width) by 4 m (downslope length) (representing delivery inputs to the buffer strips) and for both buffer strip treatments, plots measured 0.5 m by 5 m. An impermeable plastic membrane inserted to 7 cm isolated individual plots and 24 cm deep trenches isolated each of the three blocks. At the bottom of the plots, lysimeter pans collected combined overland flow and shallow subsurface flow (0-7 cm depth, collectively termed runoff) and diverted it downslope to 60 L storage tanks (Figure 4.2).
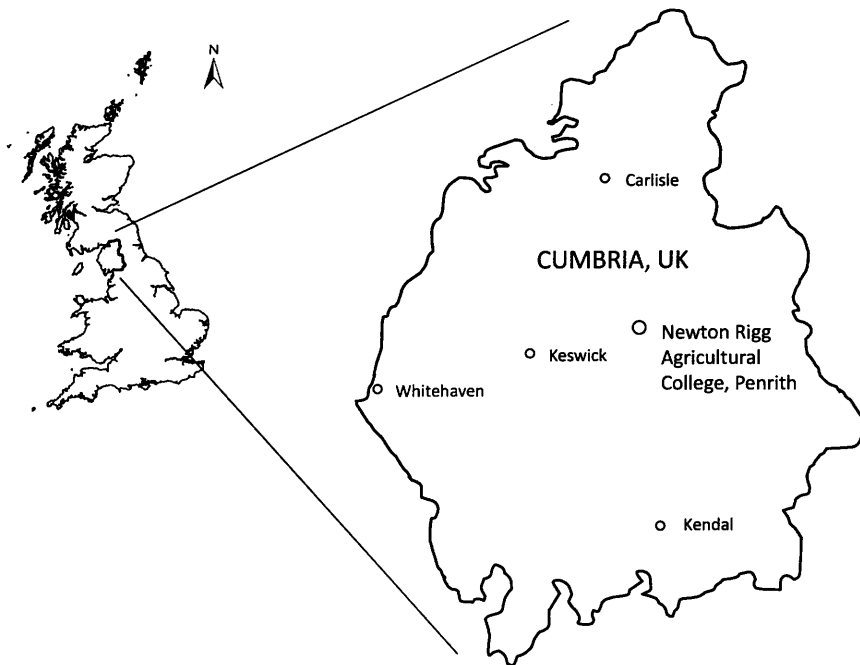
Figure 4.1. Location of the Newton Rigg Agricultural College within Cumbria, UK.
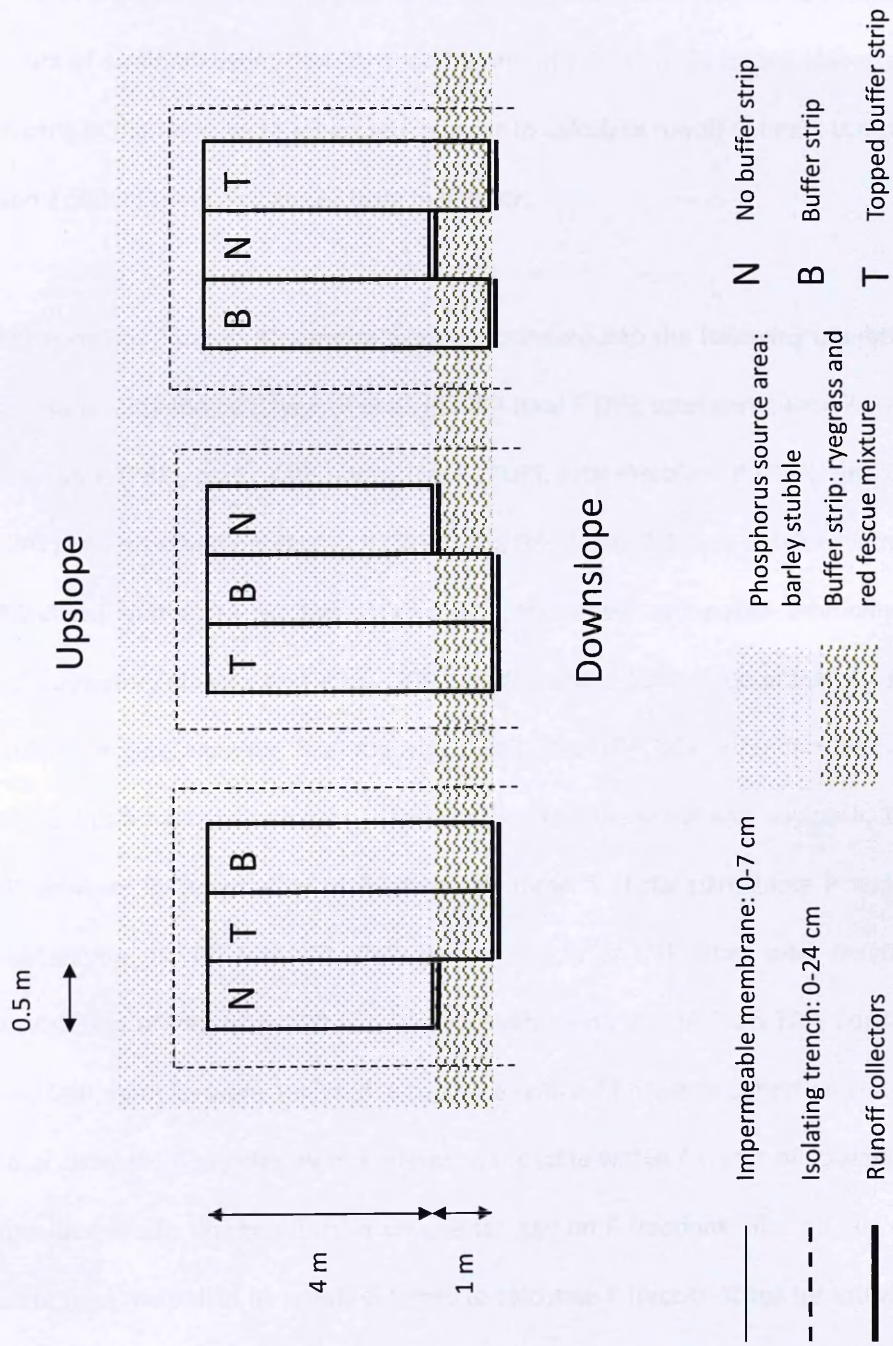
Figure 4.2. Schematic diagram of the experiment design within the experimental area (not to scale).

Upslope

Downslope

0.5 m

4 m

1 m

N T B

T B N

B N T

N No buffer strip

B Buffer strip

T Topped buffer strip

Phosphorus source area: barley stubble

Buffer strip: ryegrass and red fescue mixture

Impermeable membrane: 0-7 cm

Isolating trench: 0-24 cm

Runoff collectors

4.3.2. Sampling and analysis

An automatic tipping bucket rain gauge, situated 500 m away from the experimental area, measured rainfall in 0.2 mm increments throughout the study period: October 27th 2011 to May 27th 2012. During that period, the plots were checked for runoff samples within 24 hours of a rainfall event that exceeded 5 mm of rainfall in 24 hours. Upon sampling, water depths in the tanks were measured in order to calculate runoff volume, the contents stirred and a 500 ml sample collected from half depth.

The forms of P in runoff samples were fractionated into the following operationally defined groups as outlined by Haygarth et al. (1998): total P (TP), total particulate P (TPP), particulate reactive P (PRP), particulate unreactive P (PUP), total dissolved P (TDP), dissolved reactive P (DRP) and dissolved unreactive P (DUP). The DRP (after 0.45 µm cellulose nitrate membrane filtration) and total reactive P was determined by automated ammonium molybdate colourimetry (Murphy and Riley, 1962) with a lower limit of detection for PO_4 of 5 µg l^{-1} (AQ2+ discrete analyser, Seal Analytical, UK). The TDP (also after filtration) and TP, after manual potassium persulphate autoclave digestion (Rowland and Haygarth, 1997), was also determined by ammonium molybdate colourimetry. Total particulate P was calculated by subtraction of TDP from TP, PRP by subtraction of DRP from total reactive P, PUP by subtraction of PRP from TPP and DUP by subtraction of DRP from TDP. For total reactive P and DRP, samples were analysed in triplicate within 24 hours of collection and for total P and total dissolved P samples were analysed in triplicate within 4 weeks of collection. Appendix 2 provides details on the effect of sample storage on P fractions. Phosphorus concentrations were then multiplied by runoff volumes to calculate P fraction loads for individual plots and events.

4.3.3. Statistical analysis

The variance of concentration data for all events and individual events was analysed by mixed effects linear modelling and linear modelling respectively, to determine significant differences between treatment group means (R statistical software version 2.14.1). For P load data, linear modelling was used to determine significant differences between treatment group means for accumulated total loads and individual event loads. Linear modelling was also used to determine relationships between mean P concentrations, mean runoff quantity and mean P loads (n=9, temporal pseudoreplication averaged away) from individual plots therefore incorporating variation between blocks, treatments and plots. Plots of residuals versus fitted values were inspected to ensure model fit and the data were transformed where necessary.

4.4. Results

4.4.1. Rainfall and runoff

The study site received 444.8 mm of precipitation during the study period, 46 per cent of which, was recorded in 2011 (Figure 4.1). Rainfall quantity and maximum hourly intensity of the 19 runoff producing rainfall events recorded, ranged from 4.6 to 32.6 mm and 1 to 5.2 mm hr^{-1}, respectively.

All plots produced runoff and the mean total runoff quantity from all 9 plots during the study period was 76.8 ± 13 mm; 76 % was recorded during 2011. Treatments had little impact on accumulated total and individual event runoff quantities, although mean total runoff was notably lower from the topped buffer strip treatment (no buffer strip: 84.4 ± 19.7 mm, buffer strip: 84.5 ± 15.8 mm, and topped buffer strip: 61.5 ± 22.8 mm) (Figure 4.3).
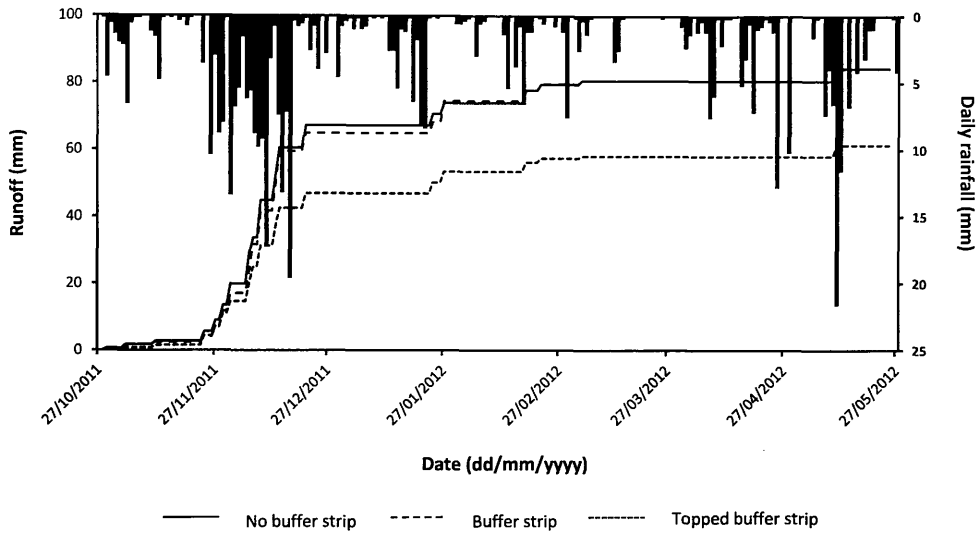
Figure 4.3. Line plot showing cumulative runoff from treatments during the study period with hanging bars showing daily rainfall.

