CRANFIELD UNIVERSITY

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Filter socks to mitigate sediment, sediment-bound phosphate and orthophosphate losses, from arable lands under extreme rainfall events

Department of Agrifood

School of Water, Energy and Environment

PhD

Academic Year: 2017-2018

Supervisors: Dr Robert Simmons and Professor Jane Rickson

Subject Advisor: Dr Ruben Sakrabani

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ABSTRACT

Agricultural diffuse pollution is a major environmental issue within the UK. Within England alone, sediment and phosphates in agricultural runoff account for 2967 rivers failing their Water Framework Directive (WFD) water quality targets. Effective end-of-pipe solution sediment control measures include silt fences, buffer strips and berms. However, with the exception of buffer strips, these are not widely used in agricultural lands. Furthermore in terms of extreme rainfall events, their long-term efficacy is limited or unproven, as well as their ability to also remove orthophosphate. Filter socks (FS) are widely used as construction site sediment control within the USA, and could provide another mitigation option; however there has been limited testing for a UK environment, and their current fill media does not aid orthophosphate removal. Phosphorus sorbing materials (PSMs) are widely used within the wastewater treatment industry to remove orthophosphate. This research evaluated the efficacy of PSM amended FS to concurrently remove sediment, sediment-bound phosphate, and orthophosphate.

In Phase 1, FS were evaluated in terms of their sediment removal ability, with and without a proprietary PSM, under UK agricultural field conditions. Runoff and eroded sediment was collected from erosion plots under a maize cropping regime. The 9-month replicated field trial results indicated variable results. The fill media produced an initial release of fines and orthophosphate after installation, although this declined over time. This flush event significantly increased the amount of sediment and orthophosphate found within the runoff of the FS compared to the runoff from the control, in sampling period 1. By the last sampling period, irrespective of fill-media (Woodchip or PAS 100 Compost), FS reduced runoff sediment load compared to the non-FS control. Orthophosphate removal was not increased by the addition of the proprietary PSM. Consequently a range of alternative PSMs were evaluated in Phase 2.

Alternative PSMs were identified from a literature review. Their ability to remove orthophosphate was established through a fully replicated column experiment over a range of orthophosphate concentrations (0.08 – 1.30 mg P l^{-1}). The results indicate that ferrihydrite and goethite ochres were significantly more effective than all other treatments, with orthophosphate removal efficiencies ranging from 51 – 99 % and 32 – 94 %, respectively. Furthermore the ferrihydrite ochre was the only PSM to reduce the orthophosphate concentration to below that of the water quality target for the Lugg river catchment (0.05 mg P l^{-1}). As the most effective PSMs, these were taken forward to Phase 3 where PSM amended FS were assessed for concurrent sediment, sediment-bound phosphate and orthophosphate removal under simulated laboratory experiments.

Efficacy and performance was established across a series of replicated laboratory experiments using a rainfall-runoff simulator. These incorporated extreme rainfall events (80 mm hr^{-1} intensity, 5 - 25 min duration), representing return periods of 5, 18, 41, 74 and 126 yr for the Lugg catchment, Herefordshire. These used an erodible sandy loam soil that represented the dominant erodible soil type of the Lugg catchment, and a 17° slope representing the 80th Percentile slope for these erodible soils within the Lugg catchment. There were no significant differences in sediment removal efficiency between the treatments, irrespective of fill media (Woodchip or PAS 100 Compost), PSM (ferrihydrite ochre, goethite ochre, proprietary product), or rainfall event. Sediment removal efficiencies ranged from 66 – 97%. Treatments consistently removed up to 88% and 82% of eroded clay and silt sized particles, which is significant for the effective removal of sediment-bound phosphate. Ferrihydrite was the most effective PSM for orthophosphate removal with removal efficiencies of up to 34%.

The 3 year trial indicated that more research is required to establish the wider validity of FS as a mitigation measure. This needs to encompass extensive field trials, incorporating their efficacy in other cropping situations with different soil types, slopes and climate conditions (e.g. annual rainfall). The research showed that PSM-amended FS are efficient at concurrently removing sediment, sediment-bound phosphate, and orthophosphate from runoff in laboratory studies, and are efficient under a range of laboratory based rainfall events. However this needs to be verified in field conditions to ensure that they remain a viable mitigation option for the future. Furthermore, research needs to be undertaken into the longevity of the materials for sediment and orthophosphate control in field conditions. .

Keywords: diffuse pollution; soil erosion; phosphate; ferrihydrite; catchment management

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LIST OF ABBREVIATIONS

2LFH	2-line ferrihydrite
6LFH	6-line ferrihydrite
BMP	Best Management Practice
BPS	Basic Payment Scheme
BS	Buffer strip
C	Compost
CAP	Common Agricultural Policy
CBA	Cost-benefit analysis
CSF	Catchment Sensitive Farming
DEFRA	Department for Environment, Food and Rural Affairs
DWTR	Drinking water treatment residual
EA	Environment Agency
EPSD	Eroded particle size distribution
EOPS	End of Pipe Solution
EU	European Union
FB	Filter berm
Fc-O	Ferrihydrite ochre
FE	Fullers Earth
FS	Filter socks
G-O	Goethite ochre
GAEC	Good Agricultural and Environmental Conditions
K	Kaolin
LVCS	Liquid Vertical Continuous Series
NMP	Nutrient Management Plan
OM	Organic matter
PO_4^{3-}	Phosphate
Pp	Proprietary product
PSD	Particle size distribution
PSE	Phosphate sorption efficiency
PSM	Phosphorus sorbing material
RE	Rainfall Event
RTP	Return Period

SA	Surface area
SAC	Special Area of Conservation
SB	Sediment-bound phosphate
SF	Silt fence
SSSI	Site of Special Scientific Interest
UK	United Kingdom
USA	United States of America
W	Woodchip
WFD	Water Framework Directive

CHAPTER 1: INTRODUCTION

1.1 Water Pollution

In England and Wales only 83% of waterbodies are meeting their water quality targets as prescribed by the EU Water Framework Directive (WFD). Agricultural activity is a major cause of diffuse pollution, and a main reason water quality standards' are being exceeded. Specifically, 487 rivers in England are failing their WFD water quality targets for sediments, and 2480 due to excessive agricultural phosphate (PO_4^{3-}) inputs. An additional 2346 are failing due to water treatment plants being unable to meet PO_4^{3-} discharge targets (Environment Agency 2015a).

Agriculture has been found to contribute 70% of sediments, 60% of nitrates and 25% of PO_4^{3-} to waterbodies (National Audit Office 2010). Annually 2.2 million tonnes of soil is lost due to erosion, costing the agricultural industry £180 - £280 million per annum (Graves et al. 2011). These sediment and nutrient inputs have a knock-on impact on to aquatic ecosystems through sedimentation, flooding and eutrophication (Smit et al. 2009, Withers et al. 2014, Glibert 2017). Aquatic species within these environments suffer from decreased light and oxygen levels, as well as increased cloudiness and shear impacts created by contact with the sediment (Birtwell 1999, Robertson et al. 2006, Kjelland et al. 2015). Consequently some of these waters also fail to meet their EU Habitats Directive targets (Natural England 2017, Natural Resources Wales 2017, Scottish Natural Heritage 2017). Furthermore it is generally accepted that climate change has resulted in significant alterations to the amount, frequency, type, intensity and energy of UK rainfall events (REs), with an increasing frequency of 'extreme' REs (IPCC 2014). These can generate high runoff volumes increasing the movement of sediments and PO_4^{3-} that subsequently compromise off-site water quality. Therefore, there is a real need to manage sediment and PO_4^{3-} inputs to waterbodies in order to meet water quality and habitat targets now, and in the long term.

One such area where water quality management is required is the Wye river catchment. The River Wye is a diverse, 135 mile, cross-border system. It is recognised as a Site of Special Scientific Interest (SSSI), with the lower stretches also recognised as a Special Area of Conservation (SAC) under the EU Habitats Directive, and is therefore important for habitats and species, as well as for flood management, abstraction, and recreation purposes. Consequently clean water is essential for the catchment, however it has been identified that the River Wye is failing its water quality targets for sediments (0.1 mg l^{-1}) and orthophosphates (0.03 mg P l^{-1} in the upper stretches, and 0.05 mg P l^{-1} in the lower stretches and the Lugg tributary). This is causing the catchment to be uncompliant with the EU WFD as well as the EU Habitats Directive.

In response to this, the Environment Agency (EA) and Natural England (NE) compiled a Nutrient Management Plan (NMP) to present strategies to enable the catchment to meet these targets. The NMP would also consider future changes within the catchment according to local legislation and plans. This research used the Lugg catchment as a case study area, both for the specific field trials, as well as its NMP water quality targets as performance criteria.

1.2 Sediment control solutions

Sediment control end-of-pipe solutions (EOPS), such as silt fences (SF), buffer strips (BS) and filter berms (FB), are already used to mitigate sediment losses from runoff (Faucette et al. 2009c, Rickson 2014, Pan et al. 2017). BS are so widely used that they are included under the Basic Payment Scheme (BPS) Greening Rules (Rural Payments Agency 2017). However their preference for removal of sand particles over clays and silts (Barling and Moore 1994, Abu-Zreig 2001), and their ability to remobilise particles (Stutter et al. 2009, Habibiandehkordi et al. 2014, Withers et al. 2014), impacts their ability to reduce overall sediment load or associated sediment-bound (SB) PO_4^{3-} (Reichenberger et al. 2007, Liu et al. 2008) which preferentially sorbs to clays and silts (Edzwald et al. 1976, Gérard 2016). The incorporation of phosphorus sorbing materials (PSMs) to EOPS has to date been limited (Faucette et al. 2008, Shipitalo et al. 2012, Habibiandehkordi et al. 2014). PSM amended BS have been trialled (Wagner et al. 2008, Habibiandehkordi et al. 2014) with some limited success, however the PSMs require frequent reapplication, and require measures to be in place to limit their detachment and transport, and subsequent remobilisation of PO_4^{3-}.

This research evaluates filter socks (FS) which have proven efficacy (Faucette et al. 2005, 2008, Shipitalo et al. 2010) in sediment control, and are widely used in the USA as a best management practice (BMP) on construction sites. FS have been shown to remove high amounts of clays, silts and sands, thereby reducing sediment load and concentration in runoff entering waterbodies, as well as associated SB PO_4^{3-} (Faucette et al. 2008, 2009a, Waters 2010). However, to date no research has investigated their efficacy as sediment control in a UK agricultural context, or their efficacy to concurrently remove soluble orthophosphate from runoff within a UK, or an agricultural context. Consequently this research has also evaluated the capability of selected PSMs to sorb soluble orthophosphate. Essentially and uniquely, the research evaluates the effectiveness of PSM-amended FS to concurrently remove sediment, SB PO_4^{3-} and soluble orthophosphate, in the context of specific water quality targets, under simulated laboratory conditions.

It is envisaged that the results of this research will provide a viable solution, which can be used to manage the impacts associated with agricultural runoff, and further opportunities to develop the measure for widespread uptake. Soil and agronomic practices such as conservation tillage (Shipitalo and Edwards 1998, Mhazo et al. 2016, Wang et al. 2017), cover cropping (De Baets et al. 2011, Zhang et al. 2017), inter cropping (Tilman et al. 2002, De Baets et al. 2011, Lenka et al. 2017), surface protection (Fiener and Auerswald 2006, Rickson et al. 2010, Mekonnen et al. 2015), and amendments (Sharpley et al. 2006, Schoumans et al. 2014) increase the overall soil health and resilience of the soil to the erosive forces of detachment and overland flow. This also reduces runoff, and therefore nutrient losses. As an EOPS, FS will not prevent the detachment phase of the soil erosion process, but can be used to manage both transport and deposition. Consequently the offsite impacts of agricultural runoff on water quality will be limited.

1.3 Research Aims and Objectives

Aim: The overall project aim is to critically evaluate whether FS can be combined with PSMs to facilitate the concurrent removal of sediment, SB PO_4^{3-} and orthophosphate from runoff. The following objectives were undertaken in order to meet this:

- **Objective 1**: Critically evaluate existing sediment control measures regarding their capability to remove sediment from runoff. This was undertaken through an extensive literature review (Chapter 2);
- **Objective 2**: Critically evaluate the effectiveness of FS to remove sediment from runoff. This was undertaken through field trials (Chapter 3) and rainfall simulation experiments (Chapter 5);
- **Objective 3**: Identify PSMs, and critically evaluate their effectiveness in removing soluble orthophosphate from runoff. This was undertaken through an extensive review of existing literature (Chapter 2), laboratory column trials (Chapter 4) and rainfall simulation experiments (Chapter 5);
- **Objective 4**: Critically evaluate the effectiveness of FS amended with PSMs in removing sediment, SB PO_4^{3-} and orthophosphate from runoff. This was undertaken through rainfall simulation trials (Chapter 5) at a range of RE return periods (RTPs);
- **Objective 5**: Carry out a cost-benefit analysis (CBA) of FS application for the reduction of sediment, SB PO_4^{3-}, and soluble orthophosphate losses from agricultural land. This involved a suitability assessment of these materials and solutions for the agricultural sector. This was undertaken using the results of the laboratory column trials (Chapter 4) and the rainfall simulation experiments (Chapter 5). Additional discussion is made on this in Chapter 6.

Case study: The study was applied to the Lugg river catchment, Herefordshire, UK; a main tributary of the River Wye.

1.4 Thesis Outline

This thesis has been written in a paper format and consequently the research phases have been written as academic journal articles or conference proceedings (Chapters 2 – 6). Chapter 2 is intended for the *Journal of Environmental Quality*. Chapter 3 was published as conference proceedings after being presented at the World Conference on Soil and Water Conservation (Cooke et al. 2017). Chapter 4 has been written as an academic article for the *Water and Environment Journal*. Chapter 5 has been written as an academic article for the *Journal of Soil and Water Conservation,* however will be submitted to the journal as two separate articles to be reformatted post-submission. Chapters 4 and 5 will be submitted for review to their target journals after completion of this thesis. Adjoining chapters (Chapters 1, 6 and 7) provide background information to the research topic, the wider context using the research outcomes, and the overall research conclusions. The chapter structure of this submission follows the research progression:

Chapter 2; 'C*ritical assessments in tackling agricultural phosphate losses; sediment control and phosphorus sorbing materials',* is a comprehensive review (Obj. 1 and 3) which details the existing knowledge surrounding EOPS, PSMs used to remove orthophosphate in the water treatment industry, processes involved in P-sorption, and factors affecting PO_4^{3-} sorption capacity. A critical assessment is then made as to which PSMs would be suitable for placement within EOPS with a focus on FS to facilitate the simultaneous removal of sediment, SB PO_4^{3-} and orthophosphate, in order to provide measures to meet existing water quality targets.

Chapter 3; '*Filter socks to mitigate runoff, soil and orthophosphate losses from arable lands under current and extreme rainfall events*' is a conference proceeding, which details the results of a replicated 9-month field trial which evaluated the efficacy of FS and selected fill media to remove sediment, SB PO_4^{3-} and orthophosphate, from agricultural runoff (Obj. 2).

Consequently this led to a series of replicated laboratory-based column experiments which exposed various PSMs (identified by the Chapter 2 review), mixed with two widely available FS fill media; woodchip (W) and compost (C), to PO_4^{3-} concentrations, ranging from 0.18 – 1.30 mg P l^{-1}. These concentrations were applied twice over a 48 hr period representing two REs. The phosphate sorption efficiency (PSE) of the selected PSMs was established through a series of mass balance equations. The PSMs selected included natural kaolin (K) and fullers earth (FE), ferrihydrite ochre (Fc-O) and goethite (G-O) by-products, and a commercial proprietary product (Pp), to allow comparison with materials that are already used in PO_4^{3-} control.

Chapter 4; 'E*fficacy of selected phosphorous sorbing materials (PSMs) to enhance the orthophosphate sorption efficiency of filter socks'* is a research paper, and details the results of the column experiments (Obj. 3 and 5) in the context of the PO_4^{3-} water quality targets for the River Lugg. A CBA of the selected PSM for PO_4^{3-} control is also discussed. The PSMs with the highest PSE, as well as the commercial Pp, were taken forward to the final phase of the research whereby they were used as PSMs within FS under laboratory conditions.

The PSMs were mixed with W or C at the same application rate as the Pp, and placed within a FS. The FS were then placed on sloped erosion rigs packed with an erodible soil and subjected to a range of RE RTPs. Efficiency of the PSM-amended FS to control sediment and SB PO_4^{3-}, and the PSMs to control orthophosphate was established for various RE RTPs. Treatment performance was evaluated in terms of PSE, and the ability to meet the Lugg catchment water quality targets.

Chapter 5; ‘*The efficacy of PSM-amended filter socks to simultaneously remove sediment, sediment-bound phosphate and orthophosphate from runoff*’, is a research article and details the results of the simulated laboratory trials in the context of the Lugg water quality targets. These results served to identify the most efficient PSMs and fill media for sediment, SB PO_4^{3-} and orthophosphate removal, and identify interactions between sediment control and PO_4^{3-}control materials (Obj. 2, 3 and 5). The applicability of PSM-amended FS for agricultural systems, based on efficacy, accessibility and cost of the materials, is also discussed.

Chapter 6; ‘*Integrated Discussion*’, does not serve to provide specific details into analytical or academic results, as these have already been discussed in the individual chapters (Chapters 2 - 6), but serves to identify the research outcomes in terms of their real world impact, i.e. to the agricultural sector and in terms of water quality improvements (Obj. 5). This chapter is essential as it identifies how the overall aim of the research was delivered, and consequently how the different chapters fit together, along with future research directions.

Chapter 7; ‘*Conclusions*’ discusses the main outcomes of this 3 year study.

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CHAPTER 2: CRITICAL ASSESSMENTS IN TACKLING AGRICULTURAL PHOSPHATE LOSSES; SEDIMENT CONTROL AND PHOSPHORUS SORBING MATERIALS

Abstract

Agriculture, soil degradation, and increased frequency of extreme REs are causing increasing soil erosion, allowing sediments, sediment-bound (SB) PO_4^{3-} and orthophosphates to enter waterbodies. This diffuse pollution is a global issue impacting on the water quality of rivers and lakes. In the EU, the water environment is protected through the WFD. There are sediment control techniques that if installed and maintained correctly can prevent sediments (and associated SB PO_4^{3-}) from travelling offsite. However many are not widely used within a European agricultural context. Furthermore PSMs are widely used within the wastewater industry for the removal of orthophosphates. An opportunity exists to combine these approaches. This paper initially reviews the performance of available sediment control structures for sediment removal, as well as their impact on PO_4^{3-} losses. Secondly, it evaluates the efficiency of widely used PSMs for removing orthophosphates from water, used within the wastewater and drinking water treatment industries. Finally, it evaluates and considers the range of options and direction of future research to combine appropriate sediment control structures with PSMs for the effective and concurrent removal of sediment, SB PO_4^{3-}, and orthophosphates, from agricultural lands in the context of the WFD.

Highlights

- Agricultural diffuse pollution is a global issue impacting water quality
- Sediment control structures effectively remove sediment and SB PO_4^{3-}
- PSMs are widely used in the water treatment industry
- The opportunity exists to combine PSMs with sediment control structures
- Concurrent sediment, SB PO_4^{3-}, and orthophosphate removal is achievable

Keywords

Agricultural diffuse pollution; soil erosion; sediment control; phosphorus sorbing materials; orthophosphate removal

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The spelling and formatting of the original paper has been adjusted to fit the format of this thesis.

2.1 Introduction

The European Union's (EU) Water Framework Directive (WFD; 2000/60/EC) is a comprehensive piece of legislation protecting the water environment, stating that by 2027 all inland and coastal waters must achieve 'good' status for a number of biological and chemical conditions, unless the measures to achieve this are disproportionately costly, or technically unfeasible. The Directive defines how to achieve this through environmental objectives and ecological targets, and diffuse pollution is one of the key challenges to achieving its objectives.

Currently in the UK, only 17% of WFD eligible waterbodies meet their water quality targets due to both point and diffuse pollution sources (Environment Agency and Natural England 2014, Environment Agency 2015b). Agricultural diffuse pollution is difficult to control effectively due to its widespread and untargeted nature across the landscape. Pollution from agricultural land is thought to deliver up to 70% of sediments, 60% of NO_3^- and 25% of PO_4^{3-} to receiving waters (National Audit Office 2010). Specifically, 487 rivers in England are failing their water quality targets for sediments, 2480 due to excessive agricultural PO_4^{3-} inputs, and another 2346 due to the water industry not being able to meet PO_4^{3-} discharge targets (Environment Agency 2015a).

This is a result of interactions between rainfall intensity, soil erosion and surface runoff processes, timing and extent of nutrient applications, and lack of effective, adoptable and cost-effective mitigation options. Agriculture can have an impact upon the amount of suspended sediments and nutrients, particularly PO_4^{3-} and NO_3^-, being delivered to the water environment (Bennett et al. 2001, Tilman et al. 2002). These have the potential to cause ecological damage, through increased turbidity, sedimentation and eutrophication (Tilman et al. 2002, Withers et al. 2014).

PO_4^{3-} from agricultural diffuse pollution originates from a combination of the inappropriate application of manure or fertilisers onto farmlands (e.g. timing, extent), and the cultivation of steeply sloping lands with erodible soils (e.g. fine silts and sands). Topography, land use (bare soil, grassland, forest, row cropping etc.) and increasingly frequent extreme REs further exacerbate PO_4^{3-} losses. However, there remains a paucity of effective, adoptable and cost-effective mitigation options. PO_4^{3-} is particularly detrimental as it is easily delivered to the receiving waters by runoff in solution, adsorbed onto the soil particles, or by combining with major elements (such as Ca, Mg, Al and Fe), after which it speeds up the eutrophication process (Bennett et al. 2001, Schoumans et al. 2014). For this reason, it is also essential that the amount of PO_4^{3-} adsorptive sediment (mainly clays), being delivered to these waters is minimised. Current methods to decrease agricultural PO_4^{3-} losses include improved manure/fertiliser management, application of lime to fields, cover cropping, and BS (Deasy et al. 2008, Schoumans et al. 2014). However, much of the PO_4^{3-} in waterbodies continues to be remediated by drinking water treatment works. This increasing need for the removal of PO_4^{3-} is expensive (Pretty et al. 2000, Houses of Parliament 2014, Department for International Trade 2015). Consequently, in-field prevention of PO_4^{3-} movement is preferred.

Current methods to decrease soil (and consequently SB PO_4^{3-}) losses from agricultural lands are focussed around agronomic and mechanical measures

(Schoumans et al. 2014), which are used either in-field to prevent initial soil particle detachment (at source), or as an EOPS to prevent the movement of eroded soil (i.e. pathway) off-site (i.e. to the receptor) as sediment. These measures include cover cropping (De Baets et al. 2011, Zhang et al. 2017), conservation tillage (Shipitalo and Edwards 1998, Mhazo et al. 2016, Wang et al. 2017), grassed waterways (Fiener and Auerswald 2006, Mekonnen et al. 2015), buffer strips (BS) (Pan et al. 2017, Van Vooren et al. 2017), filter berms (FB) (Tyler 2001, Faucette et al. 2005), filter socks (FS) (Faucette et al. 2009a, Shipitalo et al. 2010) and silt fences (SF) (US EPA 2012, Vinten et al. 2014). However, FB and SF are not yet widely used on UK agricultural lands. Whilst many of these measures are currently encouraged through the EU Common Agricultural Policy (CAP) and greening schemes (Rural Payments Agency 2017), they are still voluntary. With varying efficiencies and costs (Newell Price et al. 2011), rates of uptake are relatively low (Rickson et al. 2010, Newell Price et al. 2011).

Ideally preference would be to prevent the first phase of the soil erosion process (i.e. detachment of soil particles) in-field. However, if this cannot be achieved, and as a precautionary measure, sediment control or EOPS are necessary to prevent sediment and SB PO_4^{3-} from entering receiving water bodies.

Whilst the delivery of sediment and SB PO_4^{3-} to waterbodies can be minimised using sediment control and EOPS, these are as yet not able to prevent the delivery of soluble orthophosphate to the waters. Currently, the majority of orthophosphate is treated by the wastewater industry in treatment plants. Treatment of orthophosphate in wastewater usually involves filtration, precipitation and adsorption using metal ions (Yeoman et al. 1988, De-Bashan and Bashan 2004), biological breakdown (Yuan et al. 2012, Zuthi et al. 2013), a combination of both (Yeoman et al. 1988, Nancharaiah et al. 2016, Zou and Wang 2016), or more recently, auto-mineralisation (Pratt et al. 2012). These technologies are currently only applied to PO_4^{3-} removal in the wastewater treatment industry in order to meet discharge targets; however they would be widely beneficial for the treatment of orthophosphate within agricultural runoff (diffuse pollution), if an effective practice for their use could be found. Combining PO_4^{3-} wastewater treatment technologies with sediment control and EOPS with proven efficiency would allow sediment, SB PO_4^{3-}, and orthophosphate to be treated close to source. This could significantly reduce the PO_4^{3-} inputs to waterbodies, and consequently the treatment costs currently paid by the wastewater industry and ultimately, their customers.

Consequently in this paper, focus will be given to sediment control measures, EOPS and effective PSMs. This paper will critically evaluate the range of options available for the control of sediment, SB PO_4^{3-} and orthophosphate from agricultural lands in the context of the WFD.

2.2 Sediment Control

Soil erosion is the process by which soil is detached, transported and eventually deposited, away from its place of origin by the kinetic energy associated with rainsplash and/or runoff. Soil particles that enter waterbodies can be entrained by the current, and then undergo secondary deposition. Excessive sediment entrainment within rivers can cause waters to become turbid. Sedimentation occurs during slow flows where there is a reduction in velocity, and therefore the transport capacity of the river, which causes the sediment to fall out of suspension. Sedimentation and deposition can cause river flooding, which can cause widespread damage to both human and aquatic life.

Sediment control measures are a form of EOPS, and do not prevent the detachment phase of the soil erosion process. They prevent the impacts of soil erosion on the water environment by reducing the sediment load inputs to waterbodies (i.e. transport and deposition phases) through a dramatic reduction in runoff velocity. Consequently, they should not be used instead of traditional erosion control measures, but should supplement them within a wider erosion control management strategy, or be used to control extreme events when erosion control measures alone may not be sufficient.

Typical EOPS include SF, FB, BS, wattles and FS. There is some evidence to suggest that some of these EOPS may also be used as erosion control to prevent the initial detachment of soil particles when placed correctly within a field scenario (Rickson 2014). However more research needs to be undertaken on this to optimise their placement relative to their cost and benefit, and consequently their level of control is generally unknown across the detachment and transport phases of soil erosion within an agricultural landscape. Furthermore, empirical data on the effectiveness of these measures is limited.

2.2.1 Silt fences

SF are widely used for control of sediment movement. They consist of a stretched permeable geosynthetic material, staked into the ground. They work by creating a temporary retention pond, which allows the suspended sediment particles to be deposited whilst the runoff filters through the geotextile at reduced velocity and associated transport capacity (Robichaud and Brown 2002). They are the most commonly used sediment control measure worldwide (Cooke et al. 2015), and are considered a BMP (Keener et al. 2007, US EPA 2012).

Even though SF are commonly used, their effectiveness varies widely due to inappropriate installation, maintenance and compliance with best practice (Cooke et al. 2015). Furthermore, SF have limitations and commonly present problems upon installation (Idaho Department of Environmental Quality 2005, Morgan 2005, US EPA 2012) , namely:

- They are limited to catchment areas <2 ha;
- They cannot be used where there is a concentrated flow path;
- Many designs need the soil immediately upslope to be compacted (thus preventing undercutting) to work effectively, consequently damaging the soil structure making it more susceptible to runoff and erosion;
- The need for a deep soil/bedrock substrate to allow the fence to be staked in.

Although a failing SF is a common sight (Cooke et al. 2015) their widespread uptake is supported by laboratory studies which frequently show high sediment removal/trapping efficiencies (Barrett et al. 1998, Cooke et al. 2015). The discrepancies between laboratory and field results are due to the influence of sediment overtopping, undercutting or being diverted around the SF due to clogging of the geotextile (Barrett et al. 1998, Keener et al. 2007, Chapman et al. 2014). Furthermore, the lack of maintenance after installation exacerbates the discrepancies in efficiency (Cooke et al. 2015). Further, their high sediment removal efficiency has mainly been attributed to the removal of sand particles (up to 90% of total mass in runoff is sand). A much lower (typically only 20% of total mass in runoff) removal of silt and clay sized particles is experienced(US EPA 1993b, Wishowski et al. 1998), as these tend to be smaller than the pore size of the geotextile (Keener et al. 2007, Koerner and Koerner 2015). It is the silt and clay sized particles which have the largest impact on water quality and aquatic degradation, due to their large specific surface area (SA) and ability to adsorb and transport SB PO_4^{3-}.