4.4.2. Concentrations of phosphorus fractions

Table 4.1 summarises the mean concentrations of P fractions measured in samples from the three treatments. The buffer strip and the topped buffer strip treatments produced lower mean concentrations of PRP ($p=0.1$ and $p=0.06$ respectively) compared to the no buffer strip treatment (Table 4.1). The treatments resulted in mean concentrations of PUP that declined in the order: no buffer strip>topped buffer strip>buffer strip. The treatments significantly ($p\leq0.05$) affected mean PRP and PUP concentration during a number of individual events with mean concentrations being reduced by both the buffer strip (PRP: 4 events, PUP: 3 events) and the topped buffer strip (PRP: 5 events, PUP: 4 events) treatments compared to the no buffer treatment. These events occurred in 2011 coinciding with the highest recorded concentrations of particulate P fractions (Figure 4.4). Because the two buffer strip treatments showed a greater reduction in PRP than they did PUP concentrations, PRP became the less dominant fraction in TPP in the samples from these treatments (Figure 4.5).

Treatments resulted in very similar mean and individual event mean concentrations of DRP. Although concentrations of DUP were low compared to those of DRP, the buffer strip and the topped buffer strip treatments increased mean concentrations of DUP compared to the no buffer strip treatment (p=0.03 and p=0.04 respectively) (Table 4.1); and individual events where the two buffer strip treatments significantly ($p\leq0.05$) increased means also occurred during 2011.

Table 4.1. Mean concentrations of phosphorus fractions in runoff samples from treatment plots during the sampling period showing mean of between subjects standard error.

	No buffer strip	Buffer strip	Topped buffer strip
pH	5.89	5.74	5.34
Total P (mg l^{-1})	1.05 ± 0.31	0.70 ± 0.11	0.67 ± 0.18
Total particulate P (mg l^{-1})	0.84 ± 0.30	0.50 ± 0.12	0.48 ± 0.18
Particulate reactive P (mg l^{-1})	0.40 ± 0.14	0.19 ± 0.06*	0.15 ± 0.06*
Particulate unreactive P (mg l^{-1})	0.45 ± 0.20	0.30 ± 0.08	0.33 ± 0.13
Total dissolved P (mg l^{-1})	0.20 ± 0.05	0.20 ± 0.05	0.19 ± 0.03
Dissolved reactive P (mg l^{-1})	0.18 ± 0.05	0.17 ± 0.04	0.16 ± 0.03
Dissolved unreactive P (mg l^{-1})	0.022 ± 0.007	0.036 ± 0.009**	0.035 ± 0.001**

Asterisks indicate that buffer strip treatment groups are significantly different from the no buffer strip treatment group at the, * $p\leq0.1$ and ** $p\leq0.05$ significance level as determined by mixed effects linear modelling.
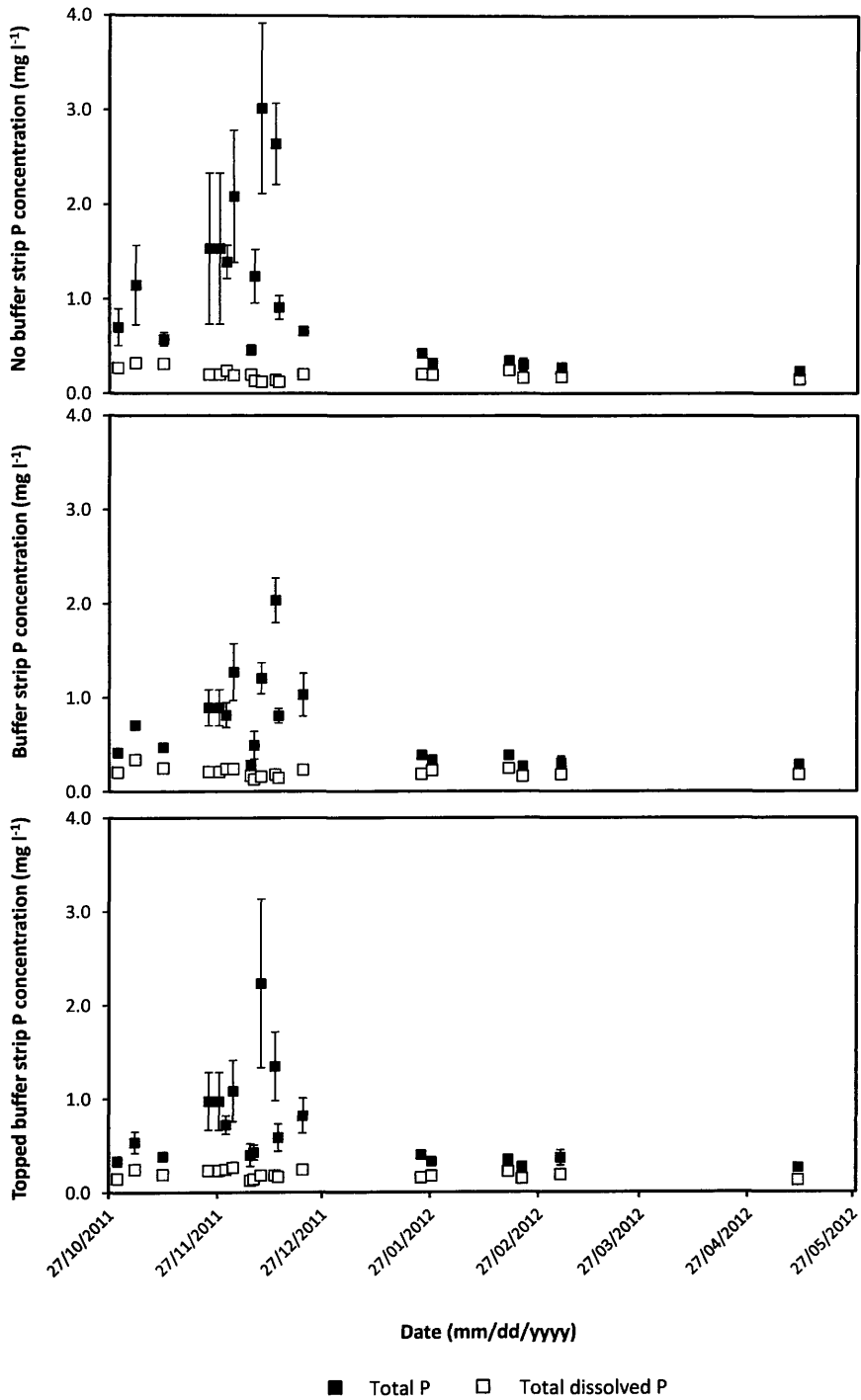
Figure 4.4. Mean concentrations of total phosphorus and total dissolved phosphorus in treatment groups (*n*=3) measured during individual runoff events. Error bars display between subjects standard error.
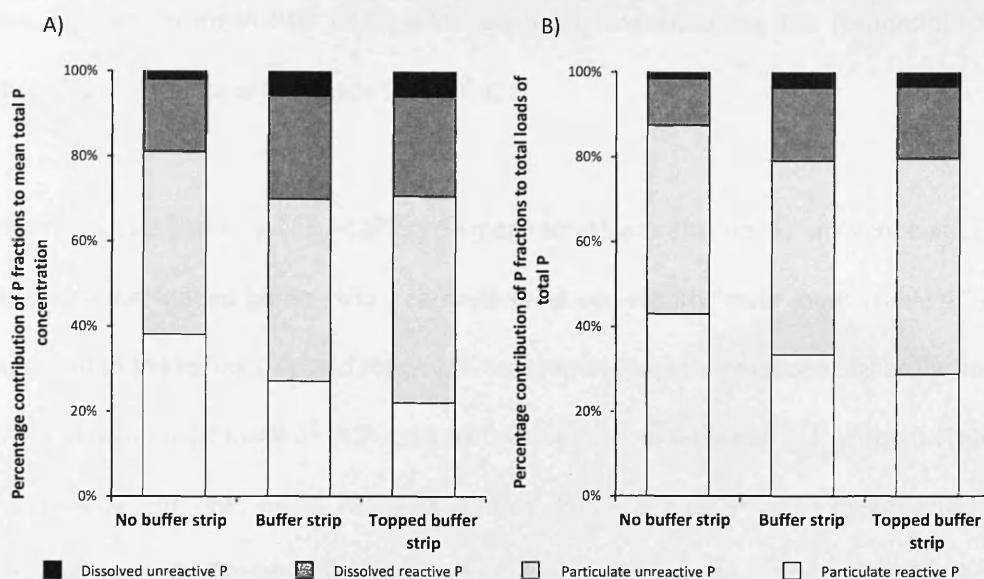
Figure 4.5. Percentage contribution of phosphorus fractions to mean concentration (A) and total loads (B) of total phosphorus within the treatment groups.

4.4.3. Loads of phosphorus fractions

Table 4.2 presents a summary of the accumulated total loads of P fractions measured from the treatment plots. The loads of all P fractions was greatest during 2011 (Figure 4.6) and this was the period when the two buffer strip treatments significantly (p=0.05) altered loads of PRP, PUP and DUP during several individual events. The topped buffer strip plots yielded lower (p=0.05) total loads and buffer strip plots yielded lower (p=0.1) total loads of PRP compared to the plots with no buffer strips (Table 4.2, Figure 4.6). Both buffer strip and topped buffer strip treatments generated lower (topped buffer strip: p=0.1) total loads of PUP compared the no buffer strip treatment group (Table 4.4, Figure 4.4). As with concentration data, PRP made a lesser contribution to TPP loads from plots assigned to both buffer strip treatments compared to those from plots assigned to the no buffer strip treatment (Figure 4.4). Mean concentration and mean runoff quantity contributed equally to

the variation in mean PUP loads, whereas, mean concentration was responsible for the majority of variation in PRP loads (Table 4.3).

No treatments had a significant effect on mean total loads and individual event loads of DRP, although the topped buffer strip treatment produced slightly lower loads (Table 4.2). Plots assigned to the buffer strip and topped buffer strip treatments produced higher (buffer strip: p=0.08) mean total loads of DUP than plots under the no buffer strip treatment (Table 4.2, Figure 4.6). For DRP, mean runoff quantities dominated variation in mean loads, which showed a very similar temporal trend to runoff quantity (Figure 4.3, Figure 4.6). On the other hand, concentration dominated variation in DUP loads (Table 4.3).

Table 4.2. Total loads of phosphorus fractions from treatment plots recorded during the sampling period showing between subjects standard error.

	No buffer strip	Buffer strip	Topped buffer strip	Buffer strip	Topped buffer strip
	kg ha^{-1}	kg ha^{-1}	kg ha^{-1}	% retention	% retention
Total P	1.34 ± 0.56^a	0.81 ± 0.19^{ab}	0.59 ± 0.29^b	39	56
Total particulate P	1.17 ± 0.57^a	0.64 ± 0.18^a	0.46 ± 0.27^a	45	61
Particulate reactive P	0.58 ± 0.32^a	0.27 ± 0.09^{ab}	0.17 ± 0.09^b	53	71
Particulate unreactive P	0.60 ± 0.25^a	0.37 ± 0.09^{ab}	0.30 ± 0.18^b	38	51
Total dissolved P	0.17 ± 0.03^a	0.17 ± 0.04^a	0.12 ± 0.02^a	-2	26
Dissolved reactive P	0.15 ± 0.02^a	0.14 ± 0.04^a	0.10 ± 0.02^a	5	32
Dissolved unreactive P	0.020 ± 0.005^a	0.029 ± 0.006^b	0.022 ± 0.002^{ab}	-47	-12

Percentage retention was calculated as the percentage difference in buffer strip/topped buffer strip P load relative to no buffer strip or 'input' P load.
Different letters between treatment groups denote groups are significantly different at the $p \leq 0.1$ significance level as determined by linear modelling.