A few studies have reported encouraging sediment removal efficiencies of SF (Robichaud and Brown 2002, Vinten et al. 2014), if properly installed and maintained. Furthermore the lower cost, easy installation and maintenance, site mobility and potential reuse make SF ideal, especially in arable settings. However these studies did not differentiate between the particle size fractions that were removed from the runoff by the SF. Therefore, in general SF are not an adequate solution for many agricultural settings where it is essential that sediment particles of all sizes are removed.

2.2.2 Filter Berms

FB are ridges placed perpendicular to runoff flow, that consist of compacted soil, rocks, compost (C) or sandbags, sometimes including a geomembrane (Idaho Department of Environmental Quality 2005, Risse and Faucette 2009). They can be temporary or permanent (if maintained), and typically divert runoff away from an area, or contain it in a retention zone (State of Oregon Department of Environmental Quality 2006, Risse and Faucette 2009). More recent designs utilising C and rock rip rap also filter sediment from runoff allowing its deposition within or immediately upslope of their structure (Clouston 1996, Faucette et al. 2005). This eventually needs to be removed; either when the FB has reached the maximum capacity of the amount of sediment it is able to retain, or when it is no longer required.

FB are commonly used in the US and are a BMP in many states; however they are not used as frequently as SF. There are well formed guidelines on the media parameters for their construction; both vegetated and unvegetated (Alexander Associates 2006). Furthermore there is guidance on best practice for their design, installation and maintenance.

Where FB are required for filtration as well as runoff diversion, sediment filtration and adsorption of nutrients is possible. Furthermore, FB aid in vegetation establishment and can be incorporated into the native soil once no longer required (Tyler 2001, Faucette et al. 2009b). However like SF, FB have a number of limitations:

- They can only be used for minor runoff flows otherwise they are likely to undergo structural failure, and the constituents are likely to be dislodged and transported in the runoff (Idaho Department of Environmental Quality 2005; Morgan et al. 2003);

- They are unsuitable for slopes >15 degrees (Idaho Department of Environmental Quality 2005; Morgan et al. 2003);
- C FB have the potential to produce an initial ‘flushing effect’ of pollutants (PO_4^{3-} and NO_3^-) and fine organic material to watercourses (Clouston 1996).

Few studies have evaluated FB performance as runoff and sediment control for agricultural lands. However they have proven to be effective for construction sites, with sediment removal efficiencies of 51 - 95%, however again, this does not differentiate between the particle size fractions that are removed (State of Oregon Department of Environmental Quality 2006, Faucette et al. 2009b).

2.2.3 Buffer Strips

BS are strips of land under permanent vegetative cover typically placed at the bottom of a slope, usually adjacent to a watercourse or drainage ditch. This includes both riparian and edge-of-field strips.

Overland flow (unconcentrated runoff) carrying sediments enters the BS which, due to the increase in surface roughness and subsequent decrease in runoff energy, allows sediments and associated pollutants (such as PO_4^{3-}) within the runoff to fall out of suspension and be deposited (SEPA 2009). Efficiency decreases with decreasing particle size (Barling and Moore 1994), and BS are not suitable for concentrated flow conditions due to the risk of erosion of the BS (Barling and Moore 1994, Morgan 2005, Sharpley et al. 2006).

UK farmers are given Entry Level Stewardship and Countryside Stewardship points for BS installation on their land (Natural England 2012) as they are recognised as effective sediment and nutrient control measures. Typically they consist of a wildflower and/or grass mix and therefore provide additional ecological benefits (Cole et al. 2015, Van Vooren et al. 2017, Westbury et al. 2017).

However a review by Rickson 2014 identified that their effectiveness for erosion control is extremely variable (0-100%; Gumiere et al. 2011; Deletic & Fletcher 2006; Reichenberger et al. 2007; Pan et al. 2017), as performance is dependent upon a wide number of factors (Liu et al. 2008). These include: vegetation species and habit, slope, soil type, runoff event, BS age, and nature of the pollutants. However, when installation and maintenance costs are considered alongside their mean effectiveness, they have been found to be good value for money (Rickson et al. 2010). Over the lifetime of a BS, if properly maintained, effectiveness has the potential to increase as soil quality conditions are improved through increased organic matter content, and in turn, increases in water holding capacity and nutrient sorbing capability (Cardinali et al. 2014), although this would be limited to localised in-field improvements. Conversely, if improperly installed or maintained, the BS can become a source of sediment and nutrients, which can result in decreases in local water quality (Rickson 2014).

Furthermore, BS are not as effective as other measures at removing PO_4^{3-} from runoff, especially that of dissolved PO_4^{3-} (Darch et al. 2015), which is typically transported through the BS within the runoff, or infiltrates into the soil matrix (Allaire et al. 2015). SB PO_4^{3-} preferentially adsorbs to clay particles. BS preferentially remove the larger sand and silt particles, therefore allowing the finer clay particles and associated PO_4^{3-} to continue off site to the watercourses (Barling and Moore 1994). Furthermore, several studies identify BS tendency to become sources of PO_4^{3-} due to remobilisation within the strip (Schmitt et al. 1999, Stutter et al. 2009, Roberts et al. 2012). Theoretically this can be overcome through the addition of PSMs to the BS surface. However in-field discrepancies with the runoff - BS contact time, and a lack of understanding of PSM efficacy in successive flows (Wagner et al. 2008, Watts and Torbert 2009, Habibiandehkordi et al. 2014) means that in practice it is hard to match laboratory levels of PO_4^{3-} adsorption.

Lastly, there are limited studies, especially with empirical data, into how BS are impacted by extreme rainfall - runoff events. Studies vary in their message, from no differences in performance (Woznicki et al. 2011, Otto et al. 2012) to reduced performance (Mullan et al. 2016). More research is required to understand the influence that climate change has on BS, as well as other sediment and erosion control measures.

2.2.4 Filter socks

FS, also known as silt socks, are large tubular structures which reduce runoff volume and velocity, and trap sediment. C FS are widely used in the US where they are considered a BMP for sediment control and stormwater management on construction sites (US EPA 2017). FS are mainly placed around drains, ditches and along slopes to limit sediment transport in runoff (US EPA 2017). They are also used in concentrated flow paths, as check dams, and as ‘terraces’ on steep slopes (Faucette et al. 2009c, Risse and Faucette 2009, USDA Natural Resources Service 2011).

Several studies have identified that C based BMPs, such as C FS, are significantly more effective sediment control measures than other BMP options, such as FB, SF and straw wattles (Faucette et al. 2007, 2009b, 2009c). Up to 97% sediment removal efficiencies have been reported from C FS (Filtrexx International 2005), although more typically they range between 65-90% efficiency for compost FS (Faucette et al. 2008, 2009a, 2009b, USDA Natural Resources Service 2011).

FS are comprised of a tubular mesh filled with C or bark meeting approved standards (mesh; (Tyler 2007), C; (Alexander Associates 2006)), with a PSD sufficient to allow runoff to flow through at a reduced velocity (Tyler and Faucette 2005, Alexander Associates 2006, Faucette et al. 2009b). This allows sediment, and consequently SB PO_4^{3-}, to deposit immediately upslope or within the FS (Faucette et al. 2008). If contact time is sufficient, dissolved PO_4^{3-} has the potential to adsorb to the exchange sites associated with the fill media (Tyler and Faucette 2005, Faucette et al. 2009a, 2013). Due to their efficacy, FS have since been adapted for different scenarios in the USA, utilising their inherent environmental and ecological sustainability. This includes adaption using additives to treat runoff contaminated with agricultural nutrients, hydrocarbons, heavy metals, and/or bacteria (Faucette et al. 2009a, USDA Natural Resources Service 2011). It also includes adaption for ecological restoration through slope stabilisation e.g. riverbanks, and the creation of green walls, all the while utilising the inherent sediment control technology. In spite of this, they are currently not widely used within an agricultural context. The limited studies which have assessed their suitability in agricultural systems show variable performance levels (Shipitalo et al. 2010, 2012) depending on soil type, slope, agricultural practice, rainfall-runoff event intensity/duration/depth, RE timing (e.g. antecedent rainfall), FS diameter, and the pollutant being targeted (sediment, nutrients, hydrocarbons and/or bacteria). Furthermore, there is the possibility of an initial flush of nutrients (PO_4^{3-} and/or NO_3^-) from the fill media into the watercourses post-installation of FS (Taylor and Trowsdale 2005, Shipitalo et al. 2010, 2012).

Although FS are widely used in the US, in the UK they have had limited uptake both in a construction and agricultural context. This is in part due to the lack of research into whether their design is transferrable to the UK. Furthermore, from an agricultural context, their effectiveness under different climate change scenarios, an increasing consideration in UK soil-related research (DEFRA 2005, 2009), is not understood. In fact, projects using FS to safeguard water quality (sediment and nutrient reduction) number less than 10 with the majority of them lacking empirical data. Those that provide empirical data find similar results to US based research (Waters 2010, ZWS 2010, Somerset Rivers Authority 2016) including that C fill media releases an initial flush of nutrients (Waters 2010). The long term significance of this flush has not yet been quantified. For sediment control, FS perform effectively under both current and extreme REs (75 year storm event; Waters, 2010). It is clear that more research is required to establish their overall performance and suitability.

2.2.5 Concluding remarks on EOPS

EOPS are essential in the protection of our waterways from diffuse pollution. However due to varying efficiencies and generally limited UK research, they should only be used in addition to within-field erosion control practices. SF and BS are widely used EOPS in the UK, however they produce highly variable sediment and PSE results (Table 2.1). FB and FS are widely used in the US, but far less within the

Table 2.1. Summary of the removal of sediment, SB PO_4^{3-} and orthophosphate by EOPS.

EOPS	Diffuse pollution removal (%)[a]		
	Sediment	**Sediment bound PO_4^{3-}**	**PO_4^{3-}**
SF[b]	65 - 99	Low. SF predominantly remove larger sand particles.	23 - 63
FB[c]	15 - 95	Medium. Higher than SF as clay, silt and sand particles will be removed.	14 - 27
BS[d]	23 - 100	60 – 74	-71 - 95
FS[e]	49 - 100	Medium. Higher than SF as clay, silt and sand particles will be removed.	28 - 99

[a] compared to bare soil
[b] values based on a combination of field and laboratory studies (Robichaud and Brown 2002, Faucette et al. 2005, 2008, Vinten et al. 2014)
[c] (State of Oregon Department of Environmental Quality 2006, Keener et al. 2007, Faucette et al. 2008, USDA Natural Resources Service 2011, Rickson 2014)
[d] (Deletic and Fletcher 2006, Hoffman et al. 2009, Gumiere et al. 2011, Rickson 2014, Darch et al. 2015)
[e] (Faucette et al. 2008, 2009a, 2013, Shipitalo et al. 2010, 2012)

UK, especially in agriculture.

FB and FS are more effective as sediment control than SF and BS, and they remove clay, silt and sand particles, rather than predominantly sand (Table 2.1), which is important for the removal of SB PO_4^{3-}. Additionally, research into the use of PSMs to manage the first flush of nutrients after their initial installation, or in areas where high PO_4^{3-} losses occur has been limited. Even so, they are considered here as a viable solution for mitigating the impacts of agricultural diffuse pollution to waterbodies.

2.3 Phosphorus sorbing materials (PSMs)

The wastewater industry regularly uses PSMs for the removal of PO_4^{3-}, thereby preventing eutrophication in receiving waters. In the UK, 11 billion litres day^{-1} of wastewater (DEFRA 2012a) is collected, with typical total-P concentrations of 5-20 mg P l^{-1} (Lenntech 2005). To reduce eutrophication and meet the WFD requirements, the maximum permissible concentration in treated effluent is 0.1 mg P l^{-1} (Shepherd et al. 2016). However the WFD target for aquatic environments in the receiving waters is often <0.025 mg P l^{-1}(Ye et al. 2017).

Removal of PO_4^{3-} from wastewater is typically achieved through screening of large solids; settlement of suspended solids; biological breakdown; and chemical treatments (DEFRA 2012a). In sensitive areas where water quality targets are <1 mg P l^{-1}, biological breakdown and further chemical treatment of the water may be required in order to achieve WFD targets (DEFRA 2012a). Chemical treatment is commonly achieved through the addition of PSMs such as Ca, Al and Fe ions. Mixing these in treatment allows coagulation, adsorption and precipitation of the PO_4^{3-}. This can then be separated and potentially reused as fertiliser in the form of sludge (Leader et al. 2008), as PO_4^{3-} desorption is typically low.

2.3.1 Typical uses of PSMs

Wetlands are often used for passive wastewater treatment. The addition of PSMs is often used to help reduce PO_4^{3-} losses in both the short and long term (Brix et al. 2001, Kadlec and Wallace 2009), and to reduce the cumulative wetland environmental footprint (Ann et al. 2000, Brix et al. 2001, Leader et al. 2008). Ballantine & Tanner, 2010 identify that P-sorption efficiency varies between constructed wetlands and restored wetlands, and influences whether these wetlands become sources or sinks of P (interchangeable over the lifetime of the wetland). Consequently when phosphate sorbing efficiency (PSE) is relatively low, the wetland benefits from the addition of a PSM to the wetland bed, or a PSM filter at its outflow. Many studies review the addition of PSMs within wetland systems to enhance PO_4^{3-} removal by increasing the PSE of the bed media (Brix et al. 2001, Cucarella and Renman 2009, Ballantine and Tanner 2010). Typical PSMs added are Ca, Al and Fe based, however the soils, sands, clays and aggregates within the bed media are also typically P-retentive, and therefore it is ideal that they have a high PSE. Sand is commonly used, however the PSE can vary widely depending on its Ca-content. This in turn influences the schemes longevity for PO_4^{3-} removal (Brix et al. 2001), although this can be enhanced through additional Ca input. In these systems particle size distribution (PSD) is important to ensure flow through the media and wetland;

sedimentation without clogging of the media, filters, and wetland outlets; and to allow sufficient contact for sustained P-removal (Ballantine and Tanner 2010).

PSMs are becoming more widely used in agriculture to mitigate against the impacts of PO_4^{3-} losses, as well as being slow-release fertilisers. Currently the most widely used PSMs in agriculture are drinking water treatment residuals (DWTRs), lime and alum (typically potassium aluminium sulfate; $KAl(SO_4)^{2\cdot}12H_2O$). These are applied to the soil surface or incorporated into manures and biosolids, and applied in-field, along watercourses, or within drainage ditches (Leader et al. 2008).

2.3.2 Typical PSM physio-chemical characteristics

Gérard (2016); Hylander, Kietlińska, Renman, & Simán (2006); Johansson Westholm (2006); and Leader et al., (2008) indicate that PSMs have the following characteristics:

- Clay sized (<2 µm);
- Presence of metal ions, particularly Ca, Al, Fe or Mg;
- pH of 6-8 for sands, silts and clays, and pH 3-8 for metal oxides;
- High hydraulic conductivity; <500 µS cm^{-1} for sands, silts and clays, <1000 µS cm^{-1} for metal oxides (Brix et al. 2001).

To be widely utilised, PSMs ideally need to be by-products, or waste materials that are generated locally but available widely (De-Bashan and Bashan 2004, Kvarnström et al. 2004, Cucarella and Renman 2009, Ippolito et al. 2011). Furthermore, ideally they should have a secondary use once saturated with PO_4^{3-}, or able to have the PO_4^{3-} removed allowing the PSMs to be reused (Kvarnström et al. 2004, Ádám et al. 2007, Leader et al. 2008).

PO_4^{3-} removal is associated with clays, due to their large specific surface area (SA), metal oxides on particle surfaces, and their intrinsic ionic charge (Gérard 2016). An extensive review undertaken by Gérard (2016) found that the majority of studies found that clays were highly effective at PO_4^{3-} sorption regardless of the presence of the metal oxides. This was mainly due to their large specific SAs, with sorption dictated by pH and ionic strength, in turn dictated by the presence of cations, which act as bridges between the negative charged sites of the clay surface and the PO_4^{3-}.

Nevertheless, there are many studies which state that metal oxides are important in PO_4^{3-} sorption, through ion and ligand exchange, and surface precipitation (Ippolito et al. 2011, Loganathan et al. 2014, Gérard 2016). In ligand exchange, PO_4^{3-} is bound to metal oxides through the creation of mononuclear and binuclear bidentate coordination bonds. This is where the ligand (ion) binds to a metal atom to form a coordination complex (complex resulting from covalent bonds), by donating two pairs of electrons to the metal atom. However, PO_4^{3-} sorption also occurs through hydrogen bonding, the weakest form of PO_4^{3-} sorption, and diffusion into pores and cavities within the PSM (Loganathan et al. 2014) which may or may not occur in the presence of metal oxides. Desorption of PO_4^{3-} from metal oxides has been found to be lower than with other materials. This confirms that metal oxides are particularly effective PSMs, and potential sources of PO_4^{3-}. The efficacy of specific metal oxides will be provided later within this paper.

2.3.3 Specific PSMs

2.3.3.1 Clays and organic soils

Soils have an inherent capability to adsorb pollutants which is highly dependent on the soil texture, organic matter content, and elemental concentrations (Harter 1969, Burkitt et al. 2006, Hongthanat 2010, Fink et al. 2014, 2016).

Clays are a soil constituent and common riverine sediment which have fine PSD (<2 µm), high SA (Table 2.2), presence of other mineral crystals and metal oxides, and layered porous hydrous structure (Uddin 2017). The structure of clay varies between species and within species depending on the pH, origin, weathered state and water availability. This variable structure determines the extent to which clays can adsorb ions, such as PO_4^{3-}. Clays with a 1:1 structure, such as kaolinite, tend to be more chemically stable due to a balanced structural charge. Montmorillonites have a 2:1 layer structure with a weak bond between layer sheets and an unbalanced charge, causing them to be more chemically reactive. Illite also has a 2:1 layer structure, however as the bonding between layer sheets is balanced, it tends to be less reactive than montmorillonite. When considered in relation to PO_4^{3-} adsorption, the PSE has been found to correlate to the finer clay-sized particles (<2 µm) within soils (Edzwald et al. 1976, Gimsing and Borggaard 2002, Burkitt et al. 2006).

Table 2.2. Specific surface area and characteristics of clay and organic PSMs.

Type	Specific SA ($m^2\ g^{-1}$)	Characteristics	Reference
Kaolinite	23.6		Gustafsson, 2001
	9.1		Manning and Goldberg, 1996
	8.8		Schroth and Sposito, 1997
	21.6		
Illite	19.0 – 53.4		Liu et al., 1999
	24.2		Manning and Goldberg, 1996
	41		Macht et al., 2011
	105 - 195		Aylmore et al., 1970
Montmorillonite	18.6		Manning and Goldberg, 1996
	12	Na-enriched	Perassi and Borgnino, 2014
	49	Ca-enriched	
	61		Macht et al., 2011
	147 - 158		Aylmore et al., 1970
Peat	144.3	Sphagnum peat	Sepúlveda-Cuevas et al., 2008
	93	Sapric peat	Kazemian et al., 2011
	69	Hemic peat	
	50	Fibrous peat	
	-	Total porosity 78.8%; 1.44 mg P g^{-1} adsorption	Na et al., 2016
Mushroom compost residue	1.2	Pleurotus mushroom compost	Kamarudzaman et al., 2014
	-	Total porosity 84.2%; 1.38 mg P g^{-1} adsorption	Na et al., 2016

However correlations between the type of clay and PSE vary in the literature. Murphy (1939) found that higher anion exchange capacities occurred in soils with kaolinitic clays, with up to double the amount of PO_4^{3-} adsorbed compared to montmorillonite dominated soils (Murphy 1939). More recently allophane clay, which has a similar structure to kaolinite, has been found to have a high PSE (Ooi et al. 2017), although this was far lower than the PSE of the metal oxides (Fe, Al, Mg) also evaluated in the study.

The impact of pH on PSE has been widely investigated with varying results. Edzwald et al. (1976), found that illite clays presented the largest PSE over montmorillonite and kaolinite clays. However this was extremely pH dependant, with illite and kaolinite having maximum adsorption at pH 4-5, whilst adsorption on montmorillonite increased linearly as pH increased. Similar results were found by Harsh & Doner (1985) with the assumption that the higher pH led to increased stability of the montmorillonites' Al-interlayers, thus increasing PSE. Conversely, Devau et al. (2011) found that the majority of PO_4^{3-} adsorption by illite occurred in the pH range neutral to alkaline, due to the presence of Ca. Gustafsson et al. (2012) found similar results in that high clay content soils had minimal solubility at pH 6-7.

Gimsing & Borggaard, (2002) identified little difference in the PSE of illite over montmorillonite, however their PSE was significantly lower as compared to goethite. In contrast, Gérard (2016) found that the PSE of clays equals or exceeds that of goethite and hematite, depending on the materials' specific SA. Together these studies suggest that clays are an important PSM, and although the clay type and pH are important, a key consideration is the clay metal oxide content (Ca, Fe, Mg, Al).

Humic substances influence a soils PSE and are found in soils in the form of organic matter (OM), humus, fulvic acids, and humic acids (Pettit 2014). Humic substances have been found to be effective at sorbing soil elements, including PO_4^{3-} (Borggaard et al. 2005), and transforming them into plant available forms. This is due to their clay size, pH neutrality, and charged surface sites (OH_- and $COOH^-$ groups). Consequently they are commonly used as a soil conditioner (Pettit 2014).

Similar to clays, there have been variable results regarding the importance that OM content has on the PSE of soils. Generally, studies state that OM increases the PSE by binding with Fe-oxides through (Fink et al. 2014, 2016):

- Cation bridging (binding with metal oxides e.g. using Al^{3+} and Fe^{3+});
- Increasing the specific SA of soil elements by inhibiting crystal growth;
- Changing the surface charges of the soil elements and soil particles.

OM in the form of peat soils and mushroom C has been found to be an effective PSM with up to 97% (Table 2.2) PO_4^{3-} removal efficiency (Na et al. 2016) due to the selective adsorption of PO_4^{3-} over other anions and the high SA; up to 200 m^2 g^{-1}; (Vohla et al. 2011). Similarly, Cui et al., (2017) found a positive correlation between OM content and adsorbed PO_4^{3-} on sediments, but did not find a correlation with any other sediment properties (including clay content). Likewise, OM removal has been found to reduce the PSE of sediments in lacustrine environments (Wang et al. 2011). When in Fe environments, OM has been found to suppress PO_4^{3-} adsorption, preferentially forming Fe-OM complexes (Sundman et al. 2016). Furthermore, large amounts of organic acid (humic and fulvic) can also decrease or delay PO_4^{3-} adsorption by competing for adsorption sites, and causing PO_4^{3-} to be repelled by changing the surface charge to a net negative, (Sibanda and Young 1986, Borggaard et al. 2005, Perassi and Borgnino 2014, Fink et al. 2016, Moreira et al. 2017).

2.3.3.2 Fe species

Fe oxides and hydroxides are widespread compounds consisting of a Fe molecule, bonded to an O molecule and/or an OH group (Cornell and Schwertmann 2003). They are more commonly referred to as 'ochre' - amorphous ferric iron oxyhydroxides that precipitate from coal mine waters during mine water treatment. UK ochre arising's are widespread and estimated to total 4500 t yr^{-1} (Sapsford et al. 2015). Ochre is currently considered a waste material as it has no clearly defined end use. It is typically landfilled at cost to The Coal Authority (£776,651 in 2016/2017) who manages the current UK mining legacy. Ochre typically contains a

Table 2.3. Specific surface area and characteristics of Fe PSMs.

Fe species	Specific SA (m^2 g^{-1})	Characteristics	Reference
Goethite	60 - 200		Schwertmann and Taylor, 1990
	51	Synthesised. Poorly crystalline.	Wei et al., 2014
	45	Synthesised. Particles acicular shape, ~ 40 nm.	Wang et al., 2013
	21 - 115	Synthesised. Various crystalline shapes.	Torrent et al., 1990
	85	Synthesised. Various crystalline shapes.	Rakovan et al., 1999
Hematite	31	Synthesised. Particles rhombohedral shape, ~ 50 nm	Wang et al., 2013
	47	Synthesised.	Ioannou and Dimirkou, 1997
	56	Synthesised.	Elzinga and Sparks, 2007
	50	Synthesised.	Lu, 2014
Ferrihydrite$_a$	348	Synthesised. Particles spherical shape, 1-3 nm.	Wang et al., 2013
	700		Willet et al., 1988
	300	Synthesised 2LFH.	Michel et al., 2010
	650	Synthesised 2LFH. Particle size ~2.6 nm.	Hiemstra and Van Riemsdijk, 2009
	280	Synthesised 6LFH. Particle size 5-6 nm.	Hiemstra and Van Riemsdijk, 2009

$_a$Ferrihydrite can be classified into 2-line (2LFH) or 6-line (6LFH). This refers to the crystal arrangement of the mineral which is dependent upon the transformations and reaction conditions.

variety of minerals, metals and sometimes toxic elements (e.g. As), with Fe-oxides being the dominant constituent.

Fe-oxides can also be found within DWTR, which are produced as a waste product from the water treatment process. They have proven to be effective PSMs with up to 99.8% efficiency (Callahan et al. 2002; Silveira et al. 2006; Gibbons et al. 2009), and have also been found to be effective in the removal of toxic elements such as selenium (Se), mercury (Hg) and arsenic (As) (Ippolito et al. 2011).

Goethite, hematite and ferrihydrite are all common Fe-(hydr)oxides that are effective at sorbing PO_4^{3-}. Transformations between them are well documented (Cornell and Schwertmann 2003, Chesworth 2008), however occur relatively slowly and therefore are unlikely to impact PSE if used as a PSM. Efficacy primarily depends on the type of Fe-(hydr)oxide, although pH also plays an important role (Hingston et al. 1968, Cornell and Schwertmann 2003, Fink et al. 2016, Ooi et al. 2017). It is well documented that, for all Fe-(hydr)oxides, PO_4^{3-} adsorption is at its maximum at lower pH values, gradually decreasing as pH increases (Hingston et al. 1968, Cornell and Schwertmann 2003). SA of the Fe-(hydr)oxide is another consideration for PSE as it impacts the number of active surface sites available for adsorption; ferrihydrite and goethite tend to have the higher SA values (Table 2.3).

Goethite

Geothite (FeO(OH)) is a hydroxide mineral which has a structure comprising a double network of $Fe_3(OH)_3$ octahedra. Adsorption of PO_4^{3-} is a function of the goethite's surface structure, SA, and ionic groups, and consequently varies from sample to sample (Torrent et al. 1990, Rakovan et al. 1999, Borgnino et al. 2009, Wei et al. 2014). The SA of goethite is reported to range from 20-200 $m^2\ g^{-1}$ (Cornell et al. 1974, Schwertmann 1988, Schwertmann and Taylor 1990, Rakovan et al. 1999, Wei et al. 2014). Most commonly, PO_4^{3-} adsorption occurs through the creation of a binuclear bond (Parfitt and Atkinson 1976, Parfitt et al. 1976, Anderson et al. 1985, Tejedor-Tejedor and Anderson 1990, Arai and Sparks 2001, Wang et al. 2013). Other authors have observed mononuclear bonding (Tejedor-Tejedor and Anderson 1990, Persson et al. 1996, Olsson et al. 2010), whilst others have found several types of complex occurring including surface precipitation (Martin et al. 1988, Tejedor-Tejedor and Anderson 1990, Li and Stanforth 2000). During adsorption PO_4^{3-} replaces the Fe hydroxyl groups with PO_4^{3-} hydroxyl groups; these are more acidic and therefore the surface charge of goethite becomes more negative. Specifically, PO_4^{3-} replaces a hydroxyl oxygen (Fe-OH), forming either $Fe\text{-}OPO_3H^-$, or $(Fe\text{-}O)_2PO_2^-$ (Parfitt and Atkinson 1976, Parfitt et al. 1976, Tejedor-Tejedor and Anderson 1990, Li and Stanforth 2000, Cornell and Schwertmann 2003, Wei et al. 2014). This is dependent on the crystal faces of the goethite, with PO_4^{3-} preferentially adsorbing on the (110) crystal faces (Torrent et al. 1990; Parfitt et al. 1976; Cornell et al. 1974; Cornell & Schwertmann 2003; Torrent et al. 1992). Rapid initial adsorption (up to 90% of the total PO_4^{3-}) is followed by a much slower prolonged adsorption (Cabrera et al. 1981, Parfitt 1989, Torrent et al. 1990, 1992). Desorption is limited, with highest desorption at lower pH values, and the reaction slowing down over time (Torrent et al. 1990, Krumina et al. 2016). This is important for ensuring that goethite does not become a PO_4^{3-}source.

Hematite

Hematite (Fe_2O_3) is one of the most abundant and stable Fe-oxide minerals (Cornell and Schwertmann 2003, Back et al. 2013) and is mined as the main Fe-ore. Similar to goethite, PO_4^{3-} adsorption depends on the hematite's surface characterisation, particularly whether it has transformed from goethite or ferrihydrite. That which transforms from ferrihydrite has higher SAs (up to 200 m^2 g^{-1}), and therefore is likely to adsorb more PO_4^{3-} (Ioannou and Dimirkou 1997, Cornell and Schwertmann 2003, Elzinga and Sparks 2007). PO_4^{3-} adsorption has been found to be variable; some studies finding that it is similar to that of ferrihydrite (Gimsing and Borggaard 2007) and others that it is less than that for ferrihydrite and goethite (Barron et al. 1988, Colombo et al. 1994) with slower adsorption and lower PO_4^{3-} affinity. High variability may be partly due to the formation of PO_4^{3-} surface complexes (Persson et al. 1996, Elzinga and Sparks 2007), which depends on pH and surface loading (Elzinga and Sparks 2007). Cornell & Schwertmann, (2003) suggest that adsorption variability is due to variations in the formation, as well as crystal morphology. Crystals that have formed as rhombohedral structures are able to adsorb more PO_4^{3-} per unit of SA than platy structures.

Ferrihydrite

Ferrihydrite ($Fe_{10}O_{14}(OH)_2$) is a common Fe-hydroxide mineral with a variable structure (Back et al. 2013). It can take the form of two crystal arrangements; 2-line ferrihydrite (2LFh), and 6-line ferrihydrite (6LFh) (Cudennec and Lecerf 2006). The line taken in formation depends on the Fe-oxide transformations and the variation in the reaction conditions (Cornell and Schwertmann 2003). There are PSD differences between 2LFh and 6LFh, which impacts upon the number of Fe^{3+} atoms within the structure, the SA, and consequently the number of reactive surface sites (Hiemstra and Van Riemsdijk 2009). 2LFh has a much higher SA than that of 6LFh (Hiemstra and Van Riemsdijk 2009), due to a smaller particle diameter of ~ 2.6 ± 0.1 nm, compared to the 6LFh particle diameter of 5-6 nm (Zhao et al. 1994, Janney et al. 2000). This suggests that 2LFh has a greater number of reactive surface sites (Hiemstra and Van Riemsdijk 2009), and therefore the type of ferrihydrite is important to consider when choosing a PSM. 2LFH has a higher SA, but 6LFH is more widely available. According to Manceau & Gatest (1997), up to 35% of Fe ions may be located at the surface; singularly coordinated to O, OH and H_2O ligands. When related to ferrihydrites high SA, this results in a much higher ion adsorption capacity (Davis et al. 1978, Michel et al. 2010, Hiemstra 2013). SA values vary widely but can generally can be placed in the range of 200-700 m^2 g^{-1} (Avotins 1975, Davis et al. 1978, Carlson and Schwertmann 1981, Eggleton and Fitzpatrick 1988). Specifically OH^- and/or H_2O is released during the adsorption process (Parfitt 1989, Cornell and Schwertmann 2003, Wang et al. 2013), likely forming monodentate and bridging bidentate configurations (Khare et al. 2007). Monodentate is the weaker bond meaning that less energy is required for PO_4^{3-} adsorption, and consequently PO_4^{3-} desorption is more likely than from a bidentate or binuclear bond (Parfitt 1989). This characteristic is important to consider when choosing a PSM for its PSE, but also for its potential reuse upon PO_4^{3-} saturation. It has been suggested that PO_4^{3-} is able to penetrate into the ferrihydrite structure, corresponding with the higher SA values of 700 m^2 g^{-1} (Willet et al. 1988), unlike that of other Fe-oxides where it is only able to adsorb to the surface Fe-OH exchange sites, or precipitate onto the surface. Ferrihydrite displays a rapid initial adsorption rate, which decreases with decreasing availability of adsorption sites as PO_4^{3-} is adsorbed (Torrent et al. 1990, 1992, Wang et al. 2013). Like that of goethite, it has been suggested that adsorption and desorption depend on the micro and nano-particle ferrihydrite crystal faces (Torrent et al. 1990, Kubicki et al. 2012). PO_4^{3-} desorption rates vary from study to study (Wang et al. 2013, Krumina et al. 2016). This is important to establish to ensure that it does not become a PO_4^{3-} source.

Overall, Fe-(hydr)oxides are considered essential PSMs that significantly reduce PO_4^{3-}, and have been widely used in the water industries for this purpose (Leader et al. 2008, Ippolito et al. 2011, Lu et al. 2016). Findings suggest that Fe-(hydr)oxides are particularly suitable for use as PSMs within existing EOPS, such as FS, due to their high SA and PSE at lower pH values, however research is needed to acquire empirical data on their efficacy for this purpose and set-up. Furthermore, the literature suggests that their PSE may be increased further with the addition of another material (e.g. Ca-oxides) which works at higher pH values in order to cover a wide runoff pH range (pH 4-8). Once saturated, they can be reused as a slow release agricultural fertiliser (Carr et al. 2004, Dobbie et al. 2005).

2.3.3.3 *Al species*

Al-oxides (Al_2O_3) or hydroxides ($Al(OH)_3$) are a commonly adopted PSM, used instead of or in addition to Fe-(hydr)oxides. Adsorption typically occurs through the same mechanisms as those of Fe-(hydr)oxides; coordination bonding, ionic bridging and surface precipitation (Ballantine and Tanner 2010, Li et al. 2016a, Zohar et al. 2017). Naturally found as the mineral Corundum, they also occur in industrial waste and by-products, including water treatment, smelting, cement production, and as a precipitate in acid mine drainage. Typical Al-oxides have porous spherical clay-sized particles, with many of the OH^- groups exposed at the surface allowing PO_4^{3-} adsorption, with further diffusion into the pores (Tanada et al. 2003). Like ferrihydrite, PO_4^{3-} is preferentially adsorbed to the OH^- groups of Al-oxides over other anions (Prasad and Power 1997, Tanada et al. 2003), making them particularly suitable for PO_4^{3-} removal. Al-oxide SA values range between 4.5 – 650 m^2 g^{-1} (Table 2.4) depending on whether they are natural or synthesised, the pH and temperature at which it was synthesised, porosity, and the surface analysis method used. Al-oxides with high SA and low crystallinity (and therefore more active surface sites) have higher PSE (Xiaofang et al. 2007), however surface analysis methods typically underestimate SA due to material microporosity (Lowell et al. 2004).

During PO_4^{3-} adsorption a mononuclear monodentate complex forms on synthesised Al-oxide (Borggaard et al. 2005), with rapid initial adsorption, and rates decreasing over time (Chen et al. 1973). Synthesised Al-oxides tend to have higher SA than natural Al-oxides (Table 2.4) and therefore more likely to have higher PSE. However, this could result in a larger amount of PO_4^{3-} desorption, at least initially.

Table 2.4. Specific surface area and characteristics of Al PSMs.

Al species	Specific SA (m^2 g^{-1})	Characteristics	Reference
Al-oxides	254	Synthesised	Goldberg et al., 2001
Al-goethite	228	Synthesised, 30% Al	Ruan and Gilkes, 1996
Al-hydroxide	252	Synthesised	Borggaard et al., 2005
Alumina	4.5	Synthesised	Karim et al., 2011
	89		Xiaofang et al., 2007
	148	Synthesised	Morterra et al., 1995
	165	Synthesised	Mekhemer et al., 2000
	186	Synthesised	Morterra et al., 1995
	203	Synthesised	Mekhemer et al., 2000
	250	Synthesised, commercial product	Samain et al., 2014
	280	Synthesised	Mekhemer et al., 2000
	340	Synthesised	Samain et al., 2014
	650	Synthesised	Y. Li et al., 2017
Boehmite	166	Synthesised	Xiaofang et al., 2007
Corundum	~16		Souto and Guitian, 2002

Alum sludge ($Al_2(SO_4)_3.16\ H_2O$) is a by-product from drinking water treatment plants and is a commonly used PSM in agriculture as it allows aluminium hydroxide phosphate formation, as well as precipitation of aluminium phosphate (Babatunde and Zhao 2010, Ballantine and Tanner 2010). PO_4^{3-} adsorption ranges from 0.3-23.9 mg P g^{-1} alum sludge (Huang and Chiswell 2000, Razali et al. 2007, Yang et al. 2008), and depends on its quality, pH and electrical conductivity as well as the concentration and pH of the PO_4^{3-} solution and of the soil (Babatunde and Zhao 2010, Dassanayake et al. 2015). Upon saturation, alum sludge can be reused as a slow release fertiliser, soil amendment, wastewater coagulant, constructed wetland substrate, or brick making substrate (Leader et al. 2008, Elangovan and Subramanian 2011, Gibbons and Gagnon 2011, Dassanayake et al. 2015, Zohar et al. 2017).

Al-oxides in the presence of high OM have proven to be a far more efficient (up to 100%) and consistent PSM (Ronkanen et al. 2016), especially those that originated from wastewater treatment. This may make Al-oxides particularly effective PSM additives if added to C EOPS.

2.3.3.4 Ca species

Ca-oxides (CaO) and hydroxides ($Ca(OH)_2$) are commonly used as PSMs in the water treatment industry and as filter media within constructed wetlands (Seo et al. 2005, Vohla et al. 2011) as they provide an essential role in PO_4^{3-} adsorption, pH regulation, and turbidity reduction through coagulation (Oates 2008). In recent years their use has become less prevalent due to issues in maintenance, handling, waste production (Nassef 2012), and the increasing viability (cost and performance) of other PSMs (e.g. Fe/Al-oxides). Calcite or lime are widely used PSMs, typically applied crushed, or as a coating on other porous materials, such as sand and clays

(Perassi and Borgnino 2014). PO_4^{3-} solution is then passed through or mixed, encouraging adsorption and precipitation. Upon saturation, the calcium phosphate ($Ca_3(PO_4)_2$) can be reused, as an agricultural slow release fertiliser or soil amendment (McLaughlin 1984, Sengupta et al. 2015), or for wastewater treatment of heavy metals (Belaicha et al. 2014, Lyczko et al. 2014). Ca-sludge is particularly suitable for agricultural reuse as it counters the traditional sludge acidity (Project on Urban Reduction of Eutrophication 2012).

Studies exploring PO_4^{3-} adsorption of Ca-oxides show that they can increase the PSE of filter materials by up to 96% (Han et al. 2017, Li et al. 2017b, Mitrogiannis et al. 2017). Results vary as to whether PO_4^{3-} is adsorbed and/or precipitated, however the likelihood is that both occur. Initial adsorption and desorption is fast indicating PO_4^{3-} precipitation, or adsorption without incorporation into the crystal lattices (House and Donaldson 1986, Sø et al. 2011, Han et al. 2017). Afterwards there occurs a nucleation process of $Ca_3(PO_4)_2$ crystals and monodentate or bidentate bonding (Prasad and Power 1997, Sø et al. 2011, Han et al. 2017).

The solution pH controls PO_4^{3-} adsorption, however initial PO_4^{3-} concentration, and surface charge (Perassi and Borgnino 2014) are also important; determined by the amount of Ca^{2+} / CO_2^{3-} ions (Madsen 2006). Solubility is affected by pH (Suzuki et al. 1986), and together these determine the resulting PO_4^{3-} speciation (Sø et al. 2011).

PO_4^{3-} adsorption increases as pH increases, and can be very low in acidic conditions (Perassi and Borgnino 2014, Xu et al. 2014c). Precipitation is the main mechanism at high PO_4^{3-} concentrations, and adsorption the main mechanism at low PO_4^{3-} concentrations (Liu et al. 2012, Yagi and Fukushi 2012).

SA is also an important consideration, and is affected by the aforementioned conditions, alongside the type of Ca-oxide and whether it is natural or synthesised. Studies show highly variable values ranging from 0.22 – 27.4 $m^2\ g^{-1}$ (Table 2.5). Consequently, a CBA may be prudent when choosing a Ca-oxide PSM as synthesised products may provide better PSE results, however the production costs may outweigh this benefit.

Table 2.5. Specific surface area and characteristics of Ca PSMs.

Ca species	**Specific SA ($m^2\ g^{-1}$)**	**Characteristics**	**Reference**
Calcite	0.2		Sø et al., 2011
	0.2 – 0.4		House and Donaldson, 1986
	0.6		Z. Li et al., 2017
	0.7	Synthesised	Suzuki et al., 1986
	4.2		Xu et al., 2014a
Calcium Carbonate	0.3 – 0.8		Amer et al., 1985
	0.6 – 8.7	Synthesised and Fe enriched	Han et al., 2017
Calcium phosphate	11.1 – 27.4	Synthesised	Lyczko et al., 2014
Dolomite	3.0		Xu et al., 2014c
Monohydrocalcite	16.4	Synthesised	Yagi and Fukushi, 2012

Ca-oxides provide appreciable PO_4^{3-} control, however studies indicate they provide less PSE than other PSMs, such as Fe/Al oxides or peat, due to their lower SA and pH dependency of the incoming solution. Consequently they may be inappropriate as the primary PSM, but it is postulated here that they may be beneficial if added in addition to other PSMs. For instance, their PSE at higher pH values may provide additional control when added to Fe-(hydr)oxides, which predominantly work within the acidic-neutral pH range. If added to EOPS, this would provide PO_4^{3-} control across a broad range of pH values (pH 4.0 – 8.0) providing wider applicability to EOPS and UK agricultural soils. This is an area of research as yet unstudied.

Mg species

Mg-oxides (MgO) and hydroxides ($Mg(OH)_2$) occur naturally as periclase and brucite, but are often synthesised for use within the wastewater treatment industry for PO_4^{3-} removal. PO_4^{3-} adsorption is through ionic bonding and surface precipitation, forming magnesium phosphate ($Mg(H_2PO_4)_2 \cdot 3H_2O$) by bonding with the O and OH groups. Struvite ($NH_4MgPO_4 \cdot 6H_2O$) often forms when in the presence of ammonia and an alkaline pH. Mg-oxides and hydroxides are PSMs which are mainly used to provide secondary adsorption capability to other metal oxides (Fe, Al, Ca). They mainly sorb PO_4^{3-} at more alkaline values, however PO_4^{3-} first preferentially sorbs to Ca-oxides (El-Nennah 1975, Kuo and Mikkelsen 1979, Busman et al. 2002). PSE of Mg-materials is ~90% (Xie et al. 2012, 2014) depending on the pH. Furthermore, like that of other metal oxides, PO_4^{3-} removal increases with SA. Where this has not been found (Xie et al. 2012, 2014, Xu et al. 2014b), sub-optimum pH or preferential adsorption to other present metal oxides was the reason

Table 2.6. Specific surface area and characteristics of Mg PSMs.

Mg species	Specific SA (m_2 g^{-1})	Characteristics	Reference
Mg-modified Bentonite	51.7	Bentonite contained montmorillonites	El Bouraie and Masoud, 2017
Mg-modified Biochar	10.2 – 12.3	Biochar from sugarcane	R. Li et al., 2016
Mg-modified $CaCO_3$	55.7	$CaCO_3$ in the form of aragonite	Xu et al., 2014b
Mg-modified Diatomite	72.5	90% PO_4^{3-} removal efficiency, equating to 44.4-52.1 mg g^{-1}	Xie et al., 2014
MgO	1 - 550	Synthesised. Maximum SA when synthesised from $MgCO_3$.	Razouk and Mikhail, 1959
	8.3	Low grade; waste product	Chimenos et al., 2003
	59.5	Synthesised, activated MgO.	Xie et al., 2012
	115	Low grade; waste product	Chimenos et al., 2003
$Mg(OH)_2$	9.8	Synthesised. Well crystallised.	Xie et al., 2012
$MgCO_3$	46.8	Synthesised. PO_4^{3-} removal capacity of 4.46 – 16.92 mg P g^{-1}	Han et al., 2017

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Values for SA (Table 2.6) vary depending on whether natural or synthesised, and if synthesised, the type of parent material and temperature at which synthesis took place.

Upon adsorption, the resultant $Mg(H_2PO_4)_2$ can be reused in concrete production to reduce its deterioration (Li and Bing 2013, Park et al. 2016). Struvite formation in wastewater treatment can often be problematic through mineralisation onto the equipment, however if obtained, it can be reused as an effective slow-release fertiliser (Doyle and Parsons 2002, Rahman et al. 2014, Talboys et al. 2016).

Mg-oxides provide appreciable PSE (up to 92%; (Xie et al. 2012)), however they are not suitable for sole inclusion into EOPS due to their pH and temperature dependency, but mainly because they are a secondary sorption material; sorption occurs once exchange sites on other metal oxides are saturated. Consequently they are suitable for inclusion in addition to other PSMs, as supplementary control at alkaline pH.

2.4 Combining sediment control with PSMs

There are several sediment control BMPs that if installed and maintained correctly can efficiently prevent these sediments (and associated SB PO_4^{3-}) from travelling offsite. Some measures, such as FS, are yet to be widely utilised within the UK, due to a lack of research into their applicability, cost-effectiveness and adoption constraints. A large body of research has been undertaken into the use of PSMs within the wastewater treatment industries. In particular, metal oxides (Fe, Al, Ca and Mg) provide effective PO_4^{3-} control (especially 2LFh). They are particularly effective when combined with each other, or with other PSMs such as clays, and organic materials (such as C or W). Combining metal oxide PSMs could allow specific PSM-enhanced EOPS to be tailored to the expected runoff pH. Furthermore, there is a research and commercial gap for effective concomitant sediment and orthophosphate control that combines PSMs with a suitable fill media in a FS, applied on site, to mitigate diffuse pollution associated with agricultural runoff. Utilising PSM enhanced FS would allow simultaneous sediment, SB PO_4^{3-} and orthophosphate removal from runoff in field. This field/catchment based approach to diffuse pollution control would decrease the need and costs associated with sediment and PO_4^{3-} treatment.

PSMs are already applied within wetlands (Ann et al. 2000, Brix et al. 2001, Leader et al. 2008, Kadlec and Wallace 2009), as well as limited application with BS (Wagner et al. 2008, Habibiandehkordi et al. 2014). Building on this research into other applicable EOPS, such as FS and FB, is necessary to provide part of the solution in meeting the UK's water quality targets, specifically diffuse pollution associated with agricultural runoff. C-based products, such as FS, have already proven effective for sediment control (Faucette et al. 2009b, Shipitalo et al. 2010), and are widely applied in the USA (as a BMP) with the addition of commercial PSM products (Faucette et al. 2009a). These commercial PSM products are not widely available in the UK, and are not likely to be widely utilised due to cost and transport constraints. Combining the effective FS sediment control with other PSMs, such as local waste materials, would incentivise wider uptake.

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CHAPTER 3: FILTER SOCKS TO MITIGATE RUNOFF, SOIL AND PHOSPHATE LOSSES FROM ARABLE LANDS UNDER CURRENT AND EXTREME RAINFALL EVENTS[1]

Abstract

Currently 83% of England's water bodies are failing prescribed water quality targets (EU WFD 2000/60/EC) due to increased turbidity, sedimentation and eutrophication. Eroded soil and orthophosphate from agricultural lands is the main reason for this, and consequently there is a need to establish methods to mitigate runoff and soil losses on vulnerable sites, to reduce these inputs to such water bodies.

This project evaluates the application, suitability and efficacy of filter socks (FS) to mitigate runoff, soil and orthophosphate losses from agricultural lands. FS are not widely used within the UK; however they are currently used as a construction site BMP for sediment control within the US. This study has established their potential efficacy within a UK agricultural context, under current and more extreme rainfall events associated with climate change.

Experimental field trials within a high-erosion area in Herefordshire, UK, evaluated the use of traditional compost FS and those filled with alternative fill media (woodchip and a commercial proprietary product). Results between FS treatments and the Control were highly variable, with few significant differences regarding sediment and orthophosphate control efficiency. Results suggest there is an initial first flush of soil and nutrients from FS, as is consistent with other research. This was evidenced by the increase in the amount of sediment and orthophosphate in the runoff in sampling period 1. However as this coincided with a period of heavy and intense rainfall, this may have created a more prolonged flush event. The commercial proprietary product did not significantly reduce orthophosphate losses compared to the non-amended FS (control). More research is required to establish FS suitability in other field situations, as well as to understand the phenomenon of the first flush event if they are to be reliable as an in-field control measure.

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[1] Cooke, A.L., Simmons, R.W., Rickson, R.J., Sakrabani, R., 2017. Filter socks to mitigate runoff, soil and phosphate losses from arable lands under current and extreme rainfall events. *World Conference on Soil and Water Conservation (CONSOWA)*, 12-16th June 2017, Lleida, Spain.

The spelling and format of the original published conference proceedings has been adjusted to fit the format of this thesis. The original proceedings can be found in Appendix 1.

3.1 Introduction

FS are little known within the UK, however they are widely used in the USA as BMPs to control sediment on construction sites. The water quality in the UK is improving; however the legacy issue of water quality problems, along with the highly variable environments in the UK, means that many waterbodies are still failing their water quality targets. For many, this is at least in part due to diffuse pollution from arable lands. It is hoped that FS may be one solution to help control sediment and PO_4^{3-} inputs to vulnerable watercourses. Controlling these inputs will satisfy water quality targets (prescribed by the EU WFD), decrease sedimentation and mitigate flooding and eutrophication processes. As a result, aquatic ecosystems will be better protected. The main focus of this research is to enhance the efficacy of FS in the control of sediment and PO_4^{3-} using a range of fill media and PSMs, and to identify whether they are a suitable option for use on agricultural lands.

PSMs are used within the wastewater industry for P adsorption from sewage sludge. They usually consist of P-sorbing resins or membranes, which are rarely used by the agricultural industry due to cost and upscaling constraints. Consequently, there is a need for alternative PSMs that can be used in agricultural settings. Appropriate field placement of FS will allow sediment capture as well as PO_4^{3-} adsorption from the runoff before it enters the drainage network. The PSM initially trialled in this study was chosen from a literature review and project based assessment criteria (ability to reduce PO_4^{3-} to meet the WFD water quality target; 0.05 mg P l^{-1}).

Climate change is projected to increase the number of extreme weather events, including higher rainfall intensities, which will ultimately increase the frequency and magnitude of runoff and soil erosion (IPCC 2014). For the UK, it has been predicted that only a 10% increase in winter rainfall could result in a 150% increase in arable soil erosion (Favis-Mortlock and Boardman 1995), with associated delivery of sediment and PO_4^{3-} load to watercourses. Therefore, it is essential that PSMs and FS are effective in mitigating the effects under current and extreme REs.

3.2 Methods

Soil erosion and runoff was monitored in a fully replicated field trial which ran for 36 weeks from July 2015 – March 2016. This encompassed the entire maize growing season (early summer to autumn), harvest (autumn), and the bare overwinter period (autumn – the end of the trial). The field site was located at 52.095354, -2.7217984 (Lat/Long) near Hereford, UK. It was chosen for its high erosion risk, fine silty soils (Cranfield University 2016); steep slope gradients (11-17^{o}); susceptibility to soil compaction and surface capping; relatively high annual rainfall (665 mm yr^{-1}), increasingly extreme REs; and erosive land use (maize with rows running up/down slope, perpendicular to the contour). These conditions meant the tenant farmer had regularly experienced soil erosion issues. Furthermore, runoff from this field after entering the field drains, eventually ended up entering the River Lugg, which is a main tributary of the Wye, and is contributing to it failing its water quality targets.

Twenty erosion plots (1.5 m wide x 15 m long) were set-up, oriented downslope; parallel to the maize rows (Figure 3.1). These plots were hydrologically isolated meaning that any runoff and erosion occurring within these plots would be isolated from that occurring in the wider field, and captured. This would then be transported to a storage tank via a Gerlach trough and pipe system. The level of runoff within the storage tanks (capacity 227 litres each), was measured remotely remotely using pre-calibrated Liquid Vertical Continuous Series (LVCS). This ensured that unnecessary sampling trips were not made, and allowed the identification of possible experimental issues from the office. Each LVCS sensor was connected to a data logger (Delta-T DT80/2), and together they monitored the levels of runoff in the tanks, as well as site precipitation, temperature and humidity as recorded by a linked on-site weather station. The data logger began logging immediately after the onset of 0.2 mm of rainfall and continued for 1 hr post-rainfall cessation.

Figure 3.1. Experimental set-up of FS field trials.

3.2.1 Treatments

The field trial investigated 5 treatments: Control (no FS); Compost FS (C FS); Woodchip FS (W FS); C FS with proprietary product (CPp FS); and W FS with proprietary product (WPp FS). Each treatment had 4 replicates which were randomly distributed across the erosion plots.

As the Control did not have a FS treatment it represented 'business-as-usual'. The trials used 8-inch diameter FS with PAS100 C or fine W used as fill media. This met the FS fill media specifications (Alexander Associates, 2006). A commercial Pp was used as the PSM, applied at the required application rate of 20 kg m_{-3} within the CPp

FS and WPp FS treatments, providing an industry ‘standard’ with which to compare alternative PSM treatments.

3.2.2 Sampling

Baseline soil sampling was undertaken to ensure that there were not significantly different conditions between erosion plots. The following analyses were undertaken: soil particle size distribution (pipette method), pH (H_2O method), organic matter content (Loss on ignition), and Total Phosphorus (acidic mjcrowave digestion method, based on British Standard BS 7755: Section 3.13:1998).

Treatment performance criteria included runoff volume (l plot^{-1}), runoff sediment concentration (g l^{-1}), sediment load (g plot^{-1}), and runoff PO_4^{3-} concentration (mg P l^{-1}). Sampling of the runoff in the tanks took place on 4 occasions (Table 3.1). These sampling occasions were dictated by the level of runoff recorded within the tanks which was monitored by the LVCS, and the timing of the previous sampling occasion. Data from the LVCS was not reliable enough to provide a volumetric runoff amount from each of the tanks. Consequently, sampling of the runoff depth (m) from the tanks was undertaken using a ruler, to calculate the volume of runoff that came from the erosion plot in that sampling period. Following this, the runoff was agitated by hand, and a 1 litre subsample taken. This was used for both sediment and orthophosphate analysis.

Sediment concentration (g ml^{-1}) was established by oven-drying a pre-weighed tin containing 250ml of agitated subsample. Once the water had evaporated off, the tin was weighed to establish the amount of sediment left (g 250ml^{-1}). This was then divided by 250ml to obtain the sediment concentration as g ml^{-1}.

Table 3.1. Sampling occasions

Sample period	Date
1	09/07/15 – 14/10/15
2	15/10/15 – 14/01/16
3	15/01/16 – 17/02/16
4	18/02/16 – 09/03/16

Following this, sediment load (g) was calculated by multiplying the sediment concentration (g ml^{-1}) by the amount of runoff (ml) measured from the erosion plot for the sampling period.

Orthophosphate concentration (mg P l^{-1}) within the runoff sample was established by the automated ascorbic acid reduction method (Clesceri et al. 1995) on the Burkard 2000-SFA auto-analyser (Burkard Scientific, Uxbridge, UK). This was done for each runoff plot and the results averaged to relate to treatment performance.

3.3 Results

Baseline sampling identified that plot soil properties were not significantly different, confirming the trials were a fair test (Table 3.2).

Table 3.2. Soil properties

Analysis		Control	C FS	CPp FS	W FS	WPp FS
pH*		6.8	6.8	7.0	7.1	6.9
Organic matter (%)		3.4	3.4	3.4	3.7	3.4
Bulk density (g cm^3)		1.1	1.0	1.0	1.0	1.0
Total P (mg P kg^{-1})		642.3	662.7	657.4	630.8	643.6
Particle Size Distribution (%)†	Sand	22.3	17.5	13.4	14.9	15.3
	Silt	56.0	61.9	66.2	64.4	62.8
	Clay	21.7	20.6	20.4	20.8	21.9

*pH determined by the H_2O method
†Particle Size Distribution (PSD) size boundaries: Sand (> 0.063 mm); Silt (0.002mm-0.063 mm); Clay (< 0.002mm).