Table 4.3. Regression statistics for mean phosphorus loads against mean runoff quantity and mean concentration of phosphorus fractions from individual plots ($n=9$), also showing percentage coefficient of variation ($n=9$).

	Total P	Total Particulate P	Particulate reactive P	Particulate unreactive P	Total dissolved P	Dissolved reactive P	Dissolved unreactive P
Runoff quantity (R^2, p)	0.63, 0.01	0.58, 0.01	0.46, 0.04	0.68, 0.006	0.40, 0.06	0.45, 0.05	0.04, 0.57
Fraction concentration (R^2, p)	0.68, 0.006	0.78, 0.002	0.87, <0.001	0.62, 0.01	0.06, 0.53	0.05, 0.57	0.57, 0.01
% coefficient of variation	68.39	80.61	98.11	68.53	32.98	34.62	31.99
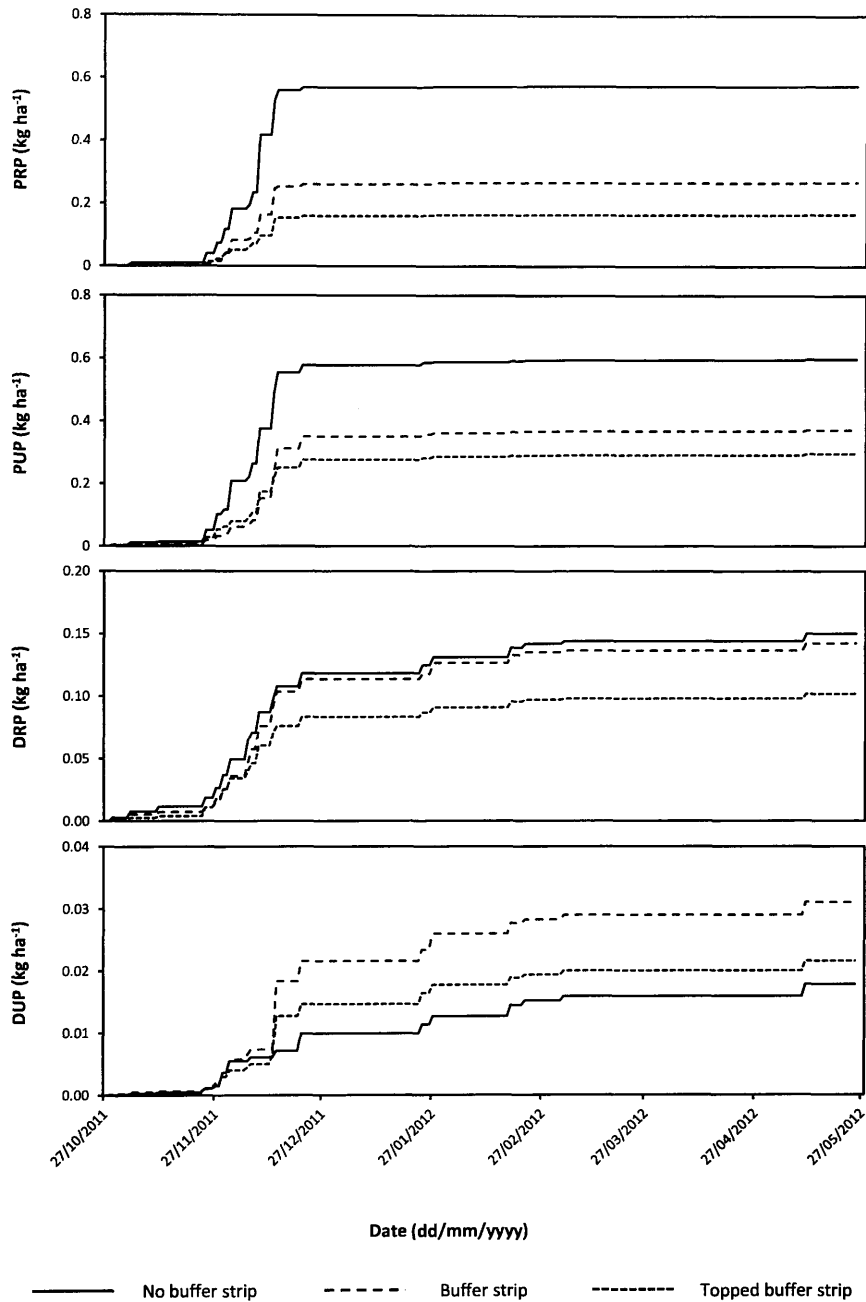
Figure 4.6. Line plots showing cumulative loads of phosphorus fractions during the study period. PRP, particulate reactive phosphorus; PUP, particulate unreactive phosphorus; DRP, dissolved reactive phosphorus; DUP, dissolved unreactive phosphorus.

4.5. Discussion

The buffer strips and topped buffer strips retained a large proportion of TP inputs from the upslope-managed land. This retention was mainly associated with a reduction in loads of particulate forms of P. Retention by unmanaged buffer strips was due to a reduction in concentration of particulate P forms as runoff quantity was not reduced. Topped buffer strips did reduce runoff quantity, possibly due to infiltration of runoff within the buffer strip soil, and this would have supplemented the reductions in concentration hence resulting in the lower loads of both particulate and dissolved P fractions compared to unmanaged buffer strips. Buffer strips therefore provide a concentration reduction mechanism and the contribution that concentration made to variation in loads of particulate P forms across the plots supports this. The proposed mechanism is that of the increased soil surface roughness in buffer strips slowing overland flow and therefore reducing its particulate transport capacity with subsequent particle deposition. It is not possible to determine the relative contribution that overland and shallow subsurface flow made to runoff quantity and P load in order to substantiate this mechanism. However, previous studies have reported higher concentrations and loads of particulate P in pathways that include surface runoff compared to those that are solely dominated by subsurface flow (Haygarth et al., 1998; Heathwaite and Dils, 2000). Compared to events in 2012, events during 2011 produced greater runoff quantities and had much lower TDP to TP concentration ratios (Figure 4.5) which could imply an increased contribution of overland flow. An increased overland flow component would activate this mechanism and buffer strips showed the greatest P retention, both on a mass and percentage basis, during these events in 2011. These observations imply that slowing of overland flow by buffer strips may be an important mechanism for the retention of particulate forms of P where little infiltration occurs within the buffer strip, for example, in areas prone to saturation excess overland flow.

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Both buffer strips and topped buffer strips retained more PRP than they did PUP. Particulate reactive P in runoff represents phosphate loosely bound to soil particles that is readily desorbable in the acid matrix of the molybdate reaction. Particulate unreactive P is comprised of phosphate and low molecular weight organic P compounds occluded in or strongly sorbed to mineral particles or high molecular weight organic compounds (Cade-Menun et al., 2010; Haygarth et al., 1998). Phosphorus associated with the PRP fraction is therefore more likely to interact with biota once delivered to the stream channel than P associated with PUP. The PRP may well be associated with larger soil particles or aggregates in runoff as studies have shown larger soil particles and water-stable aggregates to have weaker P sorption and stronger desorption compared to smaller ones despite having lower total P contents (Maguire et al., 1998; Maguire et al., 2002). This would concur with the notion that buffer strips are more likely to trap larger soil particles and aggregates with a greater mass (Syversen and Borch, 2005). Buffer strips therefore preferentially trap particles with associated P that is more likely to be available to aquatic algae and/or desorbed to the water column upon entry to the stream, which may alleviate the concern that particles holding greater total P contents are not retained (Uusi- Kämppä, 1997).

The buffer strips tested showed a minimal retention of DRP having not notably reduced loads for the data as a whole or during individual events. Dissolved reactive P measured in the samples would consist of phosphate dissolved in solution or attached to soil colloids smaller than 0.45 μm in size. The lower mass of these compounds compared to particulate P forms would make them less susceptible to the reduction in the particle transport capacity of runoff and hence buffer strips had little effect on DRP concentration. Variation in runoff quantity was responsible for the majority of variation in loads of DRP across the plots and temporal trends in DRP fractions followed closely those for runoff quantity, which shows how important runoff quantity is for determining loads of DRP. The absence of DRP retention

is therefore likely to be because buffer strips had little effect on runoff quantity. The data showed little evidence to suggest that biological processes operating within the buffer strip soils had led to an increase in DRP loads. Even topping of buffer strip vegetation had no negative impact on DRP loads in this experiment, despite the fact that studies have shown this management to increase the loads of DRP from pastures (McDowell et al., 2011; Roberson et al., 2007). This is possibly because the grasses topped in August released DRP before the commencement of runoff events in late October. Because the buffer strips had little effect on the concentration of DRP, reduction of runoff quantity by infiltration of P into buffer strip soils is likely to be a key mechanism for DRP retention.

Buffer strips and topped buffer strips showed a negative retention of DUP, i.e. low molecular weight organically complexed phosphate and condensed inorganic P compounds, as evidenced by the increased loads of DUP from the buffer strip and topped both strip treatment plots. These increases in DUP loads suggest a remobilisation of P in the buffer strip soil resulting in the increased concentrations in delivery outputs from the buffer strips. The large contribution of concentrations to variation in DUP loads also substantiates this assumption. The individual events where the buffer strip treatments had a significant impact on concentrations and loads of DUP occurred during 2011 coinciding with fresh inputs of organic matter from senescing plant leaves. Although the exact release mechanisms are unclear, concentrations of DUP leached from soils tend to increase with increasing soil organic matter (Magid *et al.*, 1996; McDowell *et al.*, 2001). Concentrations and loads would therefore increase from the current levels, which are possibly not environmentally significant, as organic matter accumulates in the buffer strip soil due to the cessation of tillage. The conduction of the experiment over only one season of organic matter inputs represents a limitation to the study and longer-term experiments measuring retention of dissolved P fractions are required.

4.6. Conclusion

This study aimed to test the hypothesis that vegetated buffer strips would reduce loads of particulate forms of P compared to inputs. Both buffer strips and topped buffer strips reduced the loads of particulate P fractions delivered. We therefore accept the hypothesis that buffer strips would reduce the loads of particulate forms of P. This would have positive implications for downstream water quality especially because buffer strips preferentially retained PRP, which would be highly available to aquatic algae and highly desorbable to the water column within the stream channel. The study also tested the hypothesis that vegetated buffer strips would increase loads of dissolved forms of P compared to inputs. Buffer strip retention of DRP was low so there was no effect on delivery but buffer strips showed a negative retention of DUP so delivery was increased. We reject the hypothesis that vegetated buffer strips would increase loads of DRP but accept the hypothesis that vegetated buffer strips would increase the loads of DUP under these experimental conditions. This suggests the P remobilised within the buffer strip soil can translate into increased delivery outputs of dissolved forms of P. It is clear that longer-term runoff experiments that capture several seasons of organic matter inputs to buffer strip soils are required to capture the resulting effect on the delivery of these forms of P.

The results show that factors internal to the buffer strip, such as plant stem growth and biological mobilisation, and factors external to the buffer strip such as rainfall-runoff conditions and concentration of P inputs, both influence the retention of different P forms making retention temporally dynamic. Our results suggest that, during soil conditions where little infiltration of runoff occurs within buffer strips soils, buffer strips may not provide the desired effect of reducing the loads dissolved forms of P and P remobilisation could even increase delivery outputs from the buffer strips. Under these soil conditions, riparian vegetated buffer strips would be most effective where the dominant mobilisation process in

the upslope-managed land is soil particle detachment with P delivery inputs dominated by particulate forms.

4.7. Acknowledgements

5. Plant root induced phosphorus leaching from riparian vegetated buffer strip soils: effects of plant species and soil management

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5.1. Abstract

Riparian vegetated buffer strips are becoming an increasingly popular option for the mitigation of phosphorus (P) transfer from agricultural fields to surface waters, as numerous studies have shown them to reduce total P delivery. The natural or introduced buffer strip vegetation provides a number of mechanisms that contribute to reducing total P losses. However, it is not clear how plant growth and the accompanying uptake of P from the soil affects the leaching of dissolved forms of P. Plant roots release carbon (C) based exudates into the soil to increase the quantities of soluble P that are available for uptake. If plants solubilise greater quantities of P than they require, excess P could be available for leaching. In addition, because different plants specialize in accessing different forms and fractions of soil P, a plant growing in a soil that is abundant in those forms and fractions could solubilise large amounts of P, resulting in elevated P leaching. This study aimed to test the hypotheses that i) plant growth can increase the leaching of dissolved inorganic P due increased C mobility in the soil, and that ii) the extent of dissolved inorganic P leaching would be

dependent on a combination plant species and soil management. We modelled the buffer strip, plant-soil system was modelled in a soil column experiment to compare the leaching of dissolved P fractions from two soils of differing management histories sown with three common riparian grass species. Columns with a mixture of ryegrass (*Lolium perenne L.*) and red fescue (*Festuca rubra L.*) increased ($p<0.05$) mean concentrations dissolved reactive P in leachate from both soils compared to columns with no plants. Dissolved organic C was also a significant factor in determining the variation in dissolved reactive P, possibly highlighting the role of plant root exudates in solubilising P. Interactions in the data suggested that different plants solubilized different quantities of P in different soils. This data supports the hypotheses, which we therefore accept under these experimental conditions. Catchment scientists and managers should consider the physiological characteristics of plants when selecting species for establishment in riparian vegetated buffer strips.

5.2. Introduction

Natural background concentrations of nitrogen (N) and phosphorus (P) in soil are insufficient to maintain agricultural production at the current level, so soils are supplemented with nutrient fertilizer often in excess of plant requirements (Holford, 1997). For this reason, N and P derived from agricultural land increasingly contributes to nutrient loadings to surface waters and, therefore, contributes to the degradation of surface water quality (Withers and Haygarth, 2007). Ceasing cultivation and fertilizer additions and allowing the proliferation of natural or introduced vegetation in riparian areas in the form of 'vegetated buffer strips' is one tool in a suite of mitigation options aimed at reducing this contribution. Much of the proposed buffering action depends on the vegetation to capture and/or take up nutrient loads during overland flow thereby reducing delivery to streams. An increased density of plant stems may slow overland flow and encourage the deposition of particle bound

nutrients and an increase in plant root density may increase soil porosity and encourage infiltration of runoff waters containing both particulate and dissolved forms of N and P (Dorioz et al., 2006; Vidon et al., 2010). It is also thought that buffer strip plants would reduce the leaching of dissolved nutrients especially due to uptake of N and P from the soil and this is certainly true for N (Scherer-Lorenzen et al., 2003). Plants take up P exclusively from the soil solution in the form of orthophosphate and because of the strong geochemical fixation of P within the soil, solution concentrations are typically low in comparison to N (Bieleski, 1973; Turner et al., 2003b). For this reason, plant requirements of P cannot be met by mass flow and diffusion to plant roots alone (Hinsinger, 2001; Schachtman et al., 1998). Plants therefore possess a range of mechanisms by which they can increase their acquisition of P; either by accessing more soil or by increasing the solubility of P in the soil. A key way in which plants influence the solubility of P is through the production and release of C based organic exudates in to the rhizosphere (Richardson et al., 2009a). These exudates may acidify or alkalinise the rhizosphere thereby increasing P availability, chelate base metals and release the associated P, stimulate microbial turnover with a resulting increase in P solubility and/or cause enzymatic mineralisation of organically complexed phosphate (Richardson et al., 2009b). The effect of these processes on P leaching has generally been overlooked because of a focus on identifying differences in leachate P concentration as a result of the addition of fertilizer of different quantity and quality (Chardon et al., 1997; Djodjic et al., 2004; Heckrath et al., 1995; Weaver et al., 1988). Studies that have investigated P leaching under different plant species have either aimed to compare plant species (Sovik and Syversen, 2008) or have been based on analysis of total P (Fraser et al., 2004; Marrs et al., 1991; Syversen and Haarstad, 2005) which may have masked changes in dissolved P forms. For this reason, it remains unclear how plant growth and the aforementioned solubilisation processes alter the leaching of dissolved forms of P and whether there is any difference between plant species, or variation between soil properties. If plant induced changes in

rhizoshpere P solubility exceed the plant's need, or ability for P uptake then excess soil solution P may be leached. Also, because plants species coexisting in an ecosystem are individually adapted to access different forms and fractions of soil P (Turner, 2008), a plant growing in a soil which is abundant in the forms and fractions of soil P for which it is specialised in accessing could solubilise large amounts of P. The resulting solubility could to lead to elevated P leaching, with some forms, particularly phosphate, being highly bioavailable to downstream algae (Boström et al., 1988).

The aim of the experiment was to test the hypotheses that i) plant growth can increase the leaching of dissolved inorganic P due increased C mobility in the soil, and that ii) the extent of dissolved inorganic P leaching would be dependent on a combination plant species and soil management. To test this, an analogue model of the buffer strip, plant-soil system was constructed in a soil column experiment measuring the leaching of dissolved P fractions from two soils of differing management histories sown with three common riparian grass species typical of different UK ecosystems.

5.3. Material and methods

5.3.1. Treatment and experimental design

Columns comprised PVC piping (7 cm diameter by 30 cm height) covered at the bottom end by nylon mesh (1 mm gauge) and with 3 cm of gravel. Columns were packed with 800 g of soil (sieved to 6 mm and air dried for 7 days at 25 °C) to a bulk density of 1 g cm^3. Two soils were used separately; both were from the Ardington soil Association, soils of this Association are characterised as having low permeability, seasonal waterlogging and a sandy silt loamy texture (25 % sand, 58 % silt and 17 % clay) (Collins et al., 2012; Soil survey of England and Wales, 1983). Both soils were collected in mid-summer 2012 from Newton Rigg Agricultural

College, Cumbria, UK (54.4°N, 2.5°W, 174 m a.s.l), within the River Eden Demonstration Test Catchment. One soil (termed 'field soil') was collected from an arable field, which was under barley production. A second soil (termed 'buffer soil') was collected from a riparian vegetated buffer strip downslope of that arable field and established in 1993 under the Countryside Stewardship scheme. Collins et al. (2012) characterised the buffer strip vegetation as, dense with high % cover of perennial forbs, high perennial flower numbers and moderate grass cover. Table 5.1 presents some selected biogeochemical properties of the two soils. Five replicates of the following plant treatments were applied to columns containing both soils separately: no plants, perennial ryegrass (*Lolium perenne L.*), red fescue (*Festuca rubra L.*), a 50:50 seed mixture of ryegrass and red fescue and barley (*Hordeum vulgare L.*). The three riparian grass species were selected on the basis of both their abundance in riparian buffer strips established under Countryside Stewardship schemes in the UK (Collins et al., 2012) and their differing natural habitat distributions (Table 5.2). Seeds were germinated in agar plates and then seedlings transferred into columns (two seedlings per column for barley and 6 for the other treatments). One week prior to and after sowing, columns were maintained at 60 % water holding capacity by daily addition of deionised water. All treatments were kept in a completely randomised design within a temperature controlled greenhouse (18 °C day and 14 °C night time temperature) with approximately 16 h of daylight supplemented with artificial lighting to maintain a minimum light intensity of 200 μmole quanta m^{-2} s^{-1}.

5.3.2. Column leaching and sampling

After 42, 47, 52, 62 and 72 days following sowing the seedlings, the columns were leached with a simulated runoff solution containing eroded sediments. The sediments used in the solution were collected from sediment traps in a barley field at Newton Rigg during winter 2011, sieved to 2 mm and air-dried for 7 days at 25 °C. For each solution, 0.34 g of sediment

was soaked in 250 ml of deionised water for 12 hours prior to dispersal on a reciprocating shaker for 1 hour immediately before each leaching cycle. The volume of each runoff solution mimicked the volume of water passing across and through a buffer strip soil (0-7 cm depth) during a runoff event of 12 mm assuming 39 % runoff. The runoff solution contained P fractions in the following concentrations: total particulate P, 0.36 ± 0.04 mg l^{-1}; dissolved reactive P, 0.079 ± 0.002 mg l^{-1}; and dissolved unreactive P, 0.008 ± 0.002 mg l^{-1}. The solutions were applied to the columns in 50 ml increments, without excessive ponding, to total 250 ml over 1 hour. Plastic cups collected leachate from the columns; the cups were then weighed to determine volume.

Table 5.1. Selected properties of the two experimental soils showing mean and standard error of the mean (*n*=3).

	Method description	Field soil	Buffer soil
pH	1:2.5 soil to deionised water	6.12	5.57
Organic matter (g kg^{-1})	Loss on ignition	74.4 ± 0.4	89.5 ± 0.0
Microbial biomass P (mg kg^{-1})	Chloroform fumigation and 0.5 M NaHCO$_3$ extraction	42.74 ± 1.45	88.04 ± 8.31
Total P (mg kg^{-1})	Sulphuric acid and hydrogen peroxide digestion	1112 ± 49	1208 ± 23
NaHCO$_3$ extractable reactive P (mg kg^{-1})	1:20 soil to 0.5 M NaHCO$_3$ extraction	38.98 ± 0.85	36.01 ± 0.19

Table 5.2. Characteristics of the three experimental plant species (Cope and Gray, 2009; Thomas and Davies, 1954).

Common name	Latin name	Habitat	Duration	Above ground characteristics	Below ground characteristics	pH range	Soil texture preference
Ryegrass	*Lolium perenne L.*	Agriculturally improved lowland pasture	Perennial	Erect, loosely tufted	Fibrous root mat, 25 cm minimum rooting depth	5.5-8	Fine and medium
Red fescue	*Festuca rubra L.*	Heathland, meadow, upland pasture	Perennial	Decumbent, loosely to densely tufted	Fibrous root mat, 30 cm minimum rooting depth	5-7.5	Fine and medium
Barely	*Hordeum vulgare L.*	Cultivated arable lowland	Annual	Erect	Fibrous root mat, 25 cm minimum rooting depth	5.5-8.5	medium

5.3.3. Laboratory analysis

Twenty hours prior to each leaching cycle, respiration from the columns was estimated by measuring CO_2 emission by infra-red gas detection (EMG-4 monitor, SRC-1 chamber, PP Systems International, USA). The concentrations of the following operationally defined fractions were determined in the leachate samples: total P (TP), total particulate P (TPP), total dissolved P (TDP), dissolved reactive P (DRP, dissolved inorganic P) and dissolved unreactive P (DUP, dissolved organic P). Dissolved reactive P (on 0.45 µm cellulose nitrate membrane filtered samples) was determined by ammonium molybdate colourimetry (Murphy and Riley, 1962). The TDP (also on filtered samples) was determined by ammonium molybdate colourimetry after an automated in-line potassium persulphate digestion according to the instrument manufacturer's instructions (San++, Skalar). Total P (on unfiltered samples) was determined by a manual autoclave acid persulphate digestion (Rowland and Haygarth, 1997) with digestates analysed colourimetrically as for DRP. Total particulate P was calculated as TPP = TP-TDP and dissolved unreactive P as DUP = TDP-DRP. Dissolved organic carbon (DOC) in the samples was measured by automated in-line acidification and phenolphthalein colourimetry (San++, Skalar).