Weather data (Tables 3.3 and 3.4) indicated 214.8 mm of rain fell during the trial, with a maximum RE intensity of 228 mm^{-1} hr^{-1} over a 7 minute duration (22/08/15), and maximum RE duration of 41 minutes (12 mm^{-1} hr^{-1} intensity, 21/09/15). The majority of REs were 1 in 1 year storms; however a 1 in 30-year and 1 in 400-year RE were also recorded.

Table 3.3. Mean rainfall characteristics for the sampling periods

Sampling period	Total rainfall (mm)	Number of rain days†	Number of REs‡	RE intensity (mm hr^{-1})		RE duration (mins)		RE frequency (yrs)	
				Mean	Max.	Mean	Max.	Min	Max
1	120	29	14	15	228	14	41	1 in 1 year	1 in 400 year
2	55.2	16	3	12	36	14	21	< 1 in 1 year	< 1 in 1 year
3	25	8	1	12	12	7	7	< 1 in 1 year	< 1 in 1 year
4	14.6	6	1	12	24	3	3	< 1 in 1 year	< 1 in 1 year

†Rain days defined as a ≥ 1.0 mm within one day.
‡Rainfall events defined as ≥1.0 mm rain over a 10 minute period.

Table 3.4. Rainfall event characteristics over the experiment for each sampling period.

		Sampling period											
		1			2			3			4		
		Mean intensity	RE freq†	Max intensity ‡	Mean intensity	RE freq†	Max intensity‡	Mean intensity	RE freq†	Max intensity ‡	Mean intensity	RE freq†	Max intensity ‡
		mm hr^{-1}	yrs	mm hr^{-1}	mm hr^{-1}	yrs	mm hr^{-1}	mm hr^{-1}	yrs	mm hr^{-1}	mm hr^{-1}	yrs	mm hr^{-1}
Rainfall event	1	54	10	72	17	1	36	12	1	12	15	1	24
	2	12	1	12	12	1	12						
	3	12	1	12	14	1	24						
	4	180	400	180									
	5	12	1	12									
	6	12	1	12									
	7	12	1	12									
	8	18	1	24									
	9	71	30	228									
	10	12	1	12									
	11	53	15	156									
	12	15	1	24									
	13	12	1	12									
	14	24	2	48									

† RE frequency based on the mean intensity of the RE

‡ Maximum intensity experienced within that RE

The results show an initial release of sediment and nutrients from the FS, and high runoff volume in the early stages (July-October 2015) of FS application, coinciding with the maximum RE intensity. This is consistent with results of other FS and C studies (Al-Bataina et al. 2016; Glanville et al. 2003; Nguyen & Marschner 2013; Waters 2010). This first ‘flush’ of runoff is shown in Table 3.5, where no statistical differences were observed between the FS treatments and the Control. After this initial period, the C FS and W FS produced statistically less runoff than the Control.

Regarding sediment concentrations, initially, the FS treatments gave statistically higher values than the Control (Table 3.5). Although there were no significant differences, by Sampling Period 4 the W FS was meeting the water quality target for sediment (0.1 mg l^{-1}). Lack of significantly different data could be due to uncontrollable plot spatial variability (e.g. microtopography, soil compaction levels). It also could have been due to a lack of replicates in Sample Periods 3 and 4, where movement of the plot boundaries only allowed 3 replicates for WPp FS and CPp FS.

Regarding sediment loads (Figure 3.2), there was a distinct first flush in Sample Period 1 whereby the majority of FS treatments displayed similar or higher sediment loads than the Control. By Sampling Periods 2-4 the FS treatments had consistently lower sediment loads than the Control (not always statistically significant). In Sampling Periods 2-4 the C FS, CPp FS and W FS treatments displayed half the sediment load of the Control.

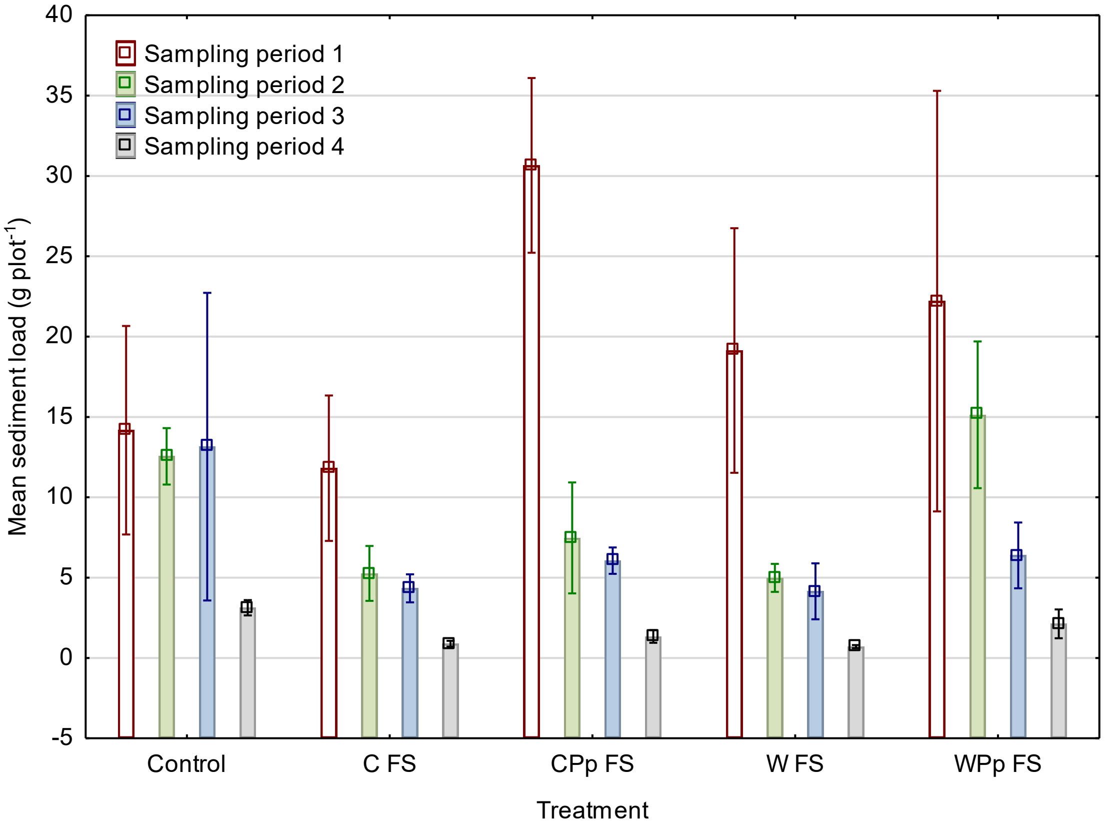

Figure 3.2. Mean (n=4) sediment load (g $plot^{-1}$) between treatments and sampling periods. Bars indicate standard error.

Table 3.5. Mean runoff volume (l plot^{-1}) compared to the control (%), and sediment concentration (g l^{-1}) for each treatment and sample period.

Treatment	**Runoff volume (l plot^{-1}) and change from the control (%)**					**Sediment concentration (g l^{-1})**			
	Sample period	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Control	Mean ±S.E	23.6^{a} ±0.0	59.1^{a} ±6.4	19.9^{a,b} ±4.7	12.6^{b} ±2.2	0.6^{a}	0.2^{a,b}	0.6^{a}	0.3^{a}
	Change (%)	-	-	-	-				
C FS	Mean ±S.E	14.8^{a} ±3.8	31.8^{b} ±3.7	11.8^{a} ±1.7	5.9^{a} ±1.2	0.7^{a,b}	0.2^{a}	0.4^{a}	0.2^{a}
	Change (%)	-37.5	-46.3	-40.7	-52.9				
W FS	Mean ±S.E	17.0^{a} ±4.1	32.5^{b} ±3.0	17.0^{a,b} ±3.9	5.2^{a} ±0.7	1.2^{a,b}	0.2^{a}	0.2^{a}	0.1^{a}
	Change (%)	-28.1	-45.0	-14.8	-58.8				
CPp FS	Mean ±S.E	16.2^{a} ±1.5	34.7^{a,b} ±12.4	27.2^{b} ±5.2	7.9^{a,b} ±2.6	2.3^{b}	0.3^{a,b}	0.3^{a}	0.2^{a}
	Change (%)	-31.3	-41.3	+36.3	-37.3				
WPp FS	Mean ±S.E	20.7^{a} ±3.8	56.1^{a,b} ±7.8	24.8^{a,b} ±4.9	13.8^{b} ±2.0	1.2^{a,b}	0.3^{b}	0.3^{a}	0.2^{a}
	Change (%)	-12.5	-5.0	+24.4	+9.8				

Sample period 3; plot 14 not included in analysis
Sample period 4 ; plots 1 and 14 not included in analysis
N.B. Within each sample period, values for litres plot^{-1}, followed by the same letter are not statistically different ($p \leq 0.05$) following one-way ANOVA and post-hoc Fisher LSD.

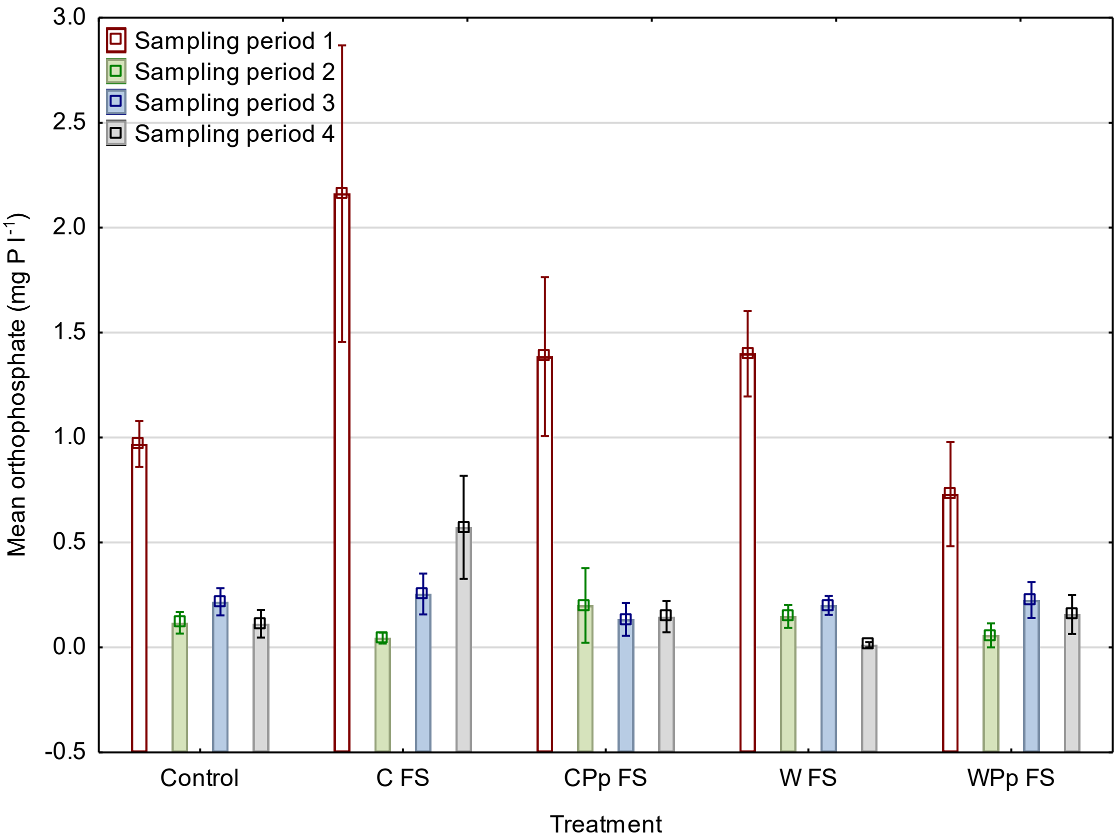

Figure 3.3. Mean (n=4) orthophosphate (mg P l^{-1}) between treatments and sampling periods. Bars indicate standard error.

Runoff PO_4^{3-} concentrations varied significantly between treatments (Figure 3.3). With the exception of the WPp FS treatments, runoff from the Control plots had statistically lower PO_4^{3-} concentrations than the FS plots in Sampling Period 1. In Sampling Periods 2 and 3, there were no statistical differences between treatments. A similar result was observed for Sampling Period 4 with the exception of the C FS and WPp FS treatments, which were associated with statistically higher runoff PO_4^{3-} concentrations. Cumulative FS treatment PO_4^{3-} concentrations were higher than those of the Control, with the exception of the WPp FS treatment. None of these were significantly higher or lower, except for that of the C FS treatment which produced significantly higher PO_4^{3-} concentrations than the Control overall.

It is suggested that the weather conditions impacted on the variability of results between sample periods, especially when comparing Sample Period 1 to Sample Periods 2-4. A longer monitoring period or more experimental sites may have captured more statistically robust differences between the FS treatments and the Control. This may have provided more reliable data on treatment efficiency which in the current experiment was masked by a prolonged first ‘flush’ period. Temporal and spatial variability in site and weather conditions highlights the challenges associated with fieldwork - more experimental sites may have made the field sample design more robust.

This is a consideration for the wider use of FS at the catchment scale where there are variable environmental and agricultural conditions. More field-based research is required into the use of FS in these different conditions; particularly their effectiveness in different soil type, slopes (length, shapes and gradients), rainfall events, crop types, and how they function when used at different times of the year (including when used at different times within a cropping or rotation cycle). Undertaking research such as this will expose the FS to different levels of sediment and orthophosphate losses, allowing their treatment efficiency to be established under a variety of scenarios.

3.4 Conclusions

The initial results from this field trial show that FS efficiency is variable. Few significant differences were found between FS treatments and the Control regarding their sediment control efficiency. Similarly, there were few significant differences between FS treatments and the control regarding their orthophosphate control capability.

Significant differences which were recorded were mainly found within Sampling Period 1 where FS treatments increased the amount of sediment and orthophosphate found within the runoff in the collection tanks. Results in Sampling Period 1 coincided with a period of high rainfall and extreme REs, where rainfall intensity was high. This may have created a prolonged first flush phase from the FS treatments whereby sediments/fines and nutrients were released from the FS fill media for longer than usual. Sampling periods 2-4 coincided with lower than average rainfall, where few REs were recorded and were weak in intensity.

More research is required into the use of FS within field conditions, and into the phenomenon of the ‘first flush’ of runoff, sediment and orthophosphate, in order to test appropriate materials which can be used as PSMs.

3.5 References

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CHAPTER 4: EFFICACY OF SELECTED PHOSPHOROUS SORBING MATERIALS (PSMS) TO ENHANCE THE ORTHOPHOSPHATE SORPTION EFFICIENCY OF FILTER SOCKS

Abstract

Agricultural PO_4^{3-} is a major cause of water quality degradation alongside eroded sediments. PO_4^{3-} easily binds to clays and silts and thus, for its effective control, mitigation measures need to remove sediments and orthophosphate in order to meet water quality targets. Research suggests that FS are an effective sediment-control method, whilst phosphorous sorbing materials (PSMs) to remove orthophosphate are widely used within the wastewater treatment industries. Potentially effective PSMs were identified from the literature; kaolin (K), fuller's earth (FE), ferrihydrite ochre (Fc-O), goethite ochre (G-O), and used as amendments for traditional compost or woodchip FS fill media. Phosphorous sorbing capability was trialled in a series of column experiments against a commercially available proprietary product (Pp), and against non-PSM amended FS fill media. The Fc-O was significantly more effective (up to 99% removal efficiency) at removing orthophosphate than the other PSMs, and was the only PSM which allowed the resultant leachate to meet the water quality target (0.05 mg P l^{-1}). Similarly, the G-O removed significantly more orthophosphate than the K, FE and the Pp, however it was not as efficient as the Fc-O, and crucially did not meet the water quality target. The K, FE and the Pp were not effective PSMs owing to lower phosphorus sorption efficiencies and higher variability of results (desorption). The applicability of the PSMs as sediment control amendments for orthophosphate control in the agricultural sector was established by way of cost benefit analysis. This indicated that the two ochre's cost £0.01 mg P^{-1} removed, which is 1100% cheaper than the widely used Pp. This research is essential in identifying and developing cost-effective mitigation measures for concurrent removal of sediment, SB PO_4^{3-} and orthophosphate losses from agricultural runoff.

Keywords

Phosphorus sorbing materials; ferrihydrite; goethite; Water Framework Directive; diffuse pollution.

The spelling and formatting of the original article has been adjusted to fit the format of this thesis.

4.1 Introduction

The EU WFD regulates the quality of the water environment through a series of targets and objectives, and is implemented and monitored by various environmental enforcement agencies throughout the UK (e.g. Environment Agency, Scottish Environmental Protection Agency, Natural Resources Wales). In England only 83% of eligible waterbodies are currently meeting their water quality targets (Environment Agency 2015a). A major contributing factor to this poor water quality is agricultural diffuse pollution which is estimated to deliver up to 70% of sediments, 60% of NO_3^- and 25% of PO_4^{3-} to receiving waters (National Audit Office 2010). Inappropriate agricultural practices, topography, the increased frequency of extreme REs, and a lack of mitigation options (Bennett et al. 2001, Tilman et al. 2002) combine to promote the generation of surface runoff, which has resulted in increased ecological degradation through eutrophication, flooding, sedimentation and turbidity within the watercourses (Tilman et al. 2002, Withers et al. 2014).

Much research focus has been given to studying the fate of PO_4^{3-} in these environments as it can be particularly detrimental to the water environment (Correll 1998). PO_4^{3-} is applied to farmland as fertiliser or manure for uptake and assimilation by crops (Bennett et al. 2001, Miller 2004). Generally PO_4^{3-} losses from agricultural lands are increasing as climate change increases the number of and severity of REs (Tilman et al. 2002, Schoumans et al. 2014), even though PO_4^{3-} fertiliser usage is decreasing (DEFRA. 2017). PO_4^{3-} is a particularly detrimental nutrient as it can be removed as a solute in runoff (Correll 1998), as well as be adsorbed to eroded fines primarily, clays (Schroth and Sposito 1997, Gimsing and Borggaard 2007), soil organic matter (Na et al. 2016, Ronkanen et al. 2016), and soil metal oxides including Fe, Al, Ca (Xu et al. 2014c, Fink et al. 2016, Uddin 2017). SB PO_4^{3-} can be managed through erosion and sediment control (Faucette et al. 2008, Waters 2010, De Baets et al. 2011), however orthophosphate can only be managed through chemical and biological adsorption (Yeoman et al. 1988, Yuan et al. 2012), breakdown or precipitation (Brix et al. 2001, Xu et al. 2014c, Antelo et al. 2015) and is easily transported in runoff and leachate. This therefore makes it more detrimental to aquatic environments as it is less easily removed from within the runoff, especially within an agricultural setting. Soil erosion and sediment control methods, such as cover cropping, tillage management, buffer strips, grassed waterways and contour cropping have been developed (Vinten et al. 2014, Mekonnen et al. 2015, Mhazo et al. 2016, Pan et al. 2017, Zhang et al. 2017). These have proven efficiency and efficacy at preventing the detachment and/or transport phases of the soil erosion process, thereby preventing adsorbed PO_4^{3-} from being moved off-site and delivered to waterbodies. However methods to mitigate against orthophosphate losses associated with runoff from agricultural lands are limited. The most effective and consistent methods are the management of fertiliser/manure application, lime application, establishment of hedges and shelter belts, and BS or changing the land use (Deasy et al. 2008, Newell Price et al. 2011, Schoumans et al. 2014). Currently, the majority of elevated PO_4^{3-} in waterbodies is remediated by wastewater treatment works (Defra, 2012).

Treatment of orthophosphate in wastewater has been the focus of much research, and involves the filtration, precipitation and adsorption of PO_4^{3-} using metal ions

(Yeoman et al. 1988, De-Bashan and Bashan 2004, Nancharaiah et al. 2016). Biological breakdown is also widely utilised (Yuan et al. 2012, Zuthi et al. 2013, Zou and Wang 2016) or more recently (but less widespread), auto-mineralisation (Pratt et al. 2012). These technologies and the materials used, although well-funded and understood, are not widely utilised outside of the wastewater treatment industry, but could prove incredibly beneficial to the agricultural sector for in-field control of PO_4^{3-}. The materials used for this purpose are known as PSMs. Wastewater with elevated levels of PO_4^{3-} is typically passed through or mixed with the PSMs allowing coagulation, adsorption and precipitation of the PO_4^{3-} (Yeoman et al. 1988, De-Bashan and Bashan 2004, Zou and Wang 2016).

PSM selection is based on a material having a high PSE. Consequently, generally an optimum PSM has the following parameters:

- particle size of <0.002 mm;
- presence of metal ions, (Fe, Al, Ca and Mg);
- high hydraulic conductivity to prevent clogging, but not so high that contact time between the PSM and solution is reduced.

Particle size distribution can often be >0.002 mm as most PSMs exhibit a crystalline structure owing to the presence of metal ions. Most typically, PSMs are synthesised materials to ensure that they meet these target specifications, however natural, waste and by-product materials, such as DWTR (Gibbons et al. 2009, Ippolito et al. 2011), corundum (Souto and Guitian 2002), Fe and Al oxides (Ooi et al. 2017), and kaolinite (Wei et al. 2014), are also used. Such materials are considered more economical as they often provide near similar PSE to synthesised products (Leader et al. 2008), but without the manufacturing costs.

Fe and Al based PSMs are most widely utilised by the wastewater treatment industry, with PO_4^{3-} sorption occurring through ion and ligand exchange (mononuclear and binuclear bidentate coordination bonds), and surface precipitation (Ippolito et al. 2011, Loganathan et al. 2014, Gérard 2016). Sorption is most effective at lower pH values, pH<5, (Hingston et al. 1968, Cornell and Schwertmann 2003), and consequently PSMs that perform better at higher pH values, such as Ca and Mg, are sometimes used in conjunction to maximise PO_4^{3-} removal. Commonly used PSMs include synthesised alumina (Mekhemer et al. 2000, Karim et al. 2011), synthesised ferrihydrite (Michel et al. 2010, Wang et al. 2013), synthesised goethite (Torrent et al. 1990, Rakovan et al. 1999), natural or synthesised calcite (Suzuki et al. 1986, Li et al. 2017b), and clays such as montmorillonite and illite (Murphy 1939, Edzwald et al. 1976, Gimsing and Borggaard 2002, Ooi et al. 2017). Synthesised materials are currently not suitable for widespread use in the agricultural sector for PO_4^{3-} control due to their comparatively high cost and inaccessibility as compared to waste and by-product PSMs.

To be compliant with WFD targets, the removal of sediment, and consequently SB PO_4^{3-}, is also a necessity for the control of PO_4^{3-} from the agricultural sector. FS have been found to remove significant amounts of sediment and associated SB PO_4^{3-} from runoff (Faucette et al. 2008, 2009b, Shipitalo et al. 2012, Cooke et al. 2017). FS are tubular meshes which are filled with C or W, and typically placed at the bottom of slopes to intercept runoff. The FS works by a) acting as a temporary bund, allowing the runoff to initially pool upslope allowing the largest sand particles to deposit; and b) reducing the velocity of the runoff as it passes through the FS allowing the smaller silt and clay particles to deposit within the FS fill media. However they are not as effective at removing orthophosphate and can even increase PO_4^{3-} in the short term as soluble ions are released from the fill media after initial installation (Waters 2010). For concurrent sediment, SB PO_4^{3-} and orthophosphate control, it would be beneficial to add efficient PSMs into the FS fill media.

The objective of this study was to critically evaluate the efficiency of natural, and by-product PSMs to remove orthophosphate from runoff, in order to meet a pre-defined water quality target of 0.05 mg P l^{-1}. Materials were selected based on their PSE as indicated by the literature, their availability, and their potential cost with regards to future adoption. The selected PSMs were mixed with typical FS fill media (C or W) with a view to farmers using these solutions for in-field sediment and PO_4^{3-} control. These fill media were selected as they are already utilised in the agricultural sector and the landscaping industry for erosion control.

4.2 Materials and Methods

4.2.1 Determination of PSE

PSE is usually determined through batch or column experiments. These expose a sorbent (PSM) to a PO_4^{3-} solution of known concentration, for a given period of time under a specific set of environmental conditions. Batch systems are most commonly used as they allow results to be easily fitted to sorption models. However, column experiments have been found to be more comparable to real-life due to the continuous flow-through of the solution, allowing the sorbent to be exposed to the same concentration at all times within the flow process (Helfferich 1995, Loganathan et al. 2014). Conversely, the sorbent in batch experiments is exposed to a continuously decreasing amount of PO_4^{3-} as the experimental time progresses. Furthermore, as the sorbent remains exposed to the solution, sorption and desorption are easily interchangeable (Gupta et al. 2012).

In column experiments, rapid sorption initially occurs in the top layer of the column material, until equilibrium is reached with the concentration of the solute. Sorption then occurs within the zone immediately below this rapid sorption layer; known as the mass transfer zone (MTZ). This MTZ moves down the column, until it reaches the base, whereby the ‘breakthrough point’ is reached. This allows the bottom layers to sorb PO_4^{3-} (Helfferich 1995), however the breakthrough adsorption capacity is less than the overall sorption capacity (Helfferich 1995, Bae et al. 2002, Gupta et al. 2012, Loganathan et al. 2014). When no further PO_4^{3-} can be sorbed, ‘exhaustion’ has been reached (Bajracharya and Barry 1995, Bae et al. 2002, Gupta et al. 2012, Loganathan et al. 2014). Due to the comparability of column experiments with real-life conditions, this was the method chosen to assess the PSE of the PSMs evaluated in this study.

4.2.2 Characteristics of FS fill media and PSMs evaluated

Baseline properties of the C and W fill media and PSMs were established through laboratory and mineralogical analysis (Table 4.1).

C and W used within the treatments were used in the condition that they arrived from the supplier (Scotbark Ltd). They were not air dried so to avoid them becoming hydrophobic, and were not wetted up, so that the target moisture content of <60% was maintained (Alexander Associates Inc., 2006). C was hand sieved prior to the experiment to ensure it met the particle size distribution (PSD) specification for C used for sediment control (Alexander Associates Inc., 2006). Similar specifications for W are not available, however hand sieving was still undertaken on the W to ensure that it's PSD (Table 4.1) and hence sediment control ability was similar to that of C. This has been identified as the optimum PSD for sediment control as it maintains runoff flow-through at rates of 15 – 38 litres min^{-1}, whilst promoting sediment deposition (Alexander Associates 2006). Total P for the C and W was determined using a Perkin Elmer Atomic Absorption Spectrometer (AAS) AnalystTM 800 following extraction with a 3:1 $HCl:HNO_3$ solution using an Anton Paar Multiwave

Table 4.1. Baseline properties of the fill media and PSMs.

Property		**Material**						
		C	**W**	**Pp**	**K**	**FE**	**Fc-O**	**G-O**
Particle size distribution (%)	<0.002 mm	0	0	4.3	99	66	2.3	40.1
	0.002 - 2 mm	0	0	95.7	1	34	97.7	59.9
	<2 mm	63	57	0	0	0	0	0
	2 - 5 mm	24	33	0	0	0	0	0
	5 - 10 mm	12	10	0	0	0	0	0
	>10 mm	1	1	0	0	0	0	0
Total P	mg P kg^{-1}	178.7 (±4.6)	148.2 (±5.0)	-				
Particle density	g cm^{-3}	1.42	1.4	2.13	2.25	2.63	3.28	4.03
Specific surface area	m^2 kg^{-1}	-			3213	730	588	945
Cation Exchange Capacity	cmol kg^{-1}	-		13.5	2.9	64	0	0
Bulk mineralogy (%)	Anatase			0	0	0.2	0	0
	Aragonite			0.1	0	0	2.3	0
	Calcite			0	0.6	2.0	50.4	14.1
	Clinoptilolite			65.8	0	0	0	0
	Ferrihydrite			0	0	0	46.6	0
	Goethite			0.5	0	0	0	84.7
	Hematite			0	0	0.7	0	0
	Kaolinite			0	95.5	0	0	0
	K-feldspar			0.1	0	21.0	0	0
	Mica			0	0	2.0	0	0
	Muscovite			0	3.9	0	0	0
	Opal-C/CT			19.0	0	0	0	0
	Plagioclase			0	0	8.2	0	0
	Quartz			1.0	0	2.0	0.7	1.2
	Smectite			13.5	0	64.0	0	0

-denotes where analysis was not available for a particular material.