After the completion of all leaching cycles, the columns were destructively sampled and plants separated into roots and shoots. Plant roots and shoots were oven dried for 5 days at 60°C, weighed and then milled before analysis for total P concentration. The resulting milled samples were then digested in concentrated nitric acid and hydrogen peroxide solution prior to determination of P concentration by malachite green colourimetry (Irving and McLaughlin, 1990). The column soils were oven dried at 105°C for 16 hours, sieved to 2 mm and then ground prior to determination of total P concentration. The soils were then digested in sulphuric acid and hydrogen peroxide (Rowland and Grimshaw, 1985) before determination

of P concentration by ammonium molybdate colourimetry (AQ2+ discrete analyser, Seal Analytical, UK).

5.3.4. Statistics

The variance of concentration data was analysed by mixed effects linear modelling to determine the main effects of and interactions between factors (R statistical software version 2.15.2). The analysis was carried out on the basis of 'soil' and 'plant' fixed factors and a 'days since sowing' random factor. Because of highly significant one-way interactions where levels of the soil factor influenced differences between treatment group means within the plant factor, models were simplified to identify significant differences between plant treatment group means within the two soil treatment groups individually. The errors presented for concentration data represent the mean of the between subjects standard error of the mean.

To understand the partitioning of P into different pools, total loads of P lost via leachate and quantities of P in soil and plant pools were calculated using concentration, volume and mass data to form an input-output P budget for the columns. Because of interactions, the analysis of these data proceeded in the same way as for concentration data with the exception of a random factor. The errors presented for budget data represent the standard error of the between subjects mean.

Linear modelling was also used to determine the effect of covariates on DRP concentrations (temporal pseudo-replication averaged away) and total loads (n=50). This was performed on the basis of the aforementioned soil and plant factors with the addition of covariates: DOC concentration and load; and plant total P concentration and contents. Assumptions of all models were checked in plots of residuals versus fitted values.

5.4. Results

5.4.1. Concentrations of dissolved nutrients in leachate and column respiration

Firstly, comparing the effects of plant treatment within soil treatments, within the field soil treatment, plant treatments had an impact on mean concentrations of DRP, which declined in the order: mixture>ryegrass>red fescue=barley=no plants. The ryegrass and mixture treatments increased mean concentrations ($p=0.05$ and $p=0.009$ respectively) compared to the no plant treatment (Table 5.3). Within the buffer soil treatment, plant treatments had a more pronounced impact on mean concentrations of DRP; means declined in the order: mixture>red fescue>ryegrass>no plants>barley (Table 5.3). The red fescue and the mixture treatments significantly increased mean concentrations ($p=0.005$ and $p=0.002$ respectively) relative to the no plant treatment whereas the barley treatment reduced mean concentration ($p<0.001$). Comparing the two soils, despite having similar total P and $NaHCO_3$ extractable reactive P concentrations (Table 5.1), columns packed with the buffer soil generated a higher mean concentration (0.76 ± 0.09 mg l^{-1}) of DRP than those packed with the field soil (0.14 ± 0.07 mg l^{-1}) ($p<0.001$). Levels of the soil factor affected the differences between the mean concentrations of DRP produced by the no plant treatment and those produced by the red fescue and barley treatments; differences were greater for the red fescue but smaller for barley treatment within the buffer soil (Figure 5.1). In addition, within the field soil, the ryegrass treatment increased mean DRP concentration compared to the red fescue treatment, but in the buffer soil, red fescue increased mean DRP concentration compared to ryegrass (Table 5.3).

Table 5.3. Mean concentrations of determinants measured in leachate samples from plant treatment groups within the field soil (A) and the buffer soil (B) (next page). Standard errors are means of between subjects standard error.

A)

	Field soil				
	No plants	Ryegrass	Red fescue	Mixture	Barley
Respiration (mg C kg^{-1} h^{-1})	-8.10 ± 3.77	6.38 ± 3.01**	11.24 ± 4.05***	8.99 ± 3.96**	70.59 ± 10.36***
pH	6.16	6.34*	6.31	6.42*	6.48*
Leachate volume (ml)	221 ± 9	214 ± 7	219 ± 11	219 ± 5	203 ± 10
Total P (mg l^{-1})	0.28 ± 0.05	0.31 ± 0.04	0.36 ± 0.07	0.27 ± 0.03	0.30 ± 0.03
Total particulate P (mg l^{-1})	0.13 ± 0.06	0.13 ± 0.05	0.23 ± 0.08	0.08 ± 0.03	0.14 ± 0.04
Total dissolved P (mg l^{-1})	0.15 ± 0.02	0.19 ± 0.03	0.14 ± 0.02	0.20 ± 0.02*	0.16 ± 0.02
Dissolved reactive P (mg l^{-1})	0.12 ± 0.01	0.16 ± 0.02*	0.12 ± 0.02	0.17 ± 0.01**	0.12 ± 0.01
Dissolved unreactive P (mg l^{-1})	0.027 ± 0.012	0.028 ± 0.008	0.016 ± 0.004	0.025 ± 0.005	0.044 ± 0.008*
Dissolved organic C (mg l^{-1})	6.47 ± 0.67	8.48 ± 0.82*	6.50 ± 0.60	9.00 ± 0.92*	10.60 ± 1.57*

B)

	Buffer soil				
	No plants	Ryegrass	Red fescue	Mixture	Barley
Respiration (mg C kg⁻¹ h⁻¹)	10.98 ± 4.67	31.11 ± 6.01*	33.31 ± 6.01*	49.25 ± 7.61***	144.05 ± 19.66***
pH	6.00	6.15*	6.13*	6.20*	6.25*
Leachate volume (ml)	215 ± 3	169 ± 11**	191 ± 5*	179 ± 9**	167 ± 8**
Total P (mg l⁻¹)	0.86 ± 0.06	1.05 ± 0.05	1.03 ± 0.05	1.13 ± 0.06	0.68 ± 0.06
Total particulate P (mg l⁻¹)	0.04 ± 0.02	0.06 ± 0.03	0.03 ± 0.01	0.06 ± 0.03	0.09 ± 0.04
Total dissolved P (mg l⁻¹)	0.82 ± 0.05	0.99 ± 0.06	1.00 ± 0.05*	1.07 ± 0.05*	0.59 ± 0.03***
Dissolved reactive P (mg l⁻¹)	0.69 ± 0.03	0.81 ± 0.05	0.89 ± 0.05**	0.97 ± 0.05**	0.45 ± 0.03***
Dissolved unreactive P (mg l⁻¹)	0.123 ± 0.019	0.185 ± 0.014*	0.111 ± 0.021	0.102 ± 0.008	0.136 ± 0.010
Dissolved organic C (mg l⁻¹)	20.10 ± 1.46	39.08 ± 2.15***	31.70 ± 2.38*	37.9 ± 1.96**	41.29 ± 2.19**

Asterisks indicate that plant treatment groups are significantly different from the no plant treatment group at the, * $p \leq 0.05$, ** $p \leq 0.01$ and *** $p \leq 0.001$ significance level as determined by mixed effects linear modelling.
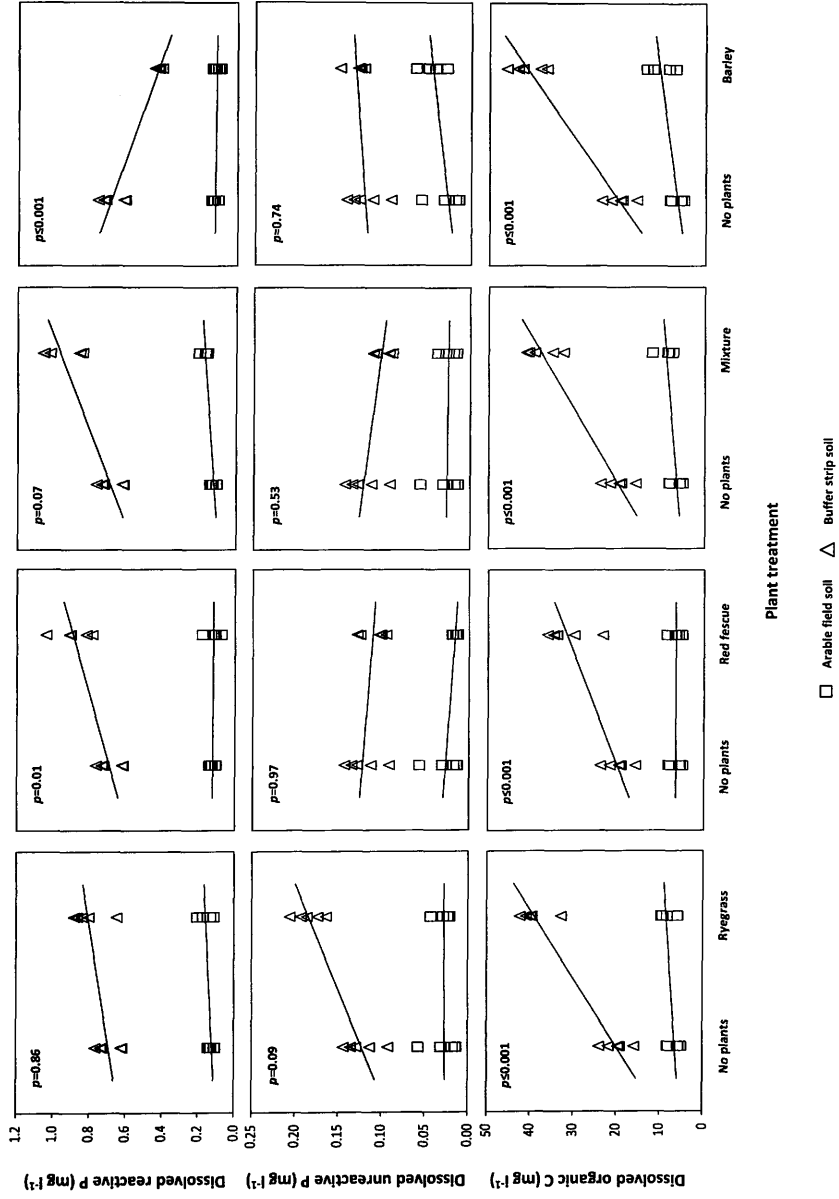
Figure 5.1. Plots of dissolved reactive, dissolved unreactive P and dissolved organic carbon concentrations (temporal pseudo-replication averaged away for graph) showing interactions between the no plant treatment group and the other plant treatment groups as affected by the soil factor. The significance of individual interactions were determined by mixed effects linear modelling.

Within the field soil, mean DUP concentrations declined in the order: barley>ryegrass>no plants>mixture>red fescue (Table 5.3). Treatments had little impact on mean concentrations of DUP except for the barley treatment which increased mean concentration compared to the no plants treatment ($p=0.04$). Within the buffer soil, mean concentrations of DUP declined in the order: ryegrass>barley>no plants>red fescue>mixture. Only the ryegrass treatment group significantly ($p=0.01$) altered mean concentration compared to the no plant treatment (Table 5.3). As for DRP, the buffer soil treatment resulted in a higher mean concentration (0.03 ± 0.01 mg l^{-1}) than did the field soil treatment (0.13 ± 0.01 mg l^{-1}) ($p<0.001$).

Table 5.3 presents the mean DOC concentrations produced by the treatments and the significant differences between them. Within both soils, mean concentrations of DOC decreased in the order: barley>mixture>ryegrass>red fescue>no plants. The soil factor affected the differences in mean concentrations of DOC produced by the no plant treatment and those produced by all other plant treatments; differences were greater within the buffer soil (Figure 5.1). The buffer soil produced higher mean concentrations of DOC than the field soil (Field soil: 8.20 ± 2.88 mg l^{-1}. Buffer soil: 34.01 ± 3.84 mg l^{-1}) ($p<0.001$).

Table 3 presents the mean column respiration from the treatments and the significant differences between them. Within the field soil, mean respirations decreased in the order: barley>red fescue>mixture>ryegrass>no plants. Within the buffer soil, mean respiration decreased in the order: barley>mixture>red fescue>ryegrass>no plants. The soil factor affected the difference in mean respiration between the no plant and the barley treatment ($p<0.001$); the difference was greater within the buffer soil. The two soil treatments respired C at different mean rates (Field soil: 17.82 ± 8.64 mg C kg^{-1} h^{-1}. Buffer soil: 53.74 ± 9.29 mg C kg^{-1} h^{-1}) ($p<0.001$).

5.4.2. Phosphorus budget

Mean cumulative loads of P fractions followed a similar pattern to those for concentration data, although, the interactions and differences tended to be less pronounced due to variation in leachate volumes. Compared to inputs, all plant treatments in both soils showed a negative retention of DRP, i.e. loads increased upon passing through the columns, but retention was lowest from both soils in the columns with the mixture treatment (Figure 5.2).
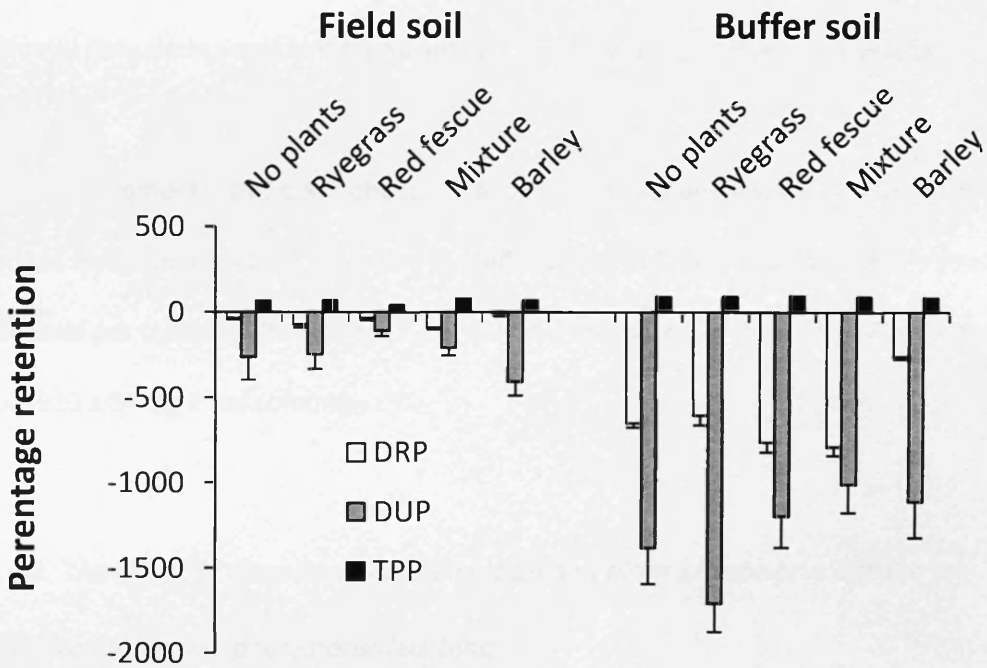
Figure 5.2. Columns depicting percentage retention of phosphorus fractions within the soil columns by plant treatment. Percentage retention was calculated, using mean accumulated P loads inputting and outputting the columns, as the difference between inputs to the columns and outputs from the columns expressed as a percentage of inputs. DRP, dissolved reactive phosphorus; DUP, dissolved unreactive phosphorus; TPP, total particulate P.

Within the field soil, barley contained higher total plant P (11.8 ± 1.3 mg P and 4.4 g biomass per column) than red fescue (6.0 ± 1.1 mg P and 0.96 g biomass per column) (p=0.02). Total P contents in ryegrass (10.1 ± 1.6 mg P and 2.1 g biomass per column) and the mixture (7.9 ±

1.0 mg P and 1.6 g biomass per column) were similar. Within the buffer soil, ryegrass (21.0 ± 1.1 mg P and 5.0 g biomass per column), the mixture (20.6 ± 1.8 mg P and 4.4 g biomass per column), and barley (23.3 ± 1.9 mg P and 7.4 g biomass per column) all contained greater plant total P than red fescue (10.4 ± 0.8 mg P and 1.8 g biomass per column) ($p<0.05$). These differences highlight the overall effect of the soil factor on differences between plant treatment means ($p=0.02$). Plant roots accumulated more P than shoots in the buffer soil and hence a more significant ($p=0.002$) overall interaction was present. Plants sown in the buffer soil had higher mean plant total P contents (15.0 ± 1.8 mg P and 3.7 g biomass per column) than those sown in the field soil (7.1 ± 1.7 mg, 1.8 g biomass per column) ($p<0.001$).

For soil P contents, the main effects of and the interactions between both soil and plant factors were not significant. Columns packed with the field soil had very similar mean total P contents per column (897 ± 30 mg P per column) compared to those packed with the buffer soil (910 ± 54 mg P per column).

5.4.3. The effect of dissolved organic carbon and plant phosphorus uptake on dissolved inorganic phosphorus leaching

To investigate whether DOC or plant uptake would explain variation in concentrations and total loads of DRP, the data were analysed with mean DOC concentration and load, and plant, root and shoot total P concentration and contents as covariates. In the simplified model which explained 98 % of variance in DRP concentration, DOC concentration was a significant ($t=2.5$, $p=0.01$) factor in explaining DRP concentrations. The slope of the relationship was not different ($p>0.05$) between the two soils but the intercept was ($p<0.001$). Slopes and intercepts within the plant groups were not different except for the barley treatment group ($p<0.05$). A similar model which explained 97 % of variance in DRP load identified DOC load as being a significant ($t=4.6$, $p<0.001$) factor in explaining DRP load.

Total plant P, plant root P or plant shoot P contents had no effect on DRP concentrations or loads. Figure 5.3 presents individual relationships between DRP and DOC concentrations within each soil.
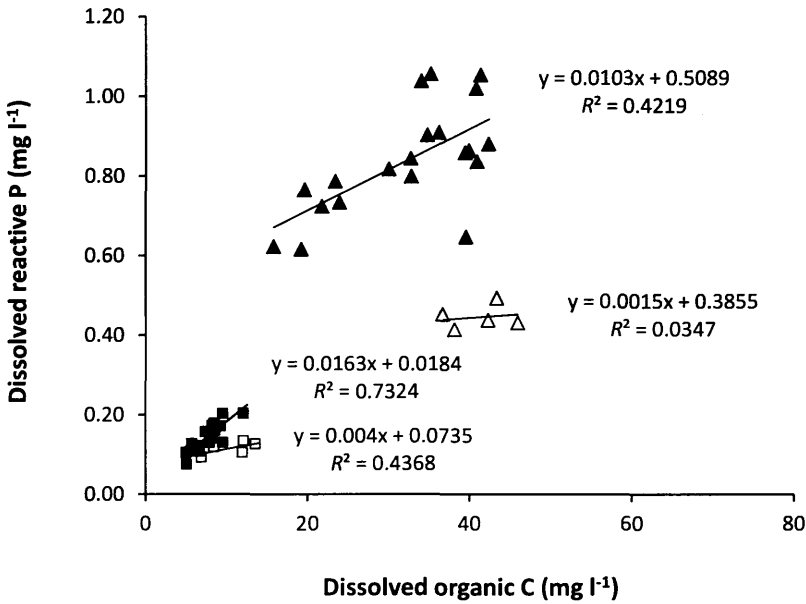
Figure 5.3. Relationships between dissolved reactive phosphorus and dissolved organic carbon concentration isolated on the basis of analysis of covariance. Squares indicate field soil and triangles indicate the buffer soil. Opacity indicates a combination of no plants, ryegrass, red fescue and mixture treatment and transparency indicates barley treatments.

5.5. Discussion

Although it is commonly suggested that plants would reduce the leaching of dissolved inorganic P from riparian buffer strip soils due to P uptake, there is little evidence for this in the literature. Here we demonstrate that in fact the opposite was the case. In the field soil 2 of the 4 treatments with plants increased DRP concentrations and loads compared to those without plants. In the buffer soil, plants had an even more pronounced impact. In contrast,

the impact of the growth of a typical arable crop species, barley, led to the expected decline in leachate DRP concentrations and loads. The notion that plants would reduce the leaching of dissolved forms of P may have been brought about because plant uptake of P from the soil has been shown to reduce sodium bicarbonate extractable fractions of inorganic P (Chen et al., 2002; Gahoonia et al., 1994) which have also been related to DRP concentration in runoff and soil leachate (Hesketh and Brookes, 2000; McDowell et al., 2001). The presence of these grasses may have also altered other fractions of soil P that are more critical for P leaching such as soil solution P. Because soil solution concentrations of P are often low (Bieleski, 1973), plants must make P more soluble in-order to meet their requirements thereby increasing the size of this fraction and this often involves the release of C based root exudates (Richardson et al., 2009a; Richardson et al., 2009b). Cereals and pasture plants transfer between 20 and 50% of total assimilated C into the soil and some of this will enter the soil solution as DOC and some will be assimilated by soil microbes (Kalbitz et al., 2000; Kuzyakov and Domanski, 2000). The increased DOC leaching under the plant treatments will therefore represent direct inputs of DOC to the soil from plants in the form of exudates and/or DOC from microbial turnover and decomposition due to increased stimulation by the exudates. To investigate whether DOC mobility in the soil or plant uptake was responsible for variations in DRP concentrations and loads the data were analysed with DOC and plant total P as covariates. The subsequent statistical analysis showed that plant uptake was not a significant factor in determining DRP concentrations or loads in the leachate; however, DOC concentration was. Presumably, plant induced DOC mobility in the soil resulted in the solubilisation of a greater quantity of P than the plants required or had the ability to take up. These findings show how plant growth and the accompanying increase in C mobility in the soil can actually increase the leaching of dissolved inorganic P. While plants that show increased P uptake may have an advantage for vegetative mining where a P legacy exists in the buffer strip soil, i.e. lowering of soil P contents by the harvesting and removal of

vegetation containing P, these species may not necessarily reduce P leaching from unmanaged buffer strips which we have shown is more dependent on C mobility in the soil.