3000 microwave digestion system (US EPA Method 3051; British Standard BS 7755: Section 3.13:1998; ISO 11047:1998).

The PSMs investigated in this study are Fc-O, G-O, K, FE and a commercially available Pp. The bulk mineralogy, CEC, PSD and particle density of the PSMs used within the study were established by X-Ray Powder Diffraction (XRPD) and X-Ray Fluorescence (XRF). XRPD was undertaken using the GM003 and GM004 accreditation methods, whilst the LTM2 WD-XRF Test Method was used to establish the XRF results. This also established the particle density of the C and W fill media. Surface area (SA) was established using laser diffraction (Mastersizer 3000; Malvern Instruments Ltd). These analyses were chosen with reference to the optimum PSM conditions, and used to understand and evaluate the methods by which PO_4^{3-} adsorption was, or was not, taking place.

Baseline characterisation of the PSMs, indicates that only K and FE have >50% of their PSD <0.002 mm which suggests that the other PSMs will not be as efficient at PO_4^{3-} adsorption. However, this method of PSD analysis does not account for crystalline structures associated with metal ion PSMs.

4.2.3 Column trial methodology

All PSMs were air dried prior to mixing. To ensure a fair test, the PSMs were mixed with the fill media at the Pp application rate (20 kg m^{-3}). Thorough mixing was ensured by adding the PSMs and fill media into bags and shaking for 1 minute until the fill media was observed to be evenly coated with the PSM. The fill media-PSM mixtures were subsequently packed into columns (10 cm length x 6.8 cm diameter polypropylene pipe with the base covered by fabric gauze) to a bulk density (BD) of 700 kg m^{-3}. This BD was chosen as it replicates the desired BD of FS when installed in-field, and equated to 0.254 kg of fill media per column. Bulk density was ensured by measuring the materials out into separate bags pre-column filling, and packing into the columns in stages whilst packing down with a stainless steel press. Once packed, each column was then clamped onto a wooden frame that connected the columns to a sample collection system (Figure 4.1).

Figure 4.1. Column trial experimental set-up.

Each column had PO_4^{3-} solution applied to achieve saturation of the treatment; based on the total porosity of the mixtures. This was calculated using a series of equations (Equations 4.1 – 4.4).

Firstly, the mean particle density of the C-PSM or W-PSM mixtures was established (Table 4.2). Where the fill media accounts for 100% of the mixture (PSM was not added), the particle densities calculated for the fill media were used (Table 4.1).

$$\text{Mean mixture particle density} = \frac{(a \times b) + (c \times d)}{100} \times 1000$$

Equation 4.1. Mean particle density of fill media-PSM mixtures

Table 4.2. Calculated particle density, porosity and volume required for saturation for each of the treatments.

Treatment	Particle density (g cm^{-3})	Porosity (%)	Volume of PO_4^{3-} solution required to achieve saturation (ml)
Non-PSM Control (C)	1.42	50.70	184
CPp	1.44	51.38	187
CK	1.45	51.85	188
CFE	1.44	51.50	187
CFc-O	1.47	52.45	191
CG-O	1.49	53.12	193
Non-PSM Control (W)	1.40	50.00	182
WPp	1.42	50.72	184
WK	1.43	51.20	186
WFE	1.42	50.84	185
WFc-O	1.45	51.81	188
WG-O	1.47	52.50	191

Where *a* is the mean particle density of the PSM (g cm^{-3}) (Table 4.1); *b* the percentage of that PSM within the C or W fill media; *c* the particle density of the fill media (Table 4.1); and *d* the percentage of the treatment that is fill media. This was then divided by 100, and multiplied by 1000 to obtain the mean mixture particle density (kg m^{-3}).

The percentage of PSM and fill media, within each treatment (*b* and *d*) is calculated using an application rate of 20 kg m^{-3} and the mass of fill media (0.245 kg) required to fill the columns. This equates to a PSM percentage of 2.8% relative to the fill media which accounts for 97.2% of each treatment.

The mean treatment particle densities (Table 4.2) calculated from Equation 4.1, were then used to determine the treatment porosity (Table 4.2); Equation 4.2.

$$\text{Porosity} = 1 - \left(\frac{f}{g}\right)$$

Equation 4.2. Porosity of the PSM-fill media treatments.

Where *f* is the target BD of the FS (700 kg m^{-3}); and *g* is the mean (n=4) treatment particle density (g cm^{-3}) for the C-PSM or W-PSM treatments (Table 4.2) and C or W fill media (Table 4.1).

To ensure normalization, treatment porosity (Table 4.2) was used to calculate the volume of PO_4^{3-} solution (ml) required to saturate the treatments (Equation 4.3) within the columns (Table 4.2) and allow optimum adsorption, as pore spaces would be filled with the PO_4^{3-} solution.

Table 4.3. Phosphate load added to the columns.

Treatment	Phosphate load* added to columns (mg P) based on intended orthophosphate concentration		
	Low	Medium	High
Non-PSM control (C)	0.015	0.048	0.239
CPp	0.015	0.049	0.243
CK	0.015	0.049	0.244
CFE	0.015	0.049	0.243
CFc-O	0.015	0.050	0.248
CG-O	0.015	0.050	0.251
Non-PSM control (W)	0.015	0.047	0.237
WPp	0.015	0.048	0.239
WK	0.015	0.048	0.242
WFE	0.015	0.048	0.241
WFc-O	0.015	0.049	0.244
WG-O	0.015	0.050	0.248

**Phosphate load calculated using the orthophosphate concentrations measured in field – low (0.08 mg P l^{-1}), medium (0.26 mg P l^{-1}), high (1.3 mg P l^{-1}).*

$$V_{SAT} = h \times k$$

Equation 4.3. Volume of solution required to achieve saturation of the treatments.

Where V_{SAT} is the volume of solution required to saturate the treatments; *h* is the column volume (363.2 cm^3); and *k* the treatment porosity.

Saturation of the fill media (Equation 4.3) was achieved with either deionised water (control), or the orthophosphate solution. The orthophosphate concentrations were selected based on values associated with runoff from the dominant erodible soils in the Lugg catchment (Cooke et al. 2017):

- low; 0.08 mg P l^{-1}
- medium; 0.26 mg P l^{-1}
- high; 1.30 mg P l^{-1}

These PO_4^{3-} concentrations are all above the water quality target for the Lugg catchment (0.05 mg P l^{-1}). These concentrations were used to calculate the PO_4^{3-} load (mg P) which was added to the treatments (Table 4.3); Equation 4.4:

$$\text{Phosphate load applied} = \left(\frac{m}{1000}\right) \times r$$

Equation 4.4. Phosphate load applied to the columns.

Where *m* is the solution PO_4^{3-} concentration converted into mg P ml^{-1}; and *r* is the volume required to achieve treatment saturation which ensures standardisation according to the PO_4^{3-} concentration applied.

All treatments were replicated in quadruplicate, resulting in a total 152 columns. Each of the columns had the orthophosphate solution, or deionised water (the control) applied twice, with the solutions poured evenly into the top of the columns using a surface gauze to minimise preferential flow paths and surface ponding. A period of 48 hours was left between the solution applications, representing the mean time between REs experienced in field trials within the Wye catchment (Cooke, 2017). In line with previous studies (Shipitalo et al. 2010, Waters 2010) two flushes (F1 and F2) were undertaken as C and W are known to release an initial flush of PO_4^{3-}. As the solution passed through the columns, the time taken for leachate initiation and leachate volume at 30 seconds, 1, 2, 5, 10, 20, 40, 60 mins post-application were monitored. During experimentation, ambient air temperature was recorded as temperature can influence PSM performance (Sugiyama and Hama 2013, Bai et al. 2017).

4.2.4 Analytical methodology

Leachate PO_4^{3-} concentration was determined using the automated ascorbic acid reduction method (Clesceri et al. 1995) on the Burkard 2000-SFA auto-analyser (Burkard Scientific, Uxbridge, UK). Treatment performance regarding leachate PO_4^{3-} concentration was assessed in comparison to the River Lugg water quality target (0.05 mg P l^{-1}). Furthermore Leachate PO_4^{3-} concentration is used in mass balance calculations to determine treatment PSE.

Total sediment within the leachate was established by taking a 20 ml subsample, placing it into an oven in a pre-weighed tin, and measuring the weight of the sediment within the tin after it has exited the oven and the water evaporated off. This sediment weight per 20 ml of leachate was then multiplied up to the total leachate volume collected from the sample. This allowed total sediment loss from the column, and consequently the sediment concentration, to be obtained. This was done for the leachate results for each flush.

4.2.4.1 Treatment PSE (%)

Determination of PSE (%) is essential in order to assess treatment performance in the context of water quality targets across both flush events. For each treatment, PSM sorption efficiency was determined using the mean (n=4) leachate PO_4^{3-} concentration for each of the treatments and the PO_4^{3-} load that was applied. Firstly, the mass of PO_4^{3-} removed (mg PO_4^{3-}) by the PSM treatments was calculated using Equation 4.5:

$$\text{Phosphate removed} = (s + t) - u$$

Equation 4.5. Phosphate removed by the treatments

Where s is the mean (n=4) leachate PO_4^{3-} load (mg PO_4^{3-}) for the control, C and W treatments where deionised water was applied; t is the mass of PO_4^{3-} applied to each treatment via the PO_4^{3-} solutions (Table 4.3); and u is the leachate PO_4^{3-} load, (mg P). Subsequently, the PO_4^{3-} sorption efficiency was calculated using Equation 4.6:

$$\text{PSE} = \frac{(\text{P0} + \text{P1}) - \text{P2}}{(\text{P0} + \text{P1})} \times 100$$

Equation 4.6. Phosphate sorption efficiency (%)

Where P0 is the mean (n=4) leachate PO_4^{3-} load (mg PO_4^{3-}) of the control, C or W where deionised water has been added; P1 is the mean (n=4) treatment PO_4^{3-} load applied (Table 4.5); PO + P1 is the total PO_4^{3-} load within each treatment; P2 is the treatment leachate PO_4^{3-} load.

4.2.4.2 Statistical Analysis

Differences in treatment performance between F1 and F2 were compared using T-tests (Statistica 13.2, Dell Inc.). Values are statistically different where $p \leq 0.05$.

Differences in treatment performance between treatments for each flush event were compared using one-way ANOVA and *post-hoc* Fisher LSD (Statistica 13.2 Dell Inc.). Values between treatments followed by the same letter are not statistically different ($p \leq 0.05$).

4.2.5 Cost-benefit calculations

To facilitate adoption of this PSM enhanced FS technology, treatment cost benefit was determined. To assess this, results from Equation 4.5 were used in conjunction with the PSM application rates and cost of the PSMs materials identified from the literature.

$$\text{PCM} = \frac{\text{PR}}{(\text{Q} + \text{V})}$$

Equation 4.7. Phosphate load removed by the total column material

Where PO_4^{3-} load removed by the total column material (PCM) is the mass of PO_4^{3-} removal per gram of column material; PR is PO_4^{3-} removal derived from Equation 4.5; Q is the mass of fill media within the columns (0.254 kg); and V is the mass of PSM within each treatment (0 kg or 0.00725 kg). Divide this by 1 to give the amount of material required for 1 mg P removal. This was then used alongside a literature search of material costs (MC), which were averaged per gram of PSM material (Equation 4.8):

$$\text{Cost of phosphate removal} = \left(\frac{1}{\text{PCM}}\right) \times \text{MC}$$

Equation 4.8. Cost of phosphate removal per gram of material.

These costs were used to assess the potential uptake of the respective PSMs within an agricultural context.

4.3 Results

4.3.1 Leachate PO_4^{3-} concentration

The leachate PO_4^{3-} concentration (Table 4.4) varied significantly between and within the C and W fill media treatments. The most successful PSM, regardless of fill media, was Fc-O which was the only PSM to consistently reduce the PO_4^{3-} concentration to below the water quality target (0.05 mg P l^{-1}) at F1.

Table 4.4. Differences in mean PO_4^{3-} concentration (mg P l^{-1}) for each PSM treatment at F1 and F2 as compared to the non-PSM Compost (C) and Woodchip (W) controls.

Compost Fill media							
PO_4^{3-} concentration*	**Flush**	**Non-PSM control (C)**	**CPp**	**CK**	**CFE**	**CFc-O**	**CG-O**
Low	F1	1.13^{c}	0.93^{c}	1.22^{c}	1.02^{c}	0.01^{a}	0.48^{b}
	F2	1.73^{d}	1.60^{d}	1.48^{cd}	1.10^{bc}	0.43^{a}	0.76^{ab}
Medium	F1	1.05^{b}	1.03^{b}	1.18^{b}	1.12^{b}	0.04^{a}	0.36^{a}
	F2	2.15^{d}	1.38^{bc}	1.73^{cd}	1.38^{bc}	0.22^{a}	0.82^{ab}
High	F1	1.47^{c}	1.73^{c}	2.00^{c}	1.68^{c}	0.04^{a}	0.90^{b}
	F2	2.40^{c}	2.20^{c}	1.98^{c}	2.03^{c}	0.49^{a}	1.08^{b}
Woodchip Fill media							
PO_4^{3-} concentration*	**Flush**	**Non-PSM control (W)**	**WPp**	**WK**	**WFE**	**WFc-O**	**WG-O**
Low	F1	14.2^{bc}	19.6^{c}	15.1^{bc}	14.5^{bc}	9.48^{b}	1.15^{a}
	F2	40.0^{b}	44.1^{b}	40.5^{b}	37.9^{b}	0.55^{a}	10.2^{a}
Medium	F1	17.5^{c}	15.5^{bc}	19.9^{c}	11.5^{abc}	2.70^{a}	6.5^{ab}
	F2	47.0^{bc}	42.4^{bc}	47.9^{c}	33.0^{b}	0.81^{a}	9.48^{a}
High	F1	18.5^{c}	13.9^{bc}	25.1^{d}	9.68^{b}	0.75^{a}	9.23^{b}
	F2	52.8^{c}	47.8^{bc}	55.1^{c}	33.2^{b}	0.70^{a}	7.48^{a}

Water quality target: 0.05 mg P l^{-1}
For each fill media, solution PO_4^{3-} concentration and Flush (F1 and F2) values in each row followed by the same letter are not significantly different following Factorial ANOVA and post-hoc Fisher LSD analysis.

4.3.1.1 Compost fill media treatments

The results indicate that for F1, at Low and High solution P concentrations, CFc-O leachate PO_4^{3-} concentrations were significantly lower as compared to all other treatments, including the non-PSM control (C). For the Medium P solution concentration at F1, the CFc-O treatment was associated with lower PO_4^{3-} concentrations than all other treatments except for CG-O, indicating that Fe-oxides are the best performing PSMs when placed in C sediment control fill media. A similar result was observed for F2 (Table 4.4).

Further, for F1 and F2, with the exception of F2 Low and Medium PO_4^{3-} solution applications, the CG-O leachate PO_4^{3-} concentrations were significantly lower than that of the C, CPp, CK and CFE treatments. The CG-O treatment did not achieve the water quality target (0.05 mg P l^{-1}), however it did reduce the PO_4^{3-} concentration to <1.0 mg P l^{-1} (Table 4.4).

Across all solution P concentrations and for both F1 and F2, the CK, CPp and CFE treatments had no impact on lowering the PO_4^{3-} concentration within the leachate as compared with the non-PSM control treatment (Table 4.2).

With the exception of the CK treatment at the High PO_4^{3-} concentration (Table 4.4), significantly higher PO_4^{3-} concentrations were found for F2 than F1 owing to the release of PO_4^{3-} from the fill media into solution during the 48hr period between the F1 and F2 events. In addition, some of the PSM PO_4^{3-} adsorption sites will have

Table 4.5. Differences in mean PO_4^{3-} sorption efficiency (%) for each treatment and flush, compared to the control.

Compost fill media							
PO_4^{3-} load*	**Flush**	**Non-PSM control (C)**	**CPp**	**CK**	**CFE**	**CFc-O**	**CG-O**
Low	F1	15.3^{c}	29.4^{c}	6.4^{c}	22.5^{c}	99.0^{a}	62.4^{b}
	F2	-47.6^{d}	-39.2^{d}	-29.0^{cd}	4.3^{bc}	61.6^{a}	31.8^{ab}
Medium	F1	30.5^{c}	31.0^{c}	20.8^{c}	24.8^{c}	97.1^{a}	75.2^{b}
	F2	-59.5^{d}	-3.3^{bc}	-30.2^{cd}	-3.3^{bc}	83.0^{a}	36.9^{ab}
High	F1	42.3^{bc}	31.8^{c}	20.7^{c}	33.8^{c}	98.3^{a}	64.1^{b}
	F2	-0.6^{c}	7.1^{c}	16.4^{c}	14.5^{c}	79.2^{a}	54.0^{b}
Woodchip fill media							
PO_4^{3-} load*	**Flush**	**Non-PSM control (W)**	**WPp**	**WK**	**WFE**	**WFc-O**	**WG-O**
Low	F1	28.6^{bc}	0.1^{c}	22.4^{bc}	25.9^{bc}	50.7^{b}	93.9^{a}
	F2	26.1^{b}	17.5^{b}	23.5^{b}	28.8^{b}	99.0^{a}	80.2^{a}
Medium	F1	12.5^{c}	21.7^{bc}	-1.2^{c}	41.9^{abc}	86.1^{a}	66.0^{ab}
	F2	13.4^{bc}	21.0^{bc}	9.9^{c}	38.2^{b}	98.5^{a}	81.7^{a}
High	F1	12.5^{c}	33.5^{bc}	-21.5^{d}	53.4^{b}	96.3^{a}	54.2^{b}
	F2	4.6^{c}	12.7^{bc}	-1.7^{c}	38.9^{b}	98.7^{a}	85.8^{a}

*PO_4^{3-} load applied via 'Low' (0.08 mg P l^{-1}); 'Medium' (0.26 mg P l^{-1}); 'High' (1.3 mg P l^{-1}) concentration PO_4^{3-} solutions. All results are compared to the PO_4^{3-} sorption efficiency of the non-PSM C or W treatments. Therefore, negative values indicate an increase in leachate PO_4^{3-} compared to the control and consequently are recorded as negative sorption efficiency.

Values within each row followed by the same letter are not significantly different following One-Way ANOVA and *post-hoc* Fisher LSD analyses.

been occupied during F1.

4.3.1.2 Woodchip fill media treatments

For the Low solution P concentration at F1, WG-O is associated with a significantly lower PO_4^{3-} concentration (1.15 mg P l^{-1}) as compared to all other treatments. For the Medium solution PO_4^{3-} concentration F1 leachate PO_4^{3-} concentration is in the order WFc-O=WG-O=WFE < WPp=WK=non-PSM control (Table 4.4). In contrast, at High solution P concentration WFc-O was associated with significantly lower PO_4^{3-} concentration as compared to all other treatments.

At F2 across all P solution concentrations, the WFc-O and WG-O treatments are associated with the lowest leachate PO_4^{3-} concentrations as compared with all other treatments. However, although significant reduction in leachate P concentration were achieved, the water quality target was not attained (Table 4.4). This is in large part due to the significantly higher leachate PO_4^{3-} concentrations at both F1 and F2 associated with the W as compared with C fill media. Leachate PO_4^{3-} concentrations following the addition of deionised water to the C and W treatments at F1 and F2 were 1.27 and 19.8 and 1.10 and 54.0 mg P l^{-1}, respectively.

The WPp, WK and WFE treatments were ineffective at reducing leachate PO_4^{3-} concentrations compared to the non-PSM W control.

4.3.2 PSM performance: PSE

PO_4^{3-} sorption efficiency (Table 4.5) was calculated using Equations 4.5 – 4.7 and used to quantify treatment performance. Significant differences in treatment PSE between F1 and F2 are shown in Table 4.6.

4.3.2.1 Compost

With the exception of CG-O at Low and Medium solution PO_4^{3-} concentrations for F2, CFc-O consistently recorded significantly higher PSE (61.6 – 99.0%) compared to all other treatments across both flushes (Table 4.6). In addition, even though background leachate PO_4^{3-} concentrations from the C fill media increased significantly from F1 to F2 for CFc-O, no significant difference in PSE was observed between F1 and F2 (Table 4.6).

Similarly, although less consistent, with the exception of Low and Medium solution PO_4^{3-} concentrations for F2 and High solution PO_4^{3-} concentrations for F1, CG-O was associated with significantly higher PSE (31.8 – 75.2%) as compared to the CPp, CK, CFE and C, treatments (Table 4.5). In contrast to CFc-O, CG-O demonstrates a significant reduction in PO_4^{3-} sorption efficiency between F1 and F2 (Table 4.6) suggesting partial saturation of P-sorption sites.

In contrast, few significant differences in PSE were observed between the CPp, CK, CFE treatments and C control. Where significant differences were observed, these were associated with negative efficiency values (Table 4.5). Negative values indicate treatments that have higher leachate PO_4^{3-}; which may in part be due to PO_4^{3-} desorption from C fill media during F1 and F2, and due to partial saturation of reactive sites within the PSMs.

Significant differences in PSE between F1 and F2 were observed for the non-PSM control, CPp and CK treatments (Table 4.6) at Low and Medium solution PO_4^{3-} concentration scenarios. This is due to negative PSE associated with F2 indicating that greater PO_4^{3-} is being released from the fill media than is sorbed by the PSM. The CPp and CK are considered ineffective, as they consistently demonstrate no significant difference in PSE as compared with the non-PSM control.

4.3.2.2 Woodchip

With the exception of the Medium solution PO_4^{3-} concentration at F1, WFc-O and WG-O are consistently associated with significantly higher PSE than all other treatments (Table 4.5) with values ranging from 50.7 – 99.0 % and 54.2 – 93.9 % respectively. In contrast to the C fill media, significant differences in PSE between F1 and F2 were observed for both WFc-O and WG-O (Table 4.6). For WG-O, this is due to PSE being significantly lower at F2 as compared with F1 for both the Low and High solution PO_4^{3-} concentration scenarios. In contrast, for WFc-O PSE, associated with the Low solution PO_4^{3-} concentration scenario, is significantly higher at F2 than F1.

Table 4.6. T-test p-values indicating significant differences (p<0.05) in PO_4^{3-} sorption efficiency between PSM treatments across Low, Medium and High solution PO_4^{3-} concentrations.

Compost fill media							
Phosphate*	**Flush**	**Non-PSM control (C)**	**CPp**	**CK**	**CFE**	**CFc-O**	**CG-O**
Low	F1	0.00	0.00*	0.05*	0.19	0.16	0.06
	F2						
Medium	F1	0.07	0.03*	0.04*	0.13	0.28	0.01*
	F2						
High	F1	0.10	0.07	0.47	0.21	0.11	0.04*
	F2						
Woodchip fill media							
Phosphate*	**Flush**	**Non-PSM control (W)**	**WPp**	**WK**	**WFE**	**WFc-O**	**WG-O**
Low	F1	0.78	0.28	0.95	0.82	0.00*	0.04*
	F2						
Medium	F1	0.94	0.96	0.59	0.85	0.21	0.33
	F2						
High	F1	0.71	0.27	0.18	0.33	0.05*	0.00*
	F2						

*T-test p values followed by an * are significantly different at 95% confidence interval.*

PSE associated with WPp (0.1 – 33.5), WFE (25.9 – 53.4) and the non-PSM control (4.6 – 28.6) are regularly significantly higher as compared to WK (-21.5 – 23.5). Further, no significant differences were found for F1 and F2 results for WPp, WFE, WK, or the non-PSM control (Table 4.6).

4.3.3 Solution retention

Table 4.7. Mean amount of solution retained by treatments.

Mean volume of PO_4^{3-} solution retained as a % of that applied*						
Compost treatments						
Flush	Non-PSM control (C)	CPp	CK	CFE	CFc-O	CG-O
F1	37.2^{a}	36.6^{a}	37.7^{a}	36.5^{a}	41.9^{a}	38.3^{a}
F2	36.5^{a}	33.4^{a}	31.5^{a}	32.4^{a}	36.4^{a}	31.9^{a}
Woodchip treatments						
Flush	Non-PSM control (W)	WPp	WK	WFE	WFc-O	WG-O
F1	48.8^{bc}	54.3^{b}	69.5^{a}	46.4^{bc}	36.8^{c}	66.0^{a}
F2	51.8^{b}	55.4^{ab}	34.1^{d}	62.8^{a}	45.9^{c}	40.7^{cd}
For that which was applied, refer to Table 4.2.						

The amount to which the PO_4^{3-} solution is retained within the treatment columns impacts on the time it is in contact with the PSMs, and therefore the ability of these to sorb PO_4^{3-} to their exchange sites. Consequently, higher solution retention should result in higher PO_4^{3-} sorption. Table 4.7 shows the mean volume of the PO_4^{3-} solution retained within the columns for each treatment and flush. No significant differences were observed in the amount of solution retained between any of the treatments.

With the exception of WFc-O, the W treatments retained between 8 – 48% more solution than the C treatments. At F1 the WK and WG-O treatments retained significantly more solution than all other treatments. At F2 the WFE treatment retained significantly more solution than all other treatments. Interestingly WFc-O retained similar amounts of solution to its CFc-O counterpart even though the other W treatments tended to retain more.

4.4 Discussion

4.4.1 PSMs

Fc-O (regardless of fill media) was most efficient at removing orthophosphate, with PSE regularly exceeding 90% (Tables 4.5). In three cases, the efficiency of the Fc-O treatments (calculated using Equation 4.6) ensured the orthophosphate within the leachate was below the prescribed water quality target of 0.05 mg l^{-1} (Table 4.4). This is a significant result showing that Fc-O is an effective PSM when trialled in a column experimental set-up. The G-O treatments were significantly less efficient (up to 94%) at F1 (Low, Medium and High) and F2 (High) when mixed with C fill media, and at High F1 when mixed with W fill media (Table 4.4). Crucially the leachate did not meet the water quality target (Table 4.4; minimum 0.36 mg P l^{-1} for Medium F1). Nevertheless, G-O still provides essential water quality benefits and may be a better option in areas of the UK where Fc-O is expensive and/or unavailable.

The consistent efficacy of the Fc-O and G-O treatments across both F1 and F2 can be explained by the mineralogical results (Table 4.1). Fc-O contains ferrihydrite and calcite. Ferrihydrite is a type of amorphous Fe-oxide, and has 2 main configurations; 2-line (2LFH) and 6-line (6LFH). The ferrihydrite present in the Fc-O is likely to be 6LFH owing to its relatively large particle size diameter (>0.002 µm; Table 4.1), which results in fewer reactive surface sites than 2LFH (Arai and Sparks 2001, Ballantine and Tanner 2010, Gérard 2016). Ferrihydrite also has exceptionally high specific surface areas; regularly up to 700 m^2 g^{-1} (Willet et al. 1988, Hiemstra and Van Riemsdijk 2009, Wang et al. 2013), which provides large numbers of reactive surface sites. Adsorption of PO_4^{3-} at these sites occurs through coordination and ionic bonding, allowing the creation of monodentate or bidentate bonds with the Fe, O and OH^- groups (Parfitt 1989, Cornell and Schwertmann 2003, Wang et al. 2013). Surface precipitation also occurs with the calcite forming calcium phosphate. The PSE of the Fc-O treatments across both C and W fill media may in part be due to the comparatively high calcite levels which may allow the Fc-O treatments to effectively sorb PO_4^{3-} at both low (ferrihydrite predominates adsorption) and higher (calcite predominates adsorption) pH values (Perassi and Borgnino 2014, Xu et al. 2014c) . If 2LFH had been utilised, it is likely that the adsorption efficiency would be even higher owing to the smaller particle sizes, its relatively larger specific SA, and thus more reactive exchange sites for adsorption to occur (Arai and Sparks 2001).

Similarly, it is postulated here that PO_4^{3-} adsorption by G-O occurs through the same mechanisms (Tejedor-Tejedor and Anderson 1990, Olsson et al. 2010, Wei et al. 2014) as that of Fc-O. The G-O contains goethite and calcite. However the amount of calcite (Table 4.1) is relatively small (14.4%) as compared to that of the Fc-O (54.1%), and as the goethite has a larger particle size and smaller specific surface area, less adsorption occurs than with Fc-O. However, goethite is more commonly found than ferrihydrite in ochre deposits as it is more stable (Cornell and Schwertmann 2003, Chesworth 2008) and therefore may be more available as a PSM for water quality control.