The data presented here provide indications that different plants may have quite different abilities in solubilising P with subsequent effects on P leaching. Ryegrass increased both DRP and DUP leaching compared to no plants within both soils. Ryegrass clearly resulted in the solubilisation of both inorganic and organic P, but didn't result in the mineralisation of this soluble organic P. Chen et al. (2002) studied P dynamics in the rhizosphere of ryegrass using a sequential soil extraction procedure and found that sodium hydroxide extractable fractions of inorganic P were depleted compared to an unplanted soil. The ryegrass rhizosphere did not, however, show a depletion of soil organic P fractions to suggest access to organic P forms. In this study, red fescue had no effect of DRP leaching compared to no plants in the field soil, but increased DRP leaching and to a greater extent than ryegrass in the buffer strip soil. Because of this and the reduced leaching of DUP from the buffer strip soil, which had greater organic matter, red fescue appeared to result in the solubilisation and mineralisation of soluble organic P. The solubilised and mineralised organic P would be available for leaching as dissolved inorganic P. There is much less evidence in the literature to support the assumptions made about red fescue but this species does typically inhabit upland meadows and pastures where organic forms of P are more likely to dominate (Floate, 1965). The mixture of the ryegrass and red fescue yielded the most DRP in leachate, which could also support the idea that the two plants are solubilising P from different forms and fractions of soil P. Barley had no effect on DRP in leachate within the arable soil but reduced DRP leaching in the buffer strip soil compared to columns with no plants. On the other hand, barley increased DUP leaching from both soils. In contrast to red fescue, barley appears to have resulted in the immobilisation of soluble inorganic P into organic P. However, barley has been shown to deplete organic P from both sterilised soil solutions (Seeling and Jungk,

1996) and sodium bicarbonate extractable soil organic P fractions (Asmar et al., 1995). The observed immobilisation into the soluble organic P fraction may therefore be due to increased microbial turnover stimulated by the root derived DOC. The interaction in column respiration where the buffer soil vastly increased the difference in respiration between no plants and barley may indicate an increased microbial activity. Barley may therefore have exuded a different quantity and/or quality of DOC that was more readily metabolised by the microbial community with the increased microbial turnover resulting in elevated organic P mobilisation and leaching (Seeling and Zasoski, 1993). These results demonstrate the difference in the nature of P leaching under different plant species as affected by the soil in which they are grown. This could have important implications for the selection of plant species to be sown in buffer strips.

Phosphorus load data from this experiment shows that the arable field soil sown with an arable barley crop leached the lowest quantities whereas the buffer strip soil sown with a mixture of the two riparian grasses leached the greatest quantities of DRP. This is contrary to the perceived role of buffer strips as sinks for dissolved P and other studies that have maintained the integrity of the soil structure have also reported similar results. Ulén and Etana (2010) leached intact soil columns collected from buffer strips and adjacent upslope fields and found that concentrations of DRP in the buffer strip soil columns were higher. In that study, soil organic matter was identified as being an important factor in promoting these concentrations, however, the changed temperature and water relations in intact core systems may have impacts on the processes controlling these dynamics. Notwithstanding this, a field study with gravity lysimeters inserted 20 cm below the soil surface showed similar results (Uusi-Kämppä, 2005) although the author provides no explanation for this. The repacking of soil columns and treatment design in our experiment allows some crude estimates of the contribution of different processes to the quantities of DRP leached to be

made. Having low biological activity, DRP in leachate from the field soil with no plants could be taken as the contribution from desorption and dissolution which would be 0.14 ± 0.01 mg per column for the leaching period. The difference between that and the contribution from the buffer soil with no plants would give a contribution from organic matter/microbial turnover of 0.60 ± 0.02 mg per column. The difference between the previous and the buffer soil planted with the mixture of grasses would leave the contribution of plant root induced leaching at 0.14 ± 0.01 mg per column. Clearly managing organic matter/microbial turnover has the potential to provide large reductions in DRP loss by leaching, but the contribution to DRP leaching from plant roots is similar to that of desorption so managing this contribution would also be beneficial. Our experiment has shown that sowing specific plant species in certain soils can help to reduce DRP leaching. A plant with the physiological characteristics of barley but the aboveground physical characteristics of ryegrass or red fescue could help to reduce plant root induced DRP leaching whilst maintaining physical particulate trapping.

5.6. Conclusion

This study aimed to test the hypothesis that plant growth can increase the leaching of dissolved inorganic P due to increased carbon mobility in the soil. Columns with the mixture of ryegrass and red fescue produced higher mean concentrations and loads of DRP in leachate from both soils than columns with no plants. Because of this and the fact that DOC was a significant factor in determining variation in DRP, we accept this hypothesis. The experiment also aimed to test the hypothesis that the extent of dissolved inorganic P leaching would be dependent on a combination of plant species and soil management. The interactions present in the data support this; for example, ryegrass produced higher DRP concentrations in leachate from the arable soil compared to red fescue, yet red fescue had higher DRP concentrations in the buffer strip soil. For this reason, we accept the proposed hypothesis. Further research is however required to determine whether natural light, water

and temperature conditions enhance or limit these effects and whether these effects would be the same in soils of varying N and P contents.

These results are contrary to the commonly held idea that buffer strip plants would reduce P leaching due to uptake. Plants displaying increased P uptake would have a benefit when used for soil P mining but the results here suggest that the increased C mobility in the soil is more critical for DRP leaching from unmanaged buffer strips. It is not clear from the results the exact source and nature of this soluble C or how and what fractions and forms of soil P are affected but an improved knowledge in these areas would allow the better management of buffer strip vegetation to reduce this root induced P leaching. In addition, screening of plant species identifying their effect on dissolved P leaching would allow catchment scientists and managers to consider the physiological characteristics of plants when selecting species for establishment of riparian vegetated buffer strips.

5.7. Acknowledgements

6. Conclusion

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The overall aim of this study was to investigate whether biological solubilisation processes operating in riparian buffer strip soils can increase the risk of dissolved P transfer, and in turn, to understand how better to manage them to minimise this. A series of experiments that addressed the specific objectives outlined in the introduction provided evidence that biological processes can increase the risk of dissolved P transfer. This chapter returns to those objectives and briefly outlines the main findings, limitations and implications. The chapter then presents a conceptual model that brings this new knowledge together into a combined understanding. Discussion of the wider implications and recommendations for future research then follow.

The first objective of the study was to determine whether microbial biomass P concentrations influence soil P solubility. Buffer strip soils showed an increased risk of dissolved P transfer compared to the adjacent field soils as evidenced by elevated inorganic P solubility. The concentration of phosphorus held within soil microorganisms, which was also elevated in the buffer strip soils, made a significant contribution to this solubility. This contribution was thought to be due to greater microbial turnover with the coupled release of phosphate to the soil solution, but inevitably, there was some uncertainty in this conclusion. It was not clear what specific fractions of the microbial community or specific community

structures that promote P solubility and what fractions and sources of organic matter stimulate their turnover.

The second objective of this study was to compare the retention of different P forms by buffer strips during delivery. Despite little reduction in runoff quantity, the narrow buffer strips reduced the loads of particulate P forms delivered by surface and shallow subsurface flow. Although buffer strips had no effect on the loads of dissolved inorganic P, buffer strips increased concentrations and loads of dissolved organic P compared to plots with no buffer strips. The increased loads of organic P from buffer strips suggested a remobilisation of P coinciding with organic matter inputs from senescing plants in autumn. The lack of difference in dissolved inorganic P may have been due to minimal build-up of organic matter in the buffer strip soil, which the previous experiment showed to be an important factor in promoting inorganic P release.

The third objective of this study was to examine the effect of the growth of different plant species in different soils on dissolved P leaching. The growth of some common buffer strip grasses increased the risk of dissolved P transfer; soil columns with grasses increased the leaching of dissolved inorganic P compared to columns with either no plants or barley. The excess leaching was due to enhanced carbon mobility in the soil. The extent of dissolved inorganic P leaching also depended on soil management history with no tillage amplifying this leaching under red fescue. It was not clear the exact source and nature of plant root derived soluble carbon or how and what fractions and forms of soil P are affected.

Figure 6.1 presents a conceptual model of vegetated buffer strip functioning that has been constructed on the basis of these findings. Being embedded in the 'P transfer continuum' and incorporating retention and remobilisation tiers, the model takes a similar form to the

one presented in the literature review but is more focussed on biological processes. Particulate forms of P dominate (approximately 90 % of load) delivery inputs from the upslope-managed land to the buffer strip with concentrations and loads varying temporally. Buffer strips typically retain 50 % of this particulate P due to physical processes that result in the deposition of particulate material containing P. The retained proportion of P inputs then becomes part of the soil continuum where there would also be geochemical interactions. Plants and microbes must acquire this physically retained P before retention within biological pools. This acquisition may involve the solubilisation of retained particulate P, native soil P and/or remobilised P. Any solubilised P not retained in biological pools could be available for leaching. After biological retention and during death, plants and microbes release a proportion of this P in soluble form, again making it available for leaching. Elevated levels of soil organic matter, for example, in older buffer strips, would increase the amount of microbial and plant P therefore increasing amount of soluble P released. How this remobilisation contributes to delivery outputs of dissolved P forms depends on soil-runoff conditions. Where little infiltration occurs within the buffer strip soil, for example, during saturated overland flow, remobilised P could result in increased delivery outputs of dissolved P forms via overland flow.
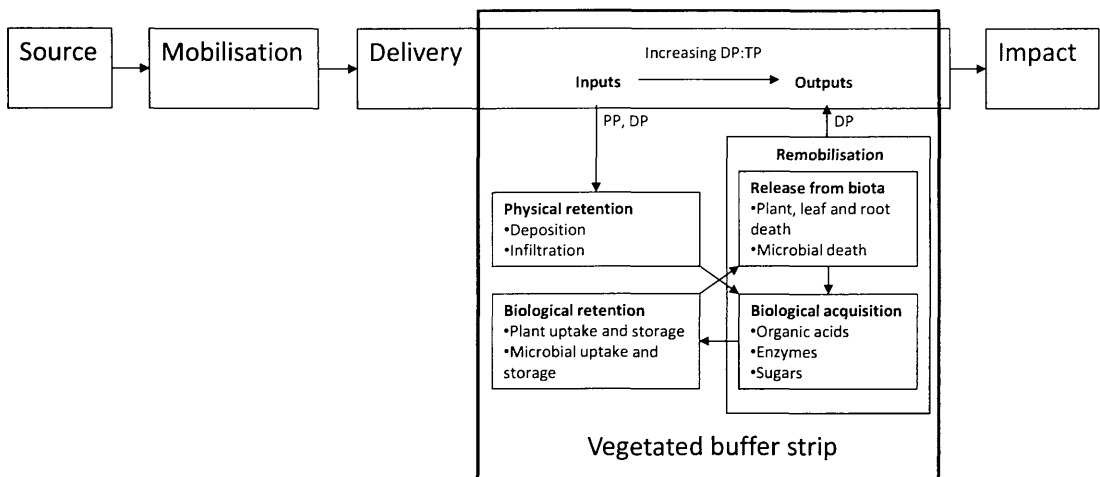
Figure 6.1. Conceptual model of vegetated buffer strip functioning with regard to biological retention and remobilisation as shown being embedded in the transfer continuum model of Haygarth et al. (2005). Arrows indicate movement of P through the transfer continuum and vegetated buffer strip retention and remobilisation tiers. DP, dissolved phosphorus; PP, particulate phosphorus; TP, total phosphorus.

Although the experiments have investigated differences in soil management, the increase in organic matter that this management creates seems to be a key factor in promoting biological P solubilisation. In the first experiment, organic matter increased microbial biomass P and its contribution to P solubility and in the third experiment, the main difference between two soils that leached vastly different quantities of P, was organic matter contents. In the latter experiment, the organic matter rich buffer strip soil magnified plant root induced P leaching under certain species. Organic matter in soils provides a number of benefits; organic matter improves soil structure and stability, promotes denitrification, provides carbon storage and encourages water retention (Johnston, 1986; Soane, 1990; Trewavas, 2004). For these reasons, there is great interest in promoting organic matter in soils by introducing no or minimum tillage in arable farming systems and by establishing buffer strips riparian areas. In arable fields, no tillage could provide an additional benefit to crops by elevating P solubility and availability to the crop; in the third experiment, barley showed increased P uptake in the buffer strip soil with a history of no tillage compared to in an arable soil with a history of regular tillage despite both soils having similar P contents.