In contrast to Fc-O and G-O, the K, Pp and FE PSMs were less efficient at sorbing PO_4^{3-} with highly variable results. This is consistent with the literature (Murphy 1939, Gimsing and Borggaard 2002, Gérard 2016). However, given the relatively large specific surface areas (Table 4.1) of K and FE and therefore potential reactive surface sites, this result was unexpected. The literature states that for K, PO_4^{3-} adsorption is mainly dictated by pH (Edzwald et al. 1976, Harsh and Doner 1985, Gustafsson et al. 2012). This impacts the charge at the K surface by causing the hydrolysis of metal-oxide and hydroxide bonds (Eslinger and Pevear 1988). The literature identifies K as being the most chemically stable of the clays near neutral pH (Murphy 1939, Shulz et al. 1992). This may be the reason why the K treatments provided generally lower and variable results as there would be fewer reactive surface sites, compared with the other PSMs investigated. The K regularly exhibited negative results. Similar results were observed by Krumina et al. 2016 which indicated that negative values originate from the saturation of the K with PO_4^{3-}, followed by removal of the labile fraction after the F2 solution application. Furthermore, during the experiment, fine K particles were regularly observed leaching out of the columns, unlike that of the other PSMs, resulting in there being less K for PO_4^{3-} adsorption. This is likely because the particle size of the K was too small for it to be retained within the relatively large pore spaces of the fill media.

FE treatments were more consistent across flushes and PO_4^{3-} applications with only one negative result reported ('Medium' at F2). Consistency is likely due to the FE having a relatively large specific SA (Table 4.1) as well as the presence of smectites, namely montmorillonite, which are more chemically reactive owing to their 2:1 layer structure, weak bond between layer sheets, and unbalanced charge (Murphy 1939, Odom 1984). Consequently, in theory, the FE provides more reactive surface sites than K for PO_4^{3-} adsorption to occur (Uddin 2017).

Pp is an industrial product used for the control of PO_4^{3-} in runoff. When compared to the non-PSM control, the Pp treatments often provide statistically similar or significantly less PO_4^{3-} sorption. When treatments are compared to the Pp results, Fc-O and G-O provide highly significant order of magnitude increases in PSE. Like K and FE, Pp was associated with variable results especially when C fill media was used. The Pp PSM did not reduce the PO_4^{3-} to the water quality target (Table 4.4).

Consequently the most appropriate PSMs out of those trialled for the control of orthophosphate losses associated with agricultural runoff are Fc-O and G-O, which would provide a more efficient and consistent alternative to Pp.

4.4.2 Fill media

Generally the results indicate a more consistent PSE from the W as compared with C fill media PSM treatments as there were less negative results reported. This is likely due to the longer retention time of the PO_4^{3-} solution within the W fill media (Table 4.7) which, retained on average 41% more of the solution in F1, and 44% more in F2, as compared with C fill media treatments. This increased retention time increases the contact time between the PO_4^{3-} solution and the PSMs allowing increased PO_4^{3-} adsorption by the PSMs.

However, this increases the likelihood of PO_4^{3-} desorption from the W fill media as demonstrated by the significantly higher leachate PO_4^{3-} concentration for the W treatment following the addition of deionised water at F2 as compared with F1 with values of 1.10 and 54.0 mg P l^{-1}, respectively. This is consistent with the findings of Shipitalo et al. (2010). The consistent PSE between C and W (Table 4.5) treatments highlight the efficiency of the PSMs. Fc-O and G-O results are particularly consistent as PSE did not decrease even when they were exposed to the high PO_4^{3-} concentrations associated with the F2 W treatments.

4.4.3 Applicability of materials to the agricultural sector

This research has highlighted the efficiency of PSMs (Fc-O and G-O) for PO_4^{3-} removal, by mixing them with fill media (C or W) in FS. To ensure widespread uptake for diffuse pollution control, both the fill media and PSMs need to be cost-effective and easy to access. Table 4.8 highlights the affordability and accessibility of the various materials used within this column study, in the UK. Furthermore it frames the average material costs (based on current 2017-18 market values) per mg of PO_4^{3-} removed, in order to relate them to specific water quality targets and the PO_4^{3-} removal required to meet these targets.

Both C and W fill media are widely available. C production is annually increasing as household recycling rates increase (WRAP 2017) with an annual production of 3.2 mt of PAS 100 (WRAP 2017) and average cost of £75 t^{-1}. W is less accessible than C as it is generally imported. National production data is limited as W is often produced as a waste and reused on site. The cost per 1 t bulk bag on average is £87 (2017). These costs were established by calculating the mean value from a market analysis of suppliers. In this analysis, a minimum of 5 suppliers were used to calculate costs except for that of the Pp where there is only 1 supplier.

Fc-O, G-O and K are most widely available within the UK. K is produced in the south west of the UK with current reserves in excess of 60 mt (Cornwall Council 2012). It is widely accessible and affordable to purchase, both direct from suppliers and online. However the cost per mg of P removed is more than that for Fc-O, G-O and Fe, and this does not account for the variation in its results especially where negative results (i.e. desorption) occur.

Natural Fc-O and G-O are widely available within the UK as ‘ochre’, found as a precipitate within mining landscapes, mine water treatment plants and water treatment plants (Hancock 2004, Sapsford et al. 2015, Shepherd et al. 2016). It can also be found naturally depositing at the outfall of agricultural drains. The average cost of ochre per mg of PO_4^{3-} removed (calculated using the 2015 costs incurred by The Coal Authority to dredge, transport and landfill) is as little as £0.01 (Table 4.8). This is particularly low as currently ochre is not commercially available to buy. The Coal Authority pays to landfill ochre from their plants as it currently is not identified as end-of-waste. This would need to be changed before ochre could be widely accessible and utilised.

The majority of FE is imported from central Europe and/or the USA as UK production has ceased owing to the working out of existing planning consents, and the remaining reserves being uneconomical to exploit (British Geological Survey 2006). Nevertheless, FE is a relatively low cost PSM even when import costs are accounted for (average £0.18 per mg of PO_4^{3-} removed). FE may therefore be considered a viable low cost PSM for PO_4^{3-} control where only small PO_4^{3-} removal is required (<0.2 mg P l^{-1}). Due to its comparatively low PSE, more FE may need to be applied at rates >20 kg m^{-3} in order to provide consistent and longer term control, and to avoid desorption.

Pp is by far the least cost effective of the PSMs, costing £11 per mg of PO_4^{3-} removed, even before importing costs are considered. Furthermore, as it is currently only available within the USA, it is not practicable for its widespread uptake, especially by the UK agricultural sector where many farmers have negligible financial margins.

4.5 Conclusions

The most effective and consistent PSM performance was given by Fc-O and G-O with PO_4^{3-} removal efficiencies of up to 99% across both C and W fill media, even with the inherently high PO_4^{3-} load released by the W fill media. This is consistent with other studies (Wang et al. 2013, Moreira et al. 2017). Fc-O consistently removed >50% of the PO_4^{3-} and was the only PSM which reduced the PO_4^{3-} concentration to below the water quality target (<0.05 mg P l^{-1}). Fc-O and G-O were the most economic to use, costing as little as £0.01 per mg of PO_4^{3-} removed. Consequently, these are recommended for wider study into the appropriate configuration for their widespread use as PSMs, e.g. application rates, point of saturation and desorption, powdered or pelletised. Furthermore, they are currently considered a waste material and are disposed of after dredging. Measures need to be undertaken to ensure they can be reused for this purpose, thereby ceasing to be a waste.

FE was also a relatively economic (£0.18 per mg of PO_4^{3-} removed) and efficient (up to 53.4% removal efficiency) PSM, however it did not reduce the concentration to below the water quality target. Given that its PO_4^{3-} removal efficiencies were significantly less than those of Fc-O and G-O, it is recommended that the use of FE as a PSM is limited to situations where lower removal efficiencies are sufficient to meet water quality targets, or during the interim stages if use of Fc-O and G-O requires end-of-waste certificates, which do not apply to FE as it is not a waste material.

K, although widely available, was not an efficient or consistent PSM with widely varying results (removal efficiencies ranging from -30.2 to 23.5%), and a higher cost (£0.23 per mg of PO_4^{3-} removed) compared to Fc-O, G-O and FE. Similarly, Pp was significantly more expensive (£11.00 per mg of PO_4^{3-} removed), and is not widely available in the UK at present. Consequently, it is not recommended that K or Pp be used as PSMs in diffuse pollution control measures in the UK agricultural sector where removal efficiency, cost and reliability are fundamental requirements.

More research is required to establish the most effective application rate of each PSM required for specific PO_4^{3-} concentrations, flows and removal efficiency targets, as well as the appropriate configuration of these PSMs (e.g. powder, processed, combined with cations). Furthermore the process of establishing an official end-of-waste certificate for Fc-O and G-O is required before their use as PSMs. Lastly this data only relates to the conditions provided by a column experimental set-up under laboratory conditions. To ensure that the PSMs and fill media are fully suitable and beneficial to the agricultural sector, research is required into their efficacy in field situations. In order to get to this stage, further research is required into their efficacy in various controlled laboratory experiments, which reflect field scenarios. If successful, it would then be appropriate to trial them in-field.

Table 4.8. Accessibility and cost of materials used in orthophosphate adsorption.

Material	Accessibility and production	Mean cost (£)		Other notes on accessibility	References
		Per 1 t bulk bag	Per mg of PO_4^{3-} removed[Φ]		
C	Widely available, widespread. UK production[1] 3.5 mt yr^{-1}	75	N/A	Increasing production owing to increasing recycling rates. Agriculture is the biggest C market.	(WRAP 2017)
W	Widely available, limited UK production data, often imported	87		Produced as waste in sawn wood production, where it is reused for wood fuel	(Forestry Commission 2017)
Pp	Not widely available or accessible. Imported from USA.	N/A	11.00*[†]	Only one supplier in the UK.	
K	Widely accessible. UK reserves in excess of 60 mt, with approx.. 1.1 mt produced annually.		0.23*	K reserves in the UK are restricted to Cornwall and Devon. Their exact extent is not available due to commercial reasons. Paper and ceramics are the main markets.	(British Geological Survey 2009, Cornwall Council 2012, Leclerc and Jackson 2016)
FE	Accessible by imports (~ 180,000 t yr^{-1}) from USA, China, Greece, India. EU produces ~21% of global output.		0.18*	Exploitable (economic) UK reserves have been exhausted. Reserves restricted to S. England, mainly Bedfordshire, Oxfordshire and the S. Bath.	(British Geological Survey 2006, Brown et al. 2012, UK Minerals Forum 2014)
Fc-O	Ochre is widely available but not currently accessible. 4500 t yr^{-1} (natural ochre). Can also be synthesised.		0.01[□]	Ochre is considered a waste material. It is currently landfilled at cost to the Coal Authority who manage the current UK mining legacy. Furthermore, discerning between goethite and ferrihydrite minerals within ochres would need undertaking.	(Sapsford et al. 2015)
G-O					

[Φ] *Mean cost (£) per mg of PO_4^{3-} removed for each treatment = (1 / (mean P removed per gram of material in columns)) * mean cost of material*

[1] *UK compost production 2014 totalled 3.5 million tonnes, with 3.2 million tonnes certified as PAS 100 (WRAP 2017).*

**Does not account for negative results where desorption occurred.*

[†] *Cost does not include air freight costs or import taxes from the USA.*

[□] *Cost calculated using 2015 dredging and landfill costs incurred by the Coal Authority.*

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CHAPTER 5: EVALUATING THE EFFICACY OF FILTER SOCKS TREATED WITH PHOSPHORUS SORBING MATERIALS (PSMS) IN REMOVING SEDIMENT, SEDIMENT-BOUND PHOSPHATE AND ORTHOPHOSPHATE FROM RUNOFF

Abstract

Agricultural sediments and PO_4^{3-} entering waterbodies are a major cause of water quality degradation. Extreme REs are predicted to increase in frequency and magnitude, thereby increasing soil erosion, runoff, and the amount of PO_4^{3-} and sediments entering waterbodies. Consequently it is essential that cost-effective and adoptable mitigation measures are developed and validated to ensure water quality targets are achievable. The use of PSMs to remove orthophosphate is standard practice for water treatment. This research has critically evaluated the use of PSM-amended C or W FS, to concurrently remove sediment, SB PO_4^{3-}, and orthophosphate from within runoff. Their efficacy under high intensity (80 mm hr^{-1}) REs was established (5, 18, 41, 75 and 126 yr RTP REs) using a pressure-fed rainfall simulator. These were evaluated on a sandy loam soil and a 17^{o} slope, representing typical erosive characteristics of the Lugg case study catchment. PSMs investigated were ferrihydrite (Fc-O), goethite (G-O) and a commercial proprietary product (Pp). Treatments (CFc-O, CG-O, CPp, WFc-O, WG-O, and WPp) were replicated in quadruplicate. Results demonstrate that FS remove 66% - 97% of sediment from runoff compared to the non-FS control. Furthermore, they remove up to 89% of the clay fraction, 82% of the silt fraction, and 75% of the sand fraction. Consequently FS treatments removed between 59% - 78% of SB PO_4^{3-} compared to the non-FS control. Crucially, all of the FS treatments met the sediment water quality target (0.1 mg l^{-1}). Fc-O and G-O amended-FS removed between 14% - 31% and 11% - 27% orthophosphate from runoff compared to the non-FS control. The Pp amended-FS varied between adding up to 6% and removing up to 26% of the orthophosphate from the runoff compared to the non-FS control. No significant differences were observed between PSM treatments where orthophosphate was removed. The water quality target (0.05 mg P l^{-1}) was not met by any of the treatments. Results indicated that there is an initial flush of fines and orthophosphate from the FS fill media.

Keywords

Filter socks; ferrihydrite; goethite; diffuse pollution; extreme rainfall events.

The spelling and formatting of the original article has been adjusted to fit the format of this thesis.

5.1 Introduction

Agricultural diffuse pollution is a main contributor to UK water quality degradation (National Audit Office 2010). Water quality targets are prescribed by the EU WFD and refer to a number of biological and chemical conditions which are related to the status of water quality. Waterbodies must meet ‘good status’ as a minimum requirement in order to be compliant. Currently in the UK, only 17% of water bodies have met these targets (Environment Agency and Natural England 2014; Environment Agency 2015). Sediments and nutrients are the main forms of diffuse pollution and enter rivers and lakes from agricultural land within runoff, causing issues such as eutrophication, sedimentation and flooding. PO_4^{3-} losses can be in the form of orthophosphate and SB PO_4^{3-} (Logan 1982), typically originating from the application of chemical and organic fertilisers (Schoumans et al. 2014). Topography, soil type, land use and rainfall all influence soil erosion rates and the associated amount of sediment and SB PO_4^{3-} being delivered to waterbodies. It is generally accepted that climate change will result in significant changes in the amount, frequency, type, intensity and kinetic energy of rainfall experienced in the UK, with an increasing propensity for ‘heavy’ and ‘extreme’ REs (IPCC 2014). With the increased frequency of such events, the amount of sediment and SB being delivered to waterbodies is likely to increase (Favis-Mortlock and Boardman 1995).

Commonly used, in-field control measures to specifically minimise PO_4^{3-} losses are limited and mainly focus on improved nutrient management and lime application (Deasy et al. 2008, Schoumans et al. 2014), cover cropping (De Baets et al. 2011, Zhang et al. 2017) and BS (Schoumans et al. 2014, Pan et al. 2017). Methods that are also often used as soil erosion mitigation (cover cropping and BS) consequently also remove the SB fraction of PO_4^{3-}. However, the majority of sediment and PO_4^{3-} is still treated ‘off-site’ at significant cost by water utility companies. Treatment to remove PO_4^{3-} involves filtration, sedimentation, precipitation and adsorption through the use of biological and/or chemical breakdown. There is a need for field-based measures and end-of-pipe-solutions (EOPS) which remove sediment and PO_4^{3-} from runoff waters before they enter waterbodies. This would reduce treatment costs by the water utility companies, as well as remove the pollutants closer to the source thereby reducing the impacts associated with being exposed to them, and limiting losses that may occur in their transport. This is consistent with the polluter pays principle whereby land managers/users pay for the loss of these pollutants from their fields, rather than the users of the waterbodies which suffer the impacts of these pollutants being lost.

FS have proven to be significantly more effective and consistent at sediment removal than other EOPS such as straw wattles, FB, BS and SF (Faucette et al. 2007, 2009b, Rickson et al. 2010, Newell Price et al. 2011). Currently, their use is mainly confined to the USA where they are a BMP for sediment control on construction sites, associated with large volumes of sediment-laden runoff entering waterbodies and drains. Placement of FS varies depending on their intended use: at the bottom of slopes; as slope interrupters or ‘terraces’; around drains; as check dams within gullies and ditches; and along river banks (Faucette et al. 2009b). As runoff passes through a FS, the fill media impart friction and turbulence to the flow, reducing runoff velocity. This causes a reduction in flow transport capacity so that sediment falls out of suspension and deposits within and immediately upslope of the FS. FS do not prevent the detachment phase of soil erosion, but are very effective at disrupting the transport and deposition phases. Consequently, FS are effective at preventing the discharge of sediment and SB PO_4^{3-} to water bodies and associated environmental impacts. Their application in an agricultural context has been limited (Shipitalo et al. 2010, 2012), especially within the UK (Somerset Rivers Authority 2016). Furthermore, it is not understood how climate change induced extreme REs will impact on their performance.

Whilst FS have proven to be effective at sediment (Cooke et al. 2017) and SB PO_4^{3-} control (Faucette et al. 2009a, 2013), currently no field-based measures are used to mitigate soluble orthophosphate losses. PSMs are widely used in the wastewater treatment industry for orthophosphate removal; however they are not widely used by the agricultural industry. There are limited studies which have assessed specific PSMs for PO_4^{3-} control within existing agricultural practices (Penn et al. 2007, Ballantine and Tanner 2010, Vohla et al. 2011, Habibiandehkordi et al. 2014). Currently orthophosphates are treated at wastewater treatment plants through adsorption by metal ions such as Fe, Al, and Ca oxides (De-Bashan and Bashan 2004, Zou and Wang 2016), or by biological breakdown (Blackall et al. 2002, Samer 2014, Nancharaiah et al. 2016).

The hypothesis is that combining FS with PSM would allow sediment, SB PO_4^{3-} and soluble orthophosphate to be treated in-field, close to source. Consequently, PO_4^{3-} inputs to waterbodies could be significantly reduced, along with associated wastewater treatment costs.

The aim of this study was to evaluate the efficacy of PSM amended FS in reducing sediment, SB PO_4^{3-} and soluble orthophosphate concentrations and loads within runoff, under a range of REs within the UK agricultural context. It is hoped PSM amended FS will be effective means of combating declining UK water quality.

5.2 Materials and Methods

In a fully replicated, controlled experiment, FS were filled with C or W, with or without PSMs. Detailed specifications (Alexander Associates 2006) have already been developed regarding the fill media (particle size, pH, moisture content) for maximising FS as sediment control. These specifications were met for the C and W fill media before mixing with PSMs. The amount of fill media-PSM mix packed into the FS was determined using the standard FS bulk density of 0.7 g cm^3 (personal communication by Britt Faucette, which was then validated) and material particle densities (Table 5.1), whilst maintaining the recommended fill media specifications (Alexander Associates 2006). The FS chosen were those commonly used on USA construction sites as sediment control. The pore size and FS diameter appropriate to the experimental design conditions was calculated using the manufacturers guidelines (Filtrex International, 2017).

Table 5.1. Baseline properties of FS materials.

Property			**Material**				
			C	**W**	**Pp**	**Fc-O**	**G-O**
Mineralogy (%)		Calcite	N/A		ND	50.4	14.1
		Goethite			0.5	0.0	84.7
		Ferrihydrite			ND	46.6	ND
		Clinoptilolite			65.8	ND	ND
		Smectite			13.5	ND	ND
		Other*			20.2	ND	1.2
CEC		cmol kg^{-1}			13.5	ND	ND
Particle size distribution (%)	Mineral	<0.002 mm			4.3	2.3	40.1
		>0.002 mm			95.7	97.7	59.9
	Organic	<2 mm	63	57	N/A		
		2-5 mm	24	33			
		5-10 mm	12	10			
		>10 mm	1	1			
Total-P		mg P kg^{-1}	178.7 (±4.6)	148.2 (±5.0)			
Particle density		g cm^{3}	1.4	1.4	2.1	3.3	4.0
Surface area (SA)		m^{2} kg^{-1}	N/A			588	945

ND = Non-detectable

**Other mineral presence includes: G-O (quartz); Pp (aragonite, K-feldspar, opal-C/CT, quartz).*

The calculation of the FS size (Filtrexx International, 2017) considers the rainfall characteristics (intensity, duration), slope and catchment area to identify the optimum FS size such that runoff flow-through is maintained, and overtopping will not occur from the runoff generated from these lands.

Table 5.2. Treatments and their treatments codes as used within text.

Treatment	**Treatment code**
Control (no FS)	Control
Compost FS	C
Compost + ferrihydrite-calcite ochre FS	CFc-O
Compost + goethite ochre FS	CG-O
Compost + proprietary product FS	CPp
Woodchip FS	W
Woodchip + ferrihydrite-calcite ochre FS	WFc-O
Woodchip + goethite ochre FS	WG-O
Woodchip + proprietary product FS	WPp

The PSMs tested included Fc-O, G-O, and a commercial Pp. These were selected based on their PO_4^{3-} removal efficiencies as reported in an extensive literature review. The Pp was included in order to compare the efficiency of the ochre PSMs to the current commercially available product for PO_4^{3-} control.

The PSMs were thoroughly mixed with the two fill media (C or W) at the Pp approved application rate of 20 kg m^3 to ensure that results were comparable. All PSMs were air dried prior to mixing, whilst the fill media was used in the same condition as it arrived. Nine treatments, including a non-FS control, each with 5 replicates were tested (Table 5.2). Five replicates were chosen to ensure that if any of the trials failed, there was still enough data to allow statistical analysis to be undertaken.

The bulk mineralogy, CEC, particle size distribution (PSD) and particle density of the PSMs used within the study were measured by X-Ray Powder Diffraction (XRPD) and X-Ray Fluorescence (XRF). The aim was to understand and evaluate the processes by which PO_4^{3-} adsorption took place. The PSD of the FS fill media was established by dry sieving. This ensured that the PSD met the required specifications for FS fill media (Alexander Associates 2006). Total-P of the PSMs and the test soil was determined using a Perkin Elmer Atomic Absorption Spectrometer (AAS) Analyst^{TM} 800 following extraction with a 3:1 $HCl:HNO_3$ solution using an Anton Paar Multiwave 3000 microwave digestion system (US EPA Method 3051; British Standard BS 7755: Section 3.13:1998; ISO 11047:1998). Surface area (SA) of the PSMs was established using laser diffraction (Mastersizer 3000; Malvern Instruments Ltd) in order to understand PSM performance (PO_4^{3-} sorption efficiency).

The test soil is representative (Table 5.3) of the dominant erodible soil of the Lugg catchment, Herefordshire and is identified as being a sandy loam of the Eardiston soil series (Cranfield University 2016). The soil is known to be at risk of water erosion and surface capping (Hollis and Hodgson 1974). The Lugg catchment was chosen for the study as it is currently failing its water quality targets due to sediment and orthophosphate entering rivers as diffuse pollution from arable lands (Environment Agency & Natural England 2014). This is not only causing the Lugg

Table 5.3. Mean (n=3) baseline characteristics of the test soil (values in parentheses indicate +/- 1 S.E.)

Analytical method			**Mean (n=3)**	**± 1 Standard Error**
Organic matter	% w/w		3.4	0.2
pH	H_2O method		6.6	0.2
Electrical conductivity	mS m^{-1}		470	10
Total P	mg P kg^{-1}		787.4	6.8
Particle size distribution*	%	Clay	14.7	0.8
		Silt	22.0	3.1
		Fine sand	22.6	4.0
		Medium sand	38.7	1.7
		Coarse sand	2.1	0.1

**Particle size distribution of clay (<0.002 mm); silt (0.002-0.063 mm); fine sand (0.063-0.212); medium sand (0.212-0.6 mm); coarse sand (0.6-2 mm)* catchment to be non-compliant with the WFD, but also means that the larger Wye catchment (for which the Lugg is a major tributary) is failing its WFD and Habitats Directive targets. Consequently there are stringent water quality targets in place for sediment (0.1 mg sediment l^{-1}) and orthophosphate (0.05 mg P l^{-1}) in the Wye and the Lugg.

After the representative soil was identified (Cranfield University 2016), a target field was identified for sampling and collection. A 30-point 600kg bulk topsoil (0-30cm depth) sample was collected from a field in arable rotation at Penalt, Herefordshire (Lat. 51.964221; Long. -2.6325534). The soil was stored at field moisture content (16%) until required. Soil pH and EC were determined on a 1:5 (w/w) soil: deionised water suspension with a Mettler Toledo MA 235 pH analyser and a Jenway 4310 Conductivity Meter respectively (BS ISO 10390:2005; BS 7755 Section 3.4:1995). Soil organic matter (OM) was determined by the Loss on Ignition (LOI) method (BS EN 13039:2000). The particle size distribution (PSD) of the soil was established using the pipette method (BS ISO 11277:2009).

The test soil has a near neutral pH, and an EC within acceptable levels (Table 5.3). The Total P (787 mg kg^{-1}) and OM levels (3.4 %) are indicative of UK arable soils (Quinton et al. 2001, Withers et al. 2001).

A rainfall simulator was pre-calibrated to two REs. First, a pre-test RE with an intensity of 24mm hr^{-1} (nozzle Lechler 460.788.17.CE at a height of 3.3m and pressure of 1.05 bar) was used to saturate the erosion trays to ensure that runoff would be generated during the FS performance test runs. Following this, the simulator was set to produce an erosive RE with an intensity of 80mm hr^{-1}(nozzle Lechler 460.848.30.CE; nozzle height of 3.3m; pressure of 1.05 bar). This erosive RE intensity was chosen on the basis of Intensity-Duration-Frequency (IDF) curves generated for the Lugg catchment. These curves identified that a RE intensity of 80 mm hr^{-1} for 25 minutes was considered an extreme event for the Lugg catchment, with a RE RTP of 1 in 126 years. Rainfall drop size distribution, raindrop fall velocities and storm KE were determined using an OTT-Parsivel 2 laser optical disdrometer (LOD; OTT Messtechnik, Kempten, Germany). The LOD was positioned at five locations within the experimental area (front, middle, back, left and right). For each location four measurements over 60 s duration were taken. The erosive RE had a KE of 7.89 J m^{-2} mm^{-1} (volume-specific i.e. the KE per mm of rainfall), equivalent to a KE of 631.5 J m^{-2} h^{-1} (time-specific i.e. the KE per hour of rainfall). Rainfall drop size ranged from 0.063 to 4.75 mm, with a median drop size (D50) of 1.05 mm.

Once calibrated, two stainless steel erosion trays (1.5 m x 0.3 m x 0.1 m) were placed onto a 2.0 x 1.0 m erosion rig, with adjustable slope gradient. The trays were packed with the test soil to a wet bulk density of 1.5 g cm^{-3}. This bulk density was chosen as it represented a typically degraded, compacted Herefordshire arable soil, capable of generating runoff. The erosion trays were placed flat for the pre-test whereby they were pre-wet under a low intensity rainfall. After infiltration of the pre-wetting rain had finished, the trays were then moved to a 17^{o} slope for the main experiment, representing a hillslope. This gradient lies within the 80th percentile (i.e. 20% of slopes were steeper than this) of Wye catchment slopes where the test soil type occurs. The gradient was established by identifying ‘medium and high risk’ erodible Wye catchment soil associations from the National Soil Resource Institute data (Cranfield University 2016). The typical slope gradients of the areas where these erodible soils occur were tabulated in increasing gradient, and the 80th percentile identified.

The pre-packed erosion trays were placed under the pre-wetting RE until surface ponding occurred. The trays were left for 2-3 minutes until the surface ponding had infiltrated into the soil, after which the trays were placed at the 17° slope prior to application of the erosive RE. FS were then placed at the bottom of this slope. A thin (<2.0 cm) layer of C or W was placed immediately upslope of the FS as described by the manufacturers’ installation protocols (Filtrexx International 2017). Care was taken to ensure contact between the FS and the edges of the erosion trays in order to avoid bypass runoff flow.