However, in riparian buffer strips established with the aim of reducing diffuse pollution, the associated increase in dissolved P transfer risk will not be beneficial, especially as P is a key macronutrient responsible for eutrophication with dissolved inorganic P being highly available to aquatic algae.

The overall aim of the study was to investigate whether biological solubilisation processes operating in riparian buffer strip soils can increase the risk of dissolved P transfer, and in turn, to understand how better to manage them to minimise this. The findings of all of these experiments show that although plant and microbial pools do provide a sink for large quantities of P in buffer strip soils, the processes that plants and microbes use to acquire P and processes associated with the release of P from biota can increase the risk of dissolved P transfer. This biological P retention and remobilisation cycle within buffer strips soils appears to be a loose one at best, with excess soluble P available for leaching after both P acquisition by and release from biota. This suggests minimal competition between plants and microbes for P possibly due to the high P contents of particulate inputs that buffer strips receive and of the agricultural soils on which buffer strips are established. It is not clear if the biological P retention and remobilisation cycle would be tighter with less excess P available for leaching in soils of lower P contents and similar experiments on soils of differing P contents would determine this. Either way, the increased biological solubilisation of P could therefore be partly responsible for the reported increases in the delivery of dissolved P forms from buffer strip soils and other soils featuring no tillage (Butler and Haygarth, 2007; Hodgkinson and Withers, 2007; McDowell and Sharpley, 2001; Uusi-Kämppä, 2005). Although we have shown here that biological solubilisation processes can increase the risk of dissolved P transfer, it remains extremely difficult to quantify the contribution that biological pools and processes make to total P loads to surface waters; indications, here and elsewhere (Blackwell et al., 2010; McDowell et al., 2007; Sharpley, 1981), suggest that the contribution could be large.

Quantifying these contributions would be an important step forward in terms of scientific understanding but would also increase research interest in this highly important area of P transfer.

The increased dissolved P transfer risk posed by buffer strips is a concern because of the bioavailability of these forms of P, and may even hinder attempts to meet Water Framework Directive chemical objectives for P. However, given the multiple benefits that buffer strips provide, for example, the reduction in particulate P transfer risk, this study was not intended as a case against buffer strip implementation but a case for management to enhance the retention of dissolved P forms. Therefore, the study also aimed to use this new knowledge to understand how better to manage biological solubilisation processes to minimise dissolved P transfer risk. It is clear that manipulation of plant and microbial pools and processes could contribute to reducing this risk. An ideal management would be one that reduces soil P contents, slows organic matter build up and limits the accompanying microbial turnover of P, reduces plant root induced P leaching and has an appropriate plant stem density to maintain physical particle trapping processes. Such a management may involve the sowing of appropriate plants in buffer strips coupled with the targeted management of that vegetation. Firstly, buffer strips could be sown with a plant that displays a high P uptake yet has minimal effect on P leaching and has dense, tufted above ground characteristics. Identifying such a plant may involve a screening process aimed at identifying plants with these characteristics. Secondly, also known as 'vegetative mining', this vegetation could be harvested and removed from the buffer strip. Van der Salm et al. (2009) showed that vegetative mining can reduce soil P contents and a coupled reduction in soil solution P concentrations were attributed to changes in sorption and desorption. The effect of vegetative mining on the biological solubilisation of P is quite unknown. This management could reduce stem-derived inputs of soluble and more stable organic matter potentially

reducing the microbial contribution to P solubility. Additional benefits may include a reduction in stem derived inputs of soluble P and an increase in plant tillering which would enhance physical particle trapping processes.

To advance our understanding of the biological P retention and remobilisation cycle in buffer strip soils and to maximise its management, research should be carried out in the following areas:

- Identification of the specific fractions of the microbial community or specific community structures that promote P solubility and what fractions and sources of organic matter stimulate their turnover would allow the targeted management of soil organic matter.

- Determining the effect of biological processes on P solubility in soils displaying a range of soil P contents would highlight the need to or not to reduce the P contents of buffer strip soil to reduce biological solubilisation.

- Studying the long-term retention of DP forms in buffer strips would help to determine whether long-term changes in soil properties, for example, organic matter build up, actually increase delivery outputs of dissolved P forms from buffer strips.

- Identifying and sowing a plant species that has a high P uptake yet has minimal effect on P leaching and has dense, tufted above ground characteristics would optimise plant induced processes for the retention of dissolved forms of P in buffer strips.

- Determining the exact sources and nature of plant root derived soluble carbon and how and what fractions and forms of soil P are affected would vastly improve our understanding of soil-plant-microbial interactions.

- Research into the effect of vegetative mining on biological solubilisation processes would increase the understanding of this management practice, which would be essential before implementation of these practices.

- Quantification of the contributions that biological P pools and processes make to surface water P loads would increase research interest in this highly important area of P transfer.

The overall message is that the solubilisation of P during acquisition by biota and the release of P from biota during death could increase the risk of dissolved P transfer and therefore the management of these pools and process would help to maximise dissolved P retention within buffer strips.

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Appendices

Appendix 1. Microbial biomass phosphorus contributions to phosphorus solubility in riparian vegetated buffer strip soils – Location of sampling sites

Hampshire, River Avon catchment

Location of buffer strip sites within Hampshire

Site Ref	Grid Ref	Stewardship Scheme	Years since establishment	Slope	Width	Landuse / Field Crop
A1	419148.73,162416.15	Countryside Stewardship (CSS)	>10 yrs	5.5-6 %	6 m	Wheat
A2	420774.08,161423.11	Entry level Stewardship (ELS)	5 yrs	4.5-6 %	6 m	Fodder Beans
A3	421362,161522	CSS	7 yrs	4 %	6 m	Winter barley
A4	421519,163468	ELS	5 yrs	4 %	6 m	Oats

Site A1. CSS: >10 year old, bordering Kennet & Avon Canal

Site A2. ELS: 5 year old, bordering Deane water

Site A3. CSS: 7 year old, bordering Deane water

Site A4. ELS: 5 year old, bordering Kennet and Avon Canal

Location of buffer strip sites within Cumbria

Site Ref	Grid Ref	Stewardship Scheme	Years since establishment	Slope	Width	Landuse / Field Crop
E1	539133.57,347768.15	ELS	4 yrs	4-10 %	6 m	Wheat
E2	540041.98,348097.34	CSS	7yrs	5.5 %	6 m	Oats
E3	530195.8,348673.11	CSS	8yrs	2-5 %	6 m	Spring OSR
E4	539229.53,347280.54	ELS	4 yrs	2-3.5 %	6 m	Wheat

Site E1. ELS: 5 year old, bordering Ravensgill Beck

Site E2. CSS: 7 year old, sheer wooded slope down to R. Petteril

Site E3. CSS: 8 year old, bordering ditch

Site E4. ELS: 4 year old, bordering Ravensgill Beck

Norfolk, River Wensum catchment

Location of buffer strip sites within Norfolk

Site Ref	Grid Ref	Steward ship Scheme	Years since establis hment	Slope	Width	Landuse / Field Crop
W1	322697.73,609017.94	ELS	5 yrs	2-4 %	6 m	Spr. Barley (harvested)
W2	325871.52,613051.43	CSS	8 yrs	2.5-3 %	6 m	Wheat (½ harvested)
W3	315763.52,594997.71	CSS	8yrs	5 %	6 m	OSR (harvested)
W4	327697.82,600814.46	ELS	5 yrs	3-4 %	6 m	Wheat

Site W1. ELS: 5 year old, bordering ditch

Site W2. CSS: 8 year old, bordering ditch

Site W3. CSS: 8 year old, bordering ditch

Site W4. ELS: 5 year old, bordering ditch

Appendix 2. Retention of phosphorus forms by a narrow vegetated buffer strip – Sorption of phosphorus to apparatus and storage vials

Experiment 1

Phosphorus (P) will interact with experimental apparatus designed to collect waters for phosphorus analysis. Materials used in the apparatus that are inserted into soil, could potentially sorb of P from the soil solution and/or water collected, introducing inaccuracy to data. The aim of this experiment was to determine any sorption of phosphorus to material used in experimental apparatus.

The experimental apparatus used to collect runoff involved a number of materials. A lysimeter pan positioned at the soil interface to collect the runoff water was made of a polyethylene tray and perforated stainless steel. Runoff waters were diverted from the collector via a PVC hose to a polyethylene barrel which provided the water storage.

Five 0.5 g samples collected from individuals of each of the four materials were weighed into 30 ml polystyrene vials. 10 ml of 0.18 mg L^{-1} PO_4 solution was decanted into each vial. Five vials had PO_4 solution but no materials and acted as controls. The vials were stored outdoors in a completely randomised design for two weeks. Reactive P concentrations of the solution were then determined by ammonium molybdate colourimetry. The data was analysed by linear modelling to determine significant differences in mean P concentrations between groups using R statistical software.

No significant difference was found between the control group and any of the other groups (Table 1). This suggested that there would be no significant sorption to the experimental apparatus between runoff events spaced two weeks apart.

Reactive P concentrations (mg L^{-1}) for solutions in vials with mean, standard deviation and standard error.

Replicate	Control	Polyethylene tray	Perforated Stainless steel	Polyethylene barrel	PVC hose
1	0.177	0.174	0.198	0.175	0.178
2	0.208	0.175	0.190	0.175	0.185
3	0.181	0.175	0.193	0.177	0.175
4	0.181	0.183	0.184	0.181	0.180
5	0.180	0.173	0.189	0.182	0.181
Mean	0.185	0.176	0.191	0.178	0.180
Standard deviation	0.013	0.004	0.005	0.003	0.004
Standard error	0.006	0.002	0.002	0.002	0.002

Experiment 2.

Samples cannot always be analysed immediately. If samples for reactive P analysis are left for longer than 24 hours hydrolysis of organic P compounds can occur increase reactive P concentrations. Analysis of samples for reactive P was therefore considered a priority which meant the samples for total P analysis were left in storage for up to 1 month. This lead to the potential for sorption of P to storage vials introducing inaccuracy to the results. The aim of this experiment was therefore to determine any sorption of phosphorus to sample containers during storage.

Nine runoff samples were collected from runoff plots in May 2012. The samples were analysed in triplicate for total P and total dissolved P after 1 week of collection and again after 4 weeks of collection. Unfiltered samples were stored in 500 ml HDPE bottles and

filtered samples were stored in 30 ml polystyrene vials. Storage was in darkness < 4°C. A Paired samples t-test was used to determine significant differences between means for the two analysis points.

After 3 weeks a significant difference in mean concentrations was found between to two groups of analyses for both total P and total dissolved P (p <0.05). Mean total P concentration was 0.264 at week 1 and 0.256 mg L^{-1} at week 4 therefore exhibiting a mean reduction of 9 µg L^{-1} over the 3 week period. Mean total dissolved P concentration was 0.153 at week 1 and 0.132 mg L^{-1} at week 4 therefore exhibiting a mean reduction of 22 µg L^{-1} over the 3 week period.

Although these are only small differences in mean concentration, they could have implications for the calculations of dissolved unreactive P in the study, as the concentrations of this fraction in runoff samples were low compared to other P fractions. This sorption of P in the vials reduced total dissolved P concentrations, which would lower the concentration of dissolved unreactive P which is calculated by subtracting dissolved reactive P from total dissolved P.