The erosive RE was applied to the test bed. Runoff sampling was undertaken at 5 minute intervals for a total duration of 25 min. This corresponded to five storm RTPs; 5, 18, 41, 75 and 126 yrs, respectively. It was essential to analyse the FS treatments at more extreme RE RTPs to understand and ensure their efficacy under future climate scenarios to ensure they remain a viable measure for sediment and PO_4^{3-} control in the future. This would also aid in understanding how they may provide additional control for specific RE RTPs alongside other mitigation measures.

Treatment performance was measured by: runoff volume (l per tray^{-1}); sediment load (g per tray^{-1}), sediment concentration (g l^{-1}) (with reference to the water quality target of 0.1 mg sediment l^{-1}); phosphate load (mg PO_4^{3-} per tray^{-1}); and orthophosphate concentration (mg P l^{-1}) (with reference to the water quality target of 0.05 mg P l^{-1}). These parameters were used to evaluate the sediment and PSE of the FS treatments, as compared to the control where FS were not used.

Runoff volume was determined by collecting runoff from the downslope outlet of the erosion trays every 5 minutes throughout the 25 minute experiment. For each sampling period, sediment concentration (g ml^{-1}) was determined (Equation 5.1) by filtering 40 ml of stirred runoff (the composite of 4 x 10ml subsamples) through a pre-weighed oven-dried Whatman 542 filter paper (Wf). This was subsequently oven-dried at 105°C for 24hrs, and weighed to give the dry weight of the sediment on the filter paper (Ws) in order to calculate the mass of sediment retained (g):

$$\text{Sediment concentration (g ml}^{-1}\text{)} = \left(\frac{\text{Ws - Wf}}{40}\right)$$

Equation 5.1. Sediment concentration (g ml^{-1})

Sediment load (g) was then calculated by multiplying the sediment concentration (g ml^{-1}) by the total runoff measured (ml) from each of the treatments (Equation 5.2):

$$\text{Sediment load (g)} = (\text{Runoff measured} + 40) \times \text{Sediment concentration}$$

Equation 5.2. Sediment load (g)

Sediment removal efficiency (%) was calculated using the sediment load (g) for each of the treatments, RE RTPs, and particle size fractions (Equation 5.3):

$$\text{Sediment removal (\%)} = 100 - \left(\frac{\text{sediment load of treatment}}{\text{sediment load of control}} \times 100\right)$$

Equation 5.3. Sediment removal efficiency (%)

The eroded particle size distribution (EPSD) of the sediment was established by laser diffraction (Mastersizer 3000; Malvern Instruments Ltd.). The purpose was to test whether the FS removed sediment sizes selectively, with a specific focus on fine materials (clays and silts; <0.063 mm) associated with SB PO_4^{3-}.

Orthophosphate in the runoff was measured using the Automated Ascorbic Acid Reduction Method (Clesceri et al. 1995) on a Burkard SFA-2000 auto-analyser. SB PO_4^{3-} (mg P) was estimated using Equation 5.4. This uses Total P (mg kg) measured within the soil, plus that which was measured in the fill media. This is divided by 1000 to convert the value into mg of P g^{-1} sediment. This was then multiplied by the total sediment (TS); the amount of sediment (g) that was measured within the runoff:

$$\text{Sediment-bound } PO_4^{3-} \text{ (mg P)} = \frac{\text{Total P}}{1000} \times \text{TS}$$

Equation 5.4. Sediment-bound PO_4^{3-}

Runoff orthophosphate concentration (mg P l^{-1}) results, and the total runoff measured (l), were also used in the calculation of the runoff soluble P (mg). This was calculated for each of the treatments, at each RE RTP (Equation 5.5):

$$\text{Soluble P in runoff (mg)} = \left(\frac{\text{orthophosphate concentration}}{1000}\right) \times \text{Total runoff}$$

Equation 5.5. Soluble P within runoff

PSE (%) i.e. the ability of the treatments to retain PO_4^{3-} from the runoff was established for each of the treatments. This used the mean runoff orthophosphate load (mg) of the control, P0, (i.e. where no FS was applied), and the runoff phosphate load (mg) of the treatment, P1. This is then multiplied by 100 to obtain the percentage value (Equation 5.6):

$$\text{PSE \%} = \left(\frac{P1 - P0}{P0}\right) \times 100$$

Equation 5.6. Orthophosphate sorption efficiency (%)

This was essential in understanding treatment performance and allowed comparisons in performance efficiency between treatments to be made.

Statistical analysis was used to evaluate treatment performance through one-way ANOVA, and post-hoc Fisher LSD in order to determine which means were significantly different from each other (Statistica 13.2 Dell Inc.). Values between treatments followed by the same letter were not statistically different ($p \leq 0.05$).

The following hypotheses were made:

1. FS will be significantly more efficient at sediment removal compared to the non-FS control, even with increasing RE severity (RTP).
2. FS will be significantly more efficient at SB PO_4^{3-}removal compared to the non-FS control , even with increasing RE severity (RTP).
3. Fc-O and G-O will be significantly more efficient at orthophosphate removal compared to the Pp PSM and the non-PSM amended FS, even with increasing RE severity (RTP).

5.3 Results

5.3.1 Runoff volume (l)

No statistical differences in runoff volume were observed between the FS treatments and the non-FS control (Figure 5.1). This was expected as FS reduces the velocity (and not volume) of runoff, giving lower flow transport capacities so allowing sediment particles to deposit upslope or within the sock itself (Faucette et al. 2008, Cooke et al. 2017). Consequently, the same volume of runoff passes through the FS.

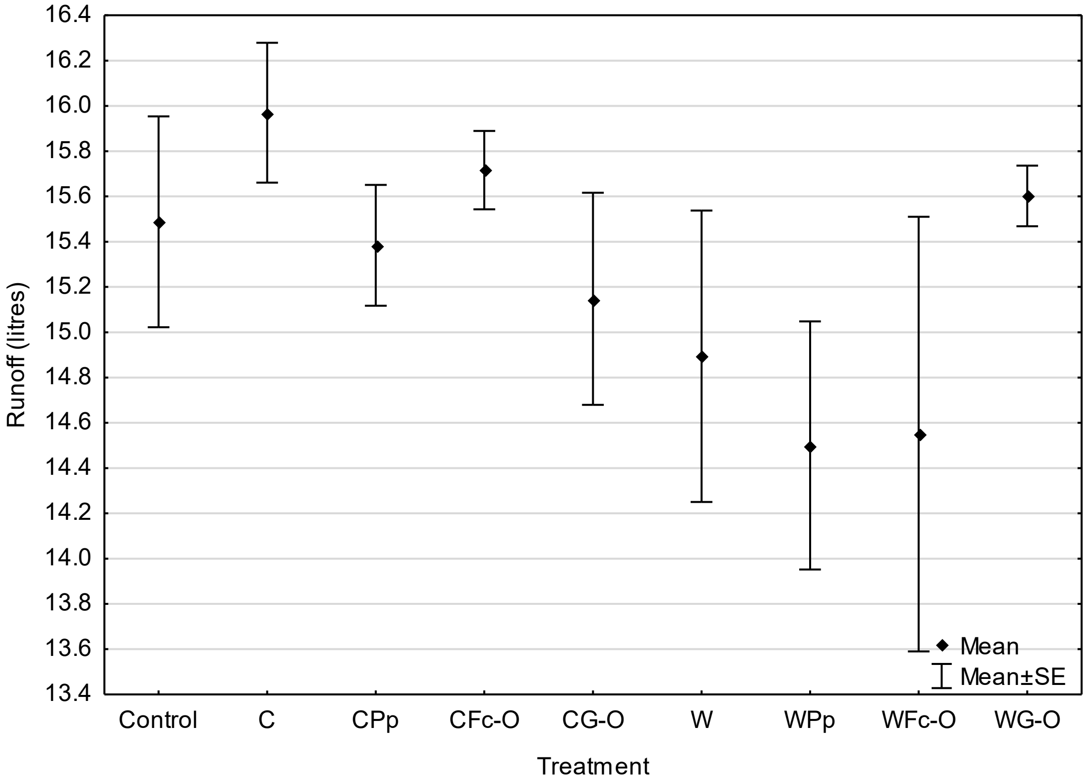

Figure 5.1. Plot of mean runoff (litres) for each treatment.

Table 5.4. Mean (n=5) FS treatment runoff volume (l per plot^{-1}) for each RTP (yr) as compared with non-FS control.

Treatment	5	18	41	75	126
Control	2.7^{bc}	5.7^{abc}	8.9^{abc}	12.1^{ab}	15.5^{ab}
C	2.9^{c}	6.1^{bc}	9.3^{c}	12.5^{b}	16.0^{b}
CPp	2.7^{bc}	5.8^{abc}	8.9^{abc}	12.1^{ab}	15.4^{ab}
CFc-O	2.8^{bc}	5.9^{bc}	9.2^{bc}	12.3^{ab}	15.7^{ab}
CG-O	2.3^{abc}	5.4^{abc}	8.5^{abc}	11.6^{ab}	15.1^{ab}
W	2.7^{bc}	5.9^{bc}	9.0^{abc}	12.1^{ab}	15.5^{ab}
WPp	1.9^{a}	4.9^{a}	7.9^{a}	11.1^{a}	14.5^{a}
WFc-O	2.2^{ab}	5.1^{ab}	8.1^{ab}	11.1^{a}	14.6^{a}
WG-O	2.7^{bc}	5.8^{abc}	9.0^{abc}	12.2^{ab}	15.6^{ab}

Within each column, values followed by the same letter are not significantly different following one-way ANOVA followed by post-hoc Fisher LSD analysis.

Generally, few statistical differences in runoff volume were found between the FS treatments for specific RTPs (Table 5.4). The only statistical difference was found at the 5 year RTP where the WPp treatment produced statistically less runoff than the control where no FS was applied. At all other RTPs, no significant statistical differences were observed in runoff volume between the control and the treatments.

There were significant differences between the different FS treatments. The WPp had significantly less runoff than the C, CPp, CFc-O, W, and WG-O treatments at the 5 year RTP. Similarly, the WPp treatment produced statistically less runoff than the C, CFc-O and W treatments at the 18 year RTP. At the 41 year RTP, WPp produced statistically less runoff than the C and CFc-O treatments. However no other significant differences between FS treatments were observed at these RTPs. Finally, at the 75 and 126 yr RTPs, WPp and WFc-O produced statistically less runoff than the C treatment; however they were not significantly different from each other. Furthermore, no other significant differences were observed between FS treatments at these more extreme events.

5.3.2 Sediment removal efficiency

As expected, sediment load (Figure 5.2) and sediment concentration (Figure 5.3), for all FS treatments, were significantly less than those for the non-FS control. However, no significant differences in these performance indicators were observed between FS treatments. This confirms that FSs are particularly efficient sediment control measures. Indeed, all FS treatments met the Wye catchment water quality target sediment concentration of 0.1 mg l^{-1} (Figure 5.3).

Furthermore no significant differences in sediment load or sediment concentration were observed between the PSM-amended FS treatments, suggesting that addition of PSMs to the FS fill media matrix does not diminish efficacy of sediment control.

Across all RERTPs, sediment removal efficiencies (Table 5.5) of 66.8 – 96.5% (C) and 65.7 – 96.4% (W) were observed compared to the non-FS control. No significant differences in sediment removal efficiency were found between any FS treatments when considering each of the RTP REs individually.

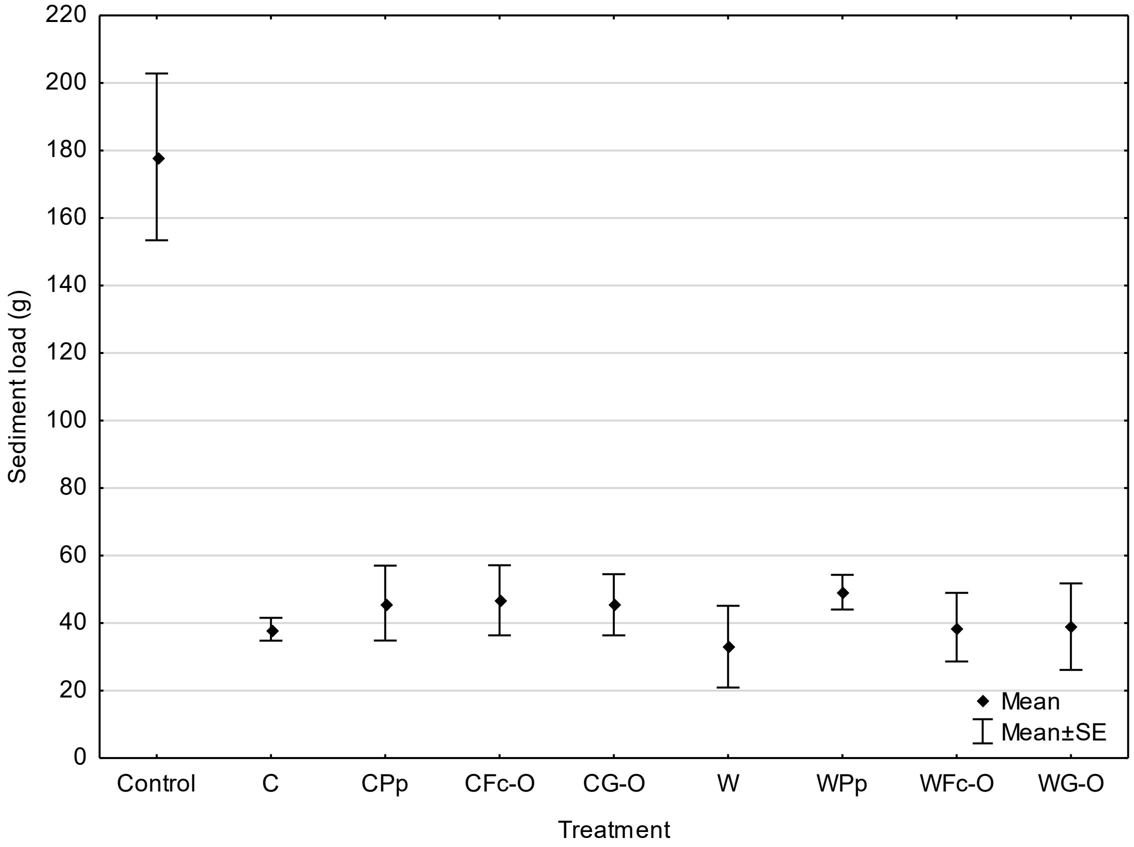

Figure 5.2. Mean sediment load for each treatment.

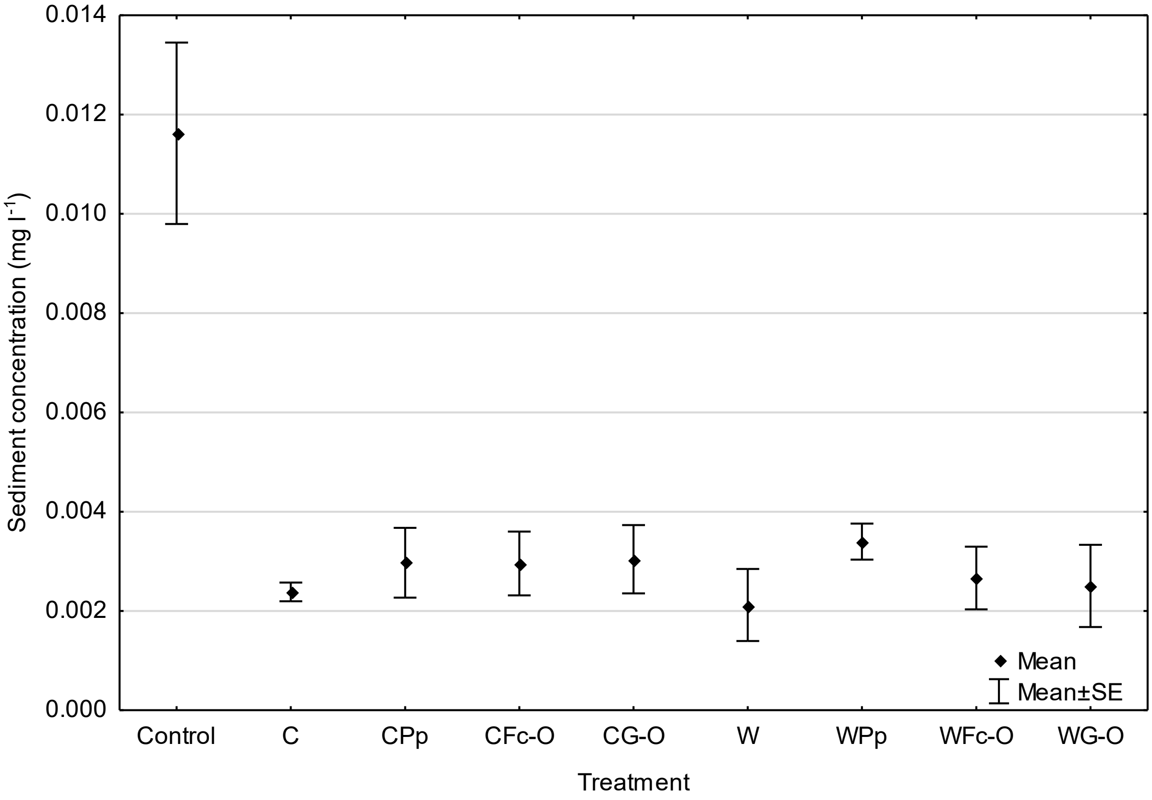

Figure 5.3. Mean sediment concentration for each treatment.

Table 5.5. Mean (n=5) FS treatment sediment removal efficiency (%) for each RTP (yr) as compared with non-FS control.

Treatment	5	18	41	75	126
C	73.5	77.1	77.5	94.3	95.6
CPp	69.9	72.8	73.4	93.5	95.0
CFc-O	66.8	71.0	72.3	92.8	94.5
CG-O	79.0	76.7	75.1	95.5	96.5
W	77.4	80.9	81.1	95.2	96.4
WPp	77.3	73.8	72.3	95.1	96.3
WFc-O	72.1	76.6	76.6	94.0	95.4
WG-O	65.7	72.5	75.6	92.6	94.4

However, mean sediment removal efficiency for all FSs significantly increased by >17.5% for the 75 and 126 yr RTP REs compared to the 5, 18 and 41 yr RTP storms.

Overall, the Eroded Particle Size Distribution (EPSD) results (Table 5.6) demonstrate that all FS treatments removed significantly more silt and clay compared to the non-FS control EPSD, however there were no significant differences between FS treatments themselves regarding the amount of sand, silt or clay retained. A large amount of sand was removed by the FS treatments; however this amount was not significantly greater than the control. This demonstrates that the significant reduction in sediment load in the runoff associated with the FS treatments (Figure 5.2) is attributed to the highly effective removal of silt and clay particles. This is the opposite to that usually found with other sediment control structures, such as SF, which easily remove sand from the runoff, whilst allowing clays and silt to continue through the geotextile (Cooke et al. 2015). The implication is that it is these finer fractions that are associated with SB PO_4^{3-}.

Clay-fraction removal efficiencies (Table 5.6) were 76.9 – 88.5% (W fill media treatments) and 80.8 – 84.6% (C fill media treatments), as compared to the non-FS control. Silt-fraction removal efficiencies varied between 72.4 – 81.6% (W), and 73.3 – 78.2% (C), whilst sand removal efficiencies varied between 25.0 – 50.0% (W) and 25.0 – 75.0% (C).

The EPSD results (Table 5.7) also show that the mass (g) of clay, silt and sand particles within the runoff all increase with storm RTP. This is due to the increasing KE associated with the higher RTPs. Table 5.8 confirms this indicating that the load increase of clay, silt and sand is correlated with increasing KE of the REs (longer duration) for all treatments and particle fractions, except that of the sand fraction for CPp and CFc-O. Although not significant, the results of CPp and CFc-O still indicate a strong relationship between the KE of the RE and the sand load.

There is no significant difference in the clay fraction loading (g) at the 5, 18, 41, 75 and 126 yr RE RTPs between FS treatments, irrespective of whether the fill media is C or W (Table 5.7). However all FS treatments reduce the amount of clay (g) in the runoff significantly compared to the control at every RE RTP. This confirms that neither type of fill media nor type of PSM have any effect on clay removal efficiency, which varies between 76.2 – 90.5% compared to the control (Figure 5.4). However, the greatest removal efficiency generally occurs for the 5, 18 and 41 yr RE RTPs.

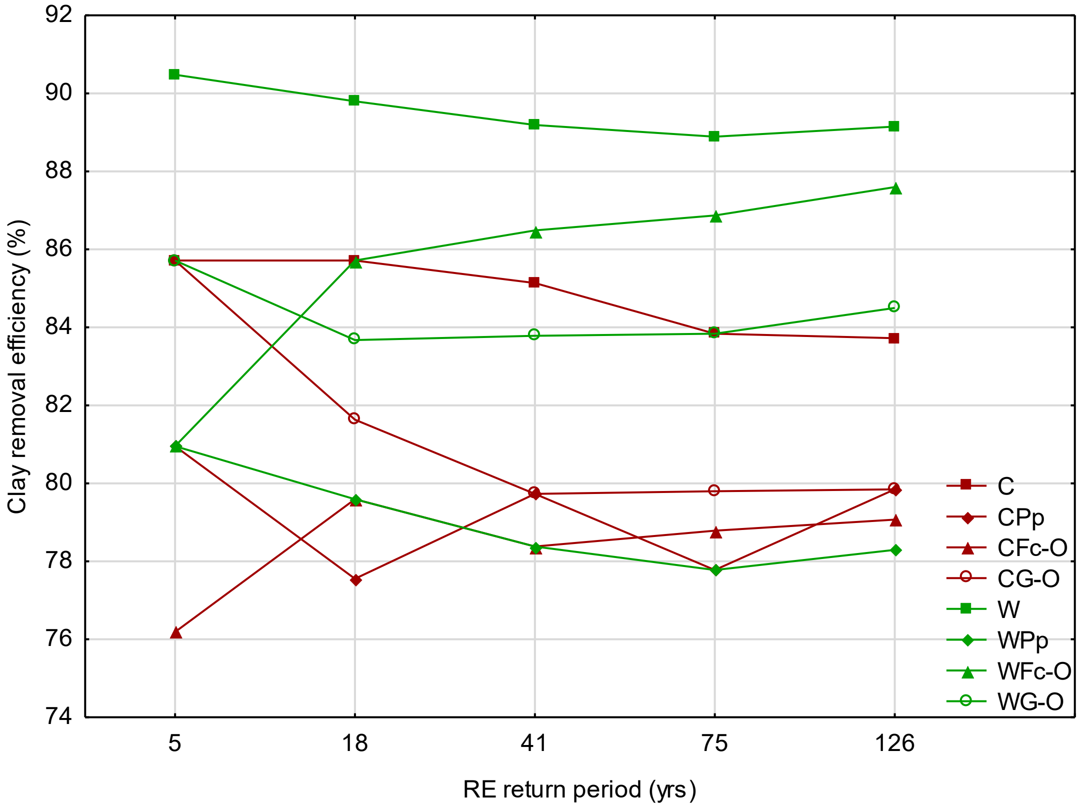

Figure 5.4. Clay removal efficiency (%) of the FS treatments, compared to the control, over the REs

Table 5.6. Mean Eroded Particle Size Distribution (EPSD) for the FS treatments as compared with the non-FS control.

Treatment	Mean (n=15) EPSD size fraction as % mass of sample (± SE)			Mean (n=25) sediment in runoff (g plot^{-1})	Mean (n=15) Total EPSD (g plot^{-1}) (± SE)			Removal efficiency (%)		
	C	Z	S		C	Z	S	C	Z	S
Control	7.2^{b} (±1.0)	91.6^{a} (±0.4)	1.2^{a} (±0.8)	35.6	2.6^{a} (±0.3)	32.6^{a} (±0.2)	0.4^{a} (±0.3)	N/A		
C	5.4^{ab} (±0.8)	93.2^{a} (±0.5)	1.4^{a} (±0.6)	7.6	0.4^{b} (±0.1)	7.1^{e} (±0)	0.1^{a} (±0)	84.6	78.2	75.0
CPp	5.7^{ab} (±0.5)	91.5^{a} (±1.2)	2.8^{ab} (±1.4)	9.2	0.5^{b} (±0.1)	8.4^{cd} (±0.1)	0.3^{a} (±0.1)	80.8	74.2	25.0
CFc-O	5.8^{ab} (±0.8)	92.7^{a} (±1.3)	1.6^{ab} (±0.6)	9.4	0.5^{b} (±0.1)	8.7^{c} (±0.1)	0.1^{a} (±0.1)	80.8	73.3	75.0
CG-O	5.7^{ab} (±0.4)	91.9^{a} (±1.0)	2.5^{ab} (±1.3)	9.1	0.5^{b} (±0)	8.4^{d} (±0.1)	0.2^{a} (±0.1)	80.8	74.2	50.0
W	4.4^{a} (±0.3)	90.7^{a} (±0.6)	5.0^{b} (±0.9)	6.6	0.3^{b} (±0)	6.0^{f} (±0)	0.3^{a} (±0.1)	88.5	81.6	25.0
WPp	5.8^{ab} (±0.5)	91.7^{a} (±0.8)	2.6^{ab} (±0.7)	9.8	0.6^{b} (±0.1)	9.0^{b} (±0.1)	0.3^{a} (±0.1)	76.9	72.4	25.0
WFc-O	4.2^{a} (±0.4)	92.4^{a} (±0.5)	3.4^{ab} (±0.8)	7.8	0.3^{b} (±0)	7.2^{e} (±0)	0.3^{a} (±0.1)	88.5	77.9	25.0
WG-O	5.2^{a} (±0.8)	92.8^{a} (±0.8)	2.0^{ab} (±1.5)	7.8	0.4^{b} (±0.1)	7.2^{e} (±0.1)	0.2^{a} (±0.1)	84.6	77.9	50.0

Within each column, values followed by the same letter are not significantly different following one-way ANOVA followed by post-hoc Fisher LSD analysis. C = clay (<0.002 mm), Z = silt (0.002 – 0.063 mm) and S = sand (>0.063 mm). Mean Total EPSD (g) based on % of Clay (C), Silt (Z) and Sand (S).

Table 5.7. Differences in mean (n=3) mass (g) of clay, silt and sand sized fractions in the runoff from the FS treatments for the RTP storms investigated as compared with the non-FS control.

RTP (yr)	Soil fraction	Treatment								
		Control	C	CPp	CFc-O	CG-O	W	WPp	WFc-O	WG-O
5	C	2.1^{a}	0.3^{b}	0.4^{b}	0.5^{b}	0.3^{b}	0.2^{b}	0.4^{b}	0.4^{b}	0.3^{b}
	Z	26.7^{a}	7.3^{d}	8.0^{c}	9.1^{b}	5.7^{e}	5.9^{e}	6.1^{e}	7.4^{d}	9.4^{b}
	S	0.6^{a}	0.2^{a}	0.3^{a}	0.2^{a}	0.1^{a}	0.5^{a}	0.3^{a}	0.4^{a}	0.4^{a}
18	C	4.9^{a}	0.7^{b}	1.1^{b}	1.0^{b}	0.9^{b}	0.5^{b}	1.0^{b}	0.7^{b}	0.8^{b}
	Z	62.5^{a}	14.6^{e}	17.0^{cd}	18.5^{b}	14.7^{e}	11.8^{f}	16.4^{d}	14.8^{e}	17.4^{c}
	S	1.1^{a}	0.4^{a}	0.6^{a}	0.4^{a}	0.3^{a}	0.8^{a}	0.5^{a}	0.5^{a}	0.5^{a}
41	C	7.4^{a}	1.1^{b}	1.5^{b}	1.6^{b}	1.5^{b}	0.8^{b}	1.6^{b}	1.0^{b}	1.2^{b}
	Z	93.9^{a}	21.6^{d}	25.4^{b}	26.0^{b}	23.5^{c}	17.6^{e}	26.1^{b}	22.1^{d}	23.3^{c}
	S	1.5^{a}	0.4^{a}	0.4^{a}	0.9^{a}	0.6^{a}	1.0^{a}	0.8^{a}	0.9^{a}	0.5^{a}
75	C	9.9^{a}	1.6^{b}	2.2^{b}	2.1^{b}	2.0^{b}	1.1^{b}	2.2^{b}	1.3^{b}	1.6^{b}
	Z	124.5^{a}	28.8^{e}	35.0^{bc}	34.0^{c}	32.7^{d}	23.5^{f}	35.8^{b}	29.0^{e}	29.4^{e}
	S	1.7^{a}	0.5^{a}	0.6^{a}	1.1^{a}	0.9^{a}	1.3^{a}	1.1^{a}	1.1^{a}	0.7^{a}
126	C	12.9^{a}	2.1^{b}	2.6^{b}	2.7^{b}	2.6^{b}	1.4^{b}	2.8^{b}	1.6^{b}	2.0^{b}
	Z	163.1^{a}	35.6^{e}	42.0^{cd}	43.3^{c}	41.8^{d}	30.0^{f}	45.1^{b}	35.9^{e}	36.1^{e}
	S	2.2^{a}	0.5^{a}	1.3^{a}	0.7^{a}	1.1^{a}	1.6^{a}	1.3^{a}	1.3^{a}	0.8^{a}

Significant differences indicated by letters and calculated by one-way ANOVA and Post-hoc Fisher LSD.

For each RTP storm, within each size fraction, values followed by the same letter are not significantly different following one-way ANOVA followed by post-hoc Fisher LSD analysis. C = clay (<0.002 mm), Z = silt (0.002 – 0.063 mm) and S = sand (>0.063 mm).

Table 5.8. Correlation (n=5) between mass of clay, silt and sand in the runoff with KE of the RE RTPs, for each of the treatments.

Treatment	Correlation coefficient		
	Clay	Silt	Sand
Control	0.999*	0.999*	0.992*
C	0.998*	0.999*	0.904*
CPp	0.996*	0.999*	0.809
CFc-O	0.999*	0.999*	0.737
CG-O	0.999*	0.999*	0.997*
W	1.000*	0.999*	0.998*
WPp	1.000*	0.999*	0.997*
WFc-O	1.000*	0.999*	0.986*
WG-O	0.999*	0.997*	0.962*

**indicates a statistically significant correlation, where increasing mass of clay, silt or sand in the runoff correlates with increasing KE of the RE.*

The FS treatments statistically reduce the mass of silt (g) in the runoff compared to the control at every RE RTP. However, the statistical differences between the different FS treatments regarding the mass of silt removed are less clear cut. The order of significance in which FS treatments remove silt mass for each RE RTP is:

- 5 yr RTP: CG-O = W = WPp > C = WFc-O >CPp > CFc-O = WG-O;
- 18 yr RTP: W > C = CG-O = WFc-O > WPp = CPp = WG-O > CFc-O;
- 41 yr RTP: W > C = WFc-O > WG-O = CG-O > CPp = CFc-O = WPp;
- 75 yr RTP: W > C = WFc-O = WG-O >CG-O > CFc-O = CPp = WPp;
- 126 yr RTP: W > C = WFc-O = WG-O> CG-O = CPp = CFc-O > WPp.

These show that amended W and C are consistently removing more silt than other FS treatments. WPp begins to remove less silt as soon as RE RTP increases, and becomes the least effective FS treatment in reducing silt at the higher RE RTP. The order of silt removal by treatments is fairly consistent for WFc-O, WG-O, CG-O, CPp and CFc-O, at all RE RTPs. Although there are significant differences in the amount of silt removed, the mass that is removed by the treatments is relatively similar. This is confirmed by the silt removal efficiency which varies between 64.8 – 81.6% (Figure 5.5). Higher silt removal efficiencies are found in the 41 to 126 yr RE RTPs.

There are no statistical differences in the mass of sand (g) between the FS treatments and the control, or between the FS treatments, at any of the RE RTPs. Sand removal efficiency is more variable than that of the clay and silt, varying between 16.7 – 83.3% (Figure 5.6).

The non-PSM amended FS treatments (i.e. C and W) retained a higher mass of clay and silt than those with PSMs added into their matrix, although this was only significant for the silt fraction (Table 5.7). As stated above and in Table 5.6, W is associated with significantly more silt retained than WPp, WFc-O and WG-O.

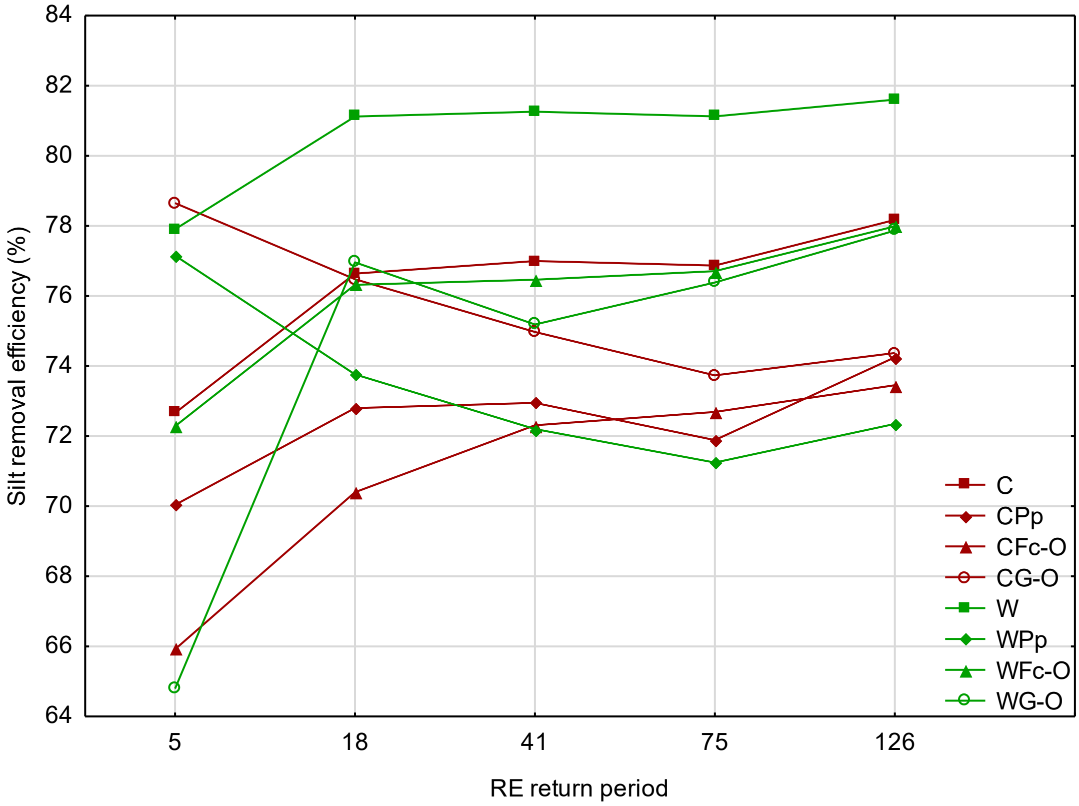

Figure 5.5. Silt removal efficiency (%) of the FS treatments, compared to the control, over the REs

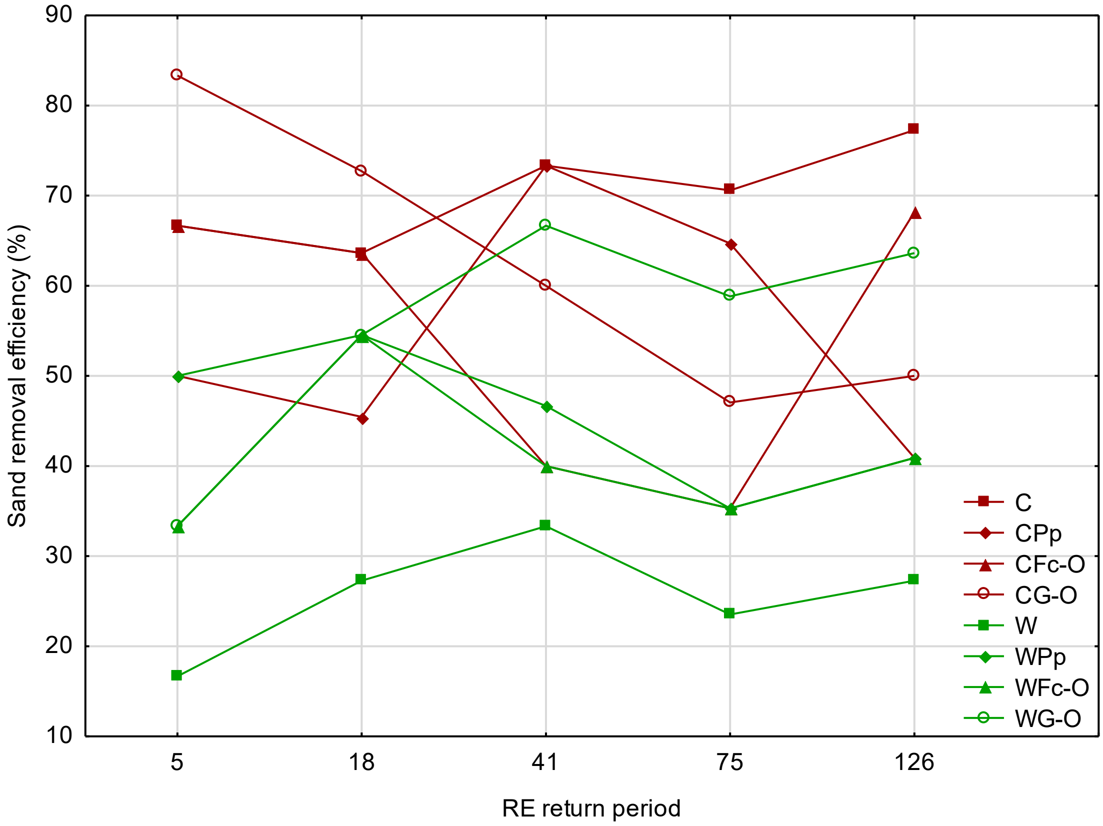

Figure 5.6. Sand removal efficiency (%) of the FS treatments, compared to the control, over the REs

C is associated with significantly more silt retained than CPp, CFc-O and CG-O. This suggests that, even though the overall sediment removal efficiency of the FS treatments is not diminished by the addition of PSMs (Table 5.6), when specific EPSD fractions are considered, the addition of the PSMs into the C or W fill media can marginally reduce the clay retention, and significantly reduce the silt retention of the FS. In turn, this limits the performance of the FS in removing SB PO_4^{3-} from the runoff. However, as discussed below, this reduction in clay and silt retention is compensated by the additional capability that the PSMs provide in adsorbing soluble orthophosphate from the runoff. Furthermore the PSM amended FS treatments still met the water quality target for sediment (0.1 mg l^{-1}).

5.3.3 Phosphate retention

For the FS and non-FS control treatments, the mean runoff orthophosphate concentrations were highly variable (Figure 5.7). The results indicate that there was no significant difference in runoff orthophosphate concentration between the non-FS control, C and CPp treatments. Although the water quality performance target of 0.05 mg P l^{-1} was not achieved, the CFc-O and WFc-O treatments were associated with significantly lower runoff orthophosphate concentrations as compared with all other treatments (Figure 5.7). Similar results were observed for PO_4^{3-} loads (Figure 5.8). In addition, it is of note that all of the W-FS treatments were associated with a significantly lower orthophosphate load than the non-FS control, C and CPp treatments (Figure 5.8).

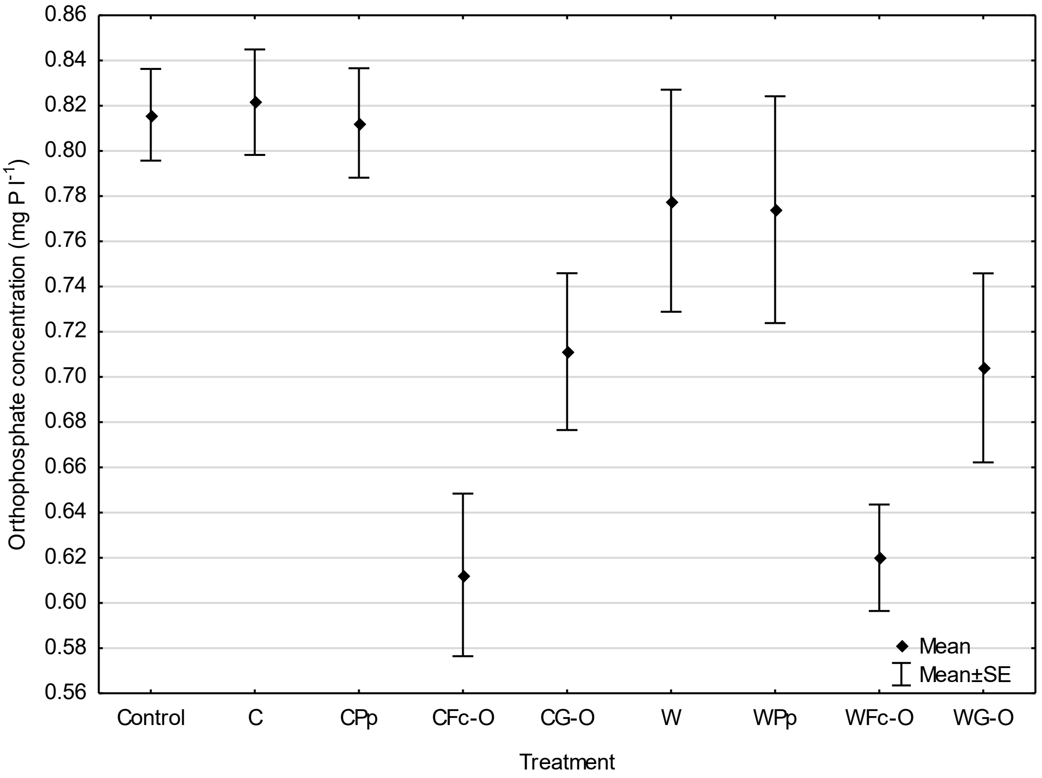

Figure 5.7. Mean runoff orthophosphate concentration (mg P l^{-1}) for each treatment

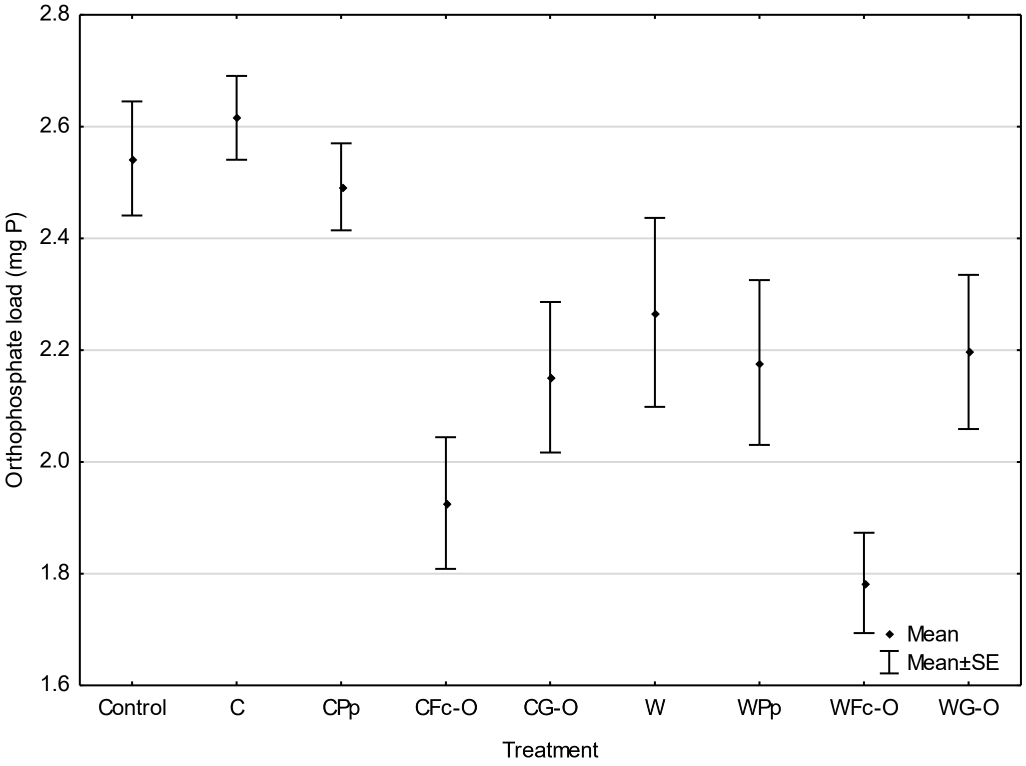

Figure 5.8. Mean runoff orthophosphate load (mg P l^{-1}) for each treatment

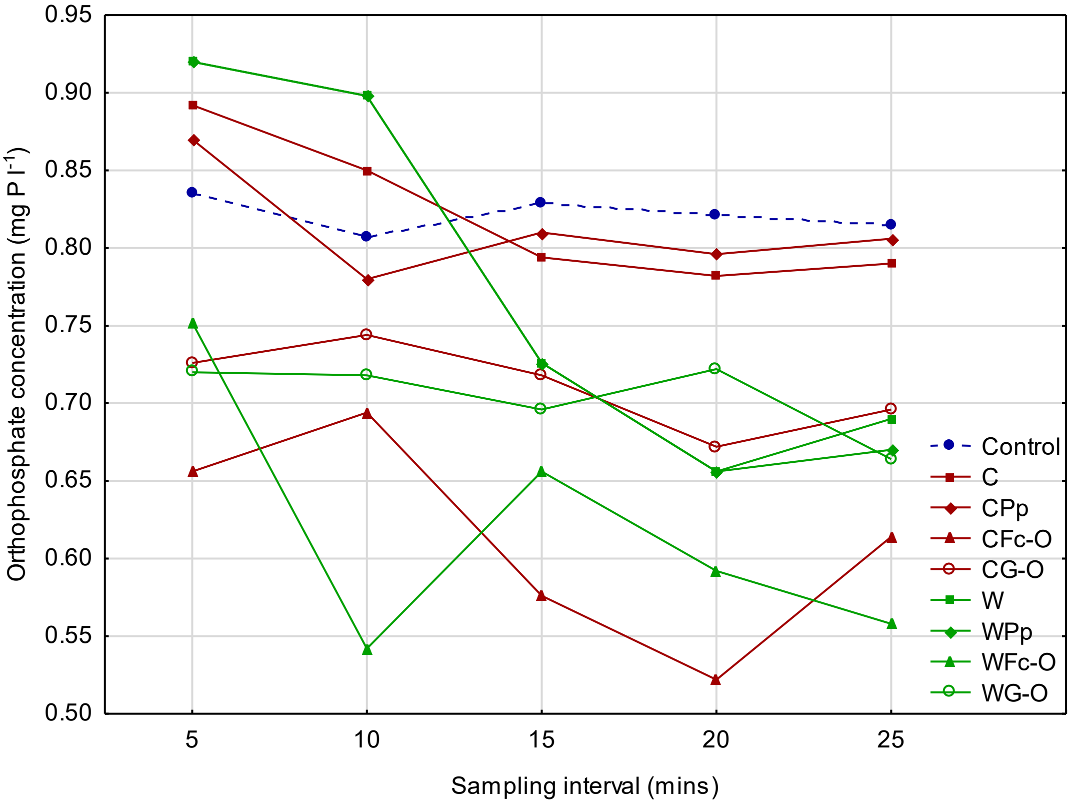

Figure 5.9. Mean runoff orthophosphate concentration (mg P l^{-1}) for each treatment at each sampling event.

PO_4^{3-} concentrations over the experimental time period (Figure 5.9) show evidence of a first flush experience. This is where soluble ions and/or fines are released from the C or W FS fill media after the initial RE following installation. It has been observed in other C and W studies (Waters 2010, Shipitalo et al. 2012, Cooke et al. 2017), but does not always occur.

The PO_4^{3-} concentration for the C and W FS treatments is higher than that for the control in the first 15 minutes of rainfall application (although not significantly so). The FS treatments with PSMs have lower PO_4^{3-} concentrations than that of the control, C and W FS treatments, indicating that the PSMs removed the PO_4^{3-} that was initially flushed out of the C and W fill media. After 15 minutes of rainfall, PO_4^{3-} concentrations gradually decrease over time for all FS treatments.

More specifically, the runoff PO_4^{3-} concentrations of the C, CPp, W, WPp and WFc-O after 5 minutes of rainfall are higher than the equivalent after 10 minutes. However this was only statistically significant for WFc-O. Although some of the results fluctuate over time (especially WFc-O and WG-O), after 15 minutes of rainfall (with the exception of CPp), all of the FS treatments had lower PO_4^{3-} concentrations compared to their initial 5 min PO_4^{3-} concentration. Again, this was only statistically significant for the C and the WFc-O treatments. This reduction in the PO_4^{3-} concentrations continued and after 25 minutes of rainfall, all treatments had lower PO_4^{3-} concentrations, significantly so for the control, WPp, and WFc-O treatments. Consequently, the Fc-O treatments, irrespective of fill media, had the highest PSE compared with all other treatments. The variation in PO_4^{3-} concentration in the Fc-O treatments varies, depending on the RE RTP, between SE ±0.01 mg P l^{-1} (5 yr RTP) and ±0.37 mg P l^{-1} (126 yr RTP). For G-O the variation in PO_4^{3-} concentration is between SE ±0.06 mg P l^{-1} (5 yr RTP) and ±0.47 mg P l^{-1} (126 yr RTP). The variation in the PO_4^{3-} concentration for the Pp treatments is between SE ±0.05 mg P l^{-1} (5 yr RTP) and 0.50 mg P l^{-1} (126 yr RTP). These indicate that not only was the PO_4^{3-} concentration reduced to the greatest extent by the Fc-O treatments but the Fc-O was more consistent in doing this as RE severity increased. Lastly, larger decreases in PO_4^{3-} concentration were seen for the Pp PSM when it was used with a W fill media rather than a C fill media.

Evidence of a first flush of PO_4^{3-} was also observed by Shipitalo et al. (2010) and Shipitalo et al. (2012). The addition of Fc-O and G-O to the FS fill media enabled the first flush PO_4^{3-} release to be lower than that from the C and W treatments. This indicates that the PSMs are adsorbing the PO_4^{3-} that is associated with the fill media as well as that associated with the soil. This prevents it from entering the watercourses.

The general trend for PO_4^{3-} loads (Table 5.9) is similar to that for PO_4^{3-} concentrations, in that they fluctuate over time. However, generally (with the exception of the Pp treatments), PO_4^{3-} load in the runoff increases over time, indicating that less PO_4^{3-} is being adsorbed by the FS as time increases. One reason for this may be that the PSMs are reaching saturation as PO_4^{3-} binds to the exchange sites. This would be confirmed through the application of successive REs.

Table 5.9. Differences in mean (n=5) runoff orthophosphate load (mg P per plot) from the FS treatments for the RTP storms investigated as compared with the non-FS control.

Treatment	**5**	**18**	**41**	**75**	**126**
Control	2.2^{ab}	4.7^{a}	7.4^{a}	10.0^{ab}	12.7^{ab}
C	2.6^{b}	5.3^{a}	7.8^{a}	10.4^{a}	13.1^{a}
CPp	2.4^{ab}	4.8^{a}	7.3^{ab}	9.8^{ab}	12.5^{ab}
CFc-O	1.8^{ab}	4.0^{ab}	5.9^{ab}	7.6^{bc}	9.6^{bc}
CG-O	1.6^{a}	4.0^{ab}	6.2^{ab}	8.3^{abc}	10.8^{abc}
W	2.5^{b}	4.6^{ab}	6.9^{ab}	9.0^{abc}	11.3^{abc}
WPp	1.7^{a}	4.3^{ab}	6.5^{ab}	8.6^{abc}	10.9^{abc}
WFc-O	1.7^{a}	3.2^{b}	5.2^{b}	7.0^{c}	8.9^{c}
WG-O	1.9^{ab}	4.2^{ab}	6.4^{ab}	8.7^{abc}	11.0^{abc}

For each RTP storm, values followed by the same letter are not significantly different following one-way ANOVA followed by post-hoc Fisher LSD analysis.

When specific RE RTPs are considered there are few statistically significant results within the data (Table 5.9). With the exception of the 5 yr RTP storm, WFc-O is the only treatment that is associated with a significantly lower PO_4^{3-} load when compared to the non-FS control. Only CG-O is associated with a statistically lower PO_4^{3-} load compared to the non-PSM amended C treatment at the 5 yr RT. Only CFc-O is associated with statistically lower PO_4^{3-} load compared to the non-PSM amended C treatment at the 75 and 126 yr RTP. This suggests that there may be some benefit in adding Fc-O PSM to the C fill media in terms of reducing PO_4^{3-} load in extreme REs, however, with all other PSMs (with the exception of G-O at the 5 yr RTP), the benefit is not clear/significant.

For the W results, only WFc-O is associated with a decrease in PO_4^{3-} load compared to the non-FS control (with the exception of the 5 yr RTP). No significant differences were observed between the PSM amended FS treatments, and the non-PSM amended W treatment with the exception of WFc-O at the 5 yr RTP. This suggests that there is no benefit in adding PSM to the W fill media in terms of reducing PO_4^{3-} load.

This translates into variable PO_4^{3-} removal efficiencies across the treatments (Table 5.10). Positive values indicate where more PO_4^{3-} has been added to the runoff compared to the non-FS control, whilst negative values indicate where PO_4^{3-} has been removed compared to the control. The percentage of PO_4^{3-} removal observed compared to the control ranged from +14.4% to -31.1%.

Table 5.10. Differences in mean (n=5) orthophosphate removal efficiency (%) associated with the FS treatments for the RTP storms investigated as compared with the non-FS control.

Treatment	5	18	41	75	126
Control	N/A				
C	14.4^{d}	13.5^{a}	7.0^{b}	4.0^{c}	2.9^{c}
CPp	6.0^{cd}	2.0^{a}	-1.2^{b}	-1.8^{bc}	-2.0^{bc}
CFc-O	-18.7^{abc}	-14.4^{ab}	-19.5^{ab}	-24.4^{ab}	-24.2^{ab}
CG-O	-27.1^{a}	-16.1^{ab}	-15.7^{ab}	-16.9^{abc}	-15.4^{abc}
W	12.3^{cd}	-1.7^{ab}	-5.9^{ab}	-9.9^{abc}	-10.8^{abc}
WPp	-26.1^{a}	-7.7^{ab}	-10.8^{ab}	-13.5^{abc}	-14.4^{abc}
WFc-O	-25.8^{ab}	-31.1^{b}	-28.8^{a}	-29.6^{a}	-29.9^{a}
WG-O	-13.5^{abcd}	-11.3^{ab}	-13.0^{ab}	-12.8^{abc}	-13.6^{abc}

For each RTP storm, values followed by the same letter are not significantly different following one-way ANOVA followed by post-hoc Fisher LSD analysis. Negative values indicate that PO_4^{3-} has been removed from the runoff, whilst positive values indicate PO_4^{3-} addition.

Across all RE RTPs, the non-PSM amended C treatment added PO_4^{3-} to the runoff, indicating a prolonged flush of PO_4^{3-} from the fill media. On the other hand, the W treatment, after an initial flush associated with the 5 yr RTP event, had increasing PO_4^{3-} removal efficiency, reaching a maximum of -10.8% for the 126 yr storm. This suggests that the W fill media had a strong capability for PO_4^{3-} adsorption. However as there were no significant differences between the results of the non-PSM amended C and W treatments, this is speculation. The flush associated with the C fill media is confirmed by the CPp amended treatment which added PO_4^{3-} at the 5 and 18 yr RTP, after which it gave a removal efficiency ranging from -1.2 – 2.0% (Table 5.10). The WPp removed significant amounts of PO_4^{3-} for 18, 41, 75 and 126 yr RTP, but significant differences in removal efficiency between the CPp and WPp were only found at the 5yr RTP. Similarly lower removal efficiency by the CFc-O treatment is observed at all RE RTPs compared to the WFc-O treatments (although not significantly so). Lastly, no significant differences in removal efficiency were observed between the results for the CG-O and the WG-O treatments at any of the RE RTPs. The WG-O removal efficiency remained fairly constant at all RE RTPs.

There are no significant differences in the PO_4^{3-} retention efficiency of the PSM-amended C treatments compared to the non-PSM C treatments, or between the PSM-amended W treatments compared to the non-PSM W treatments (Table 5.11) the RE RTPs. The best performing and most consistent PSMs were the Fc-O treatments which had large, but not statistically different, PO_4^{3-} removal efficiencies. CFc-O and WFc-O consistently removed more PO_4^{3-} than the non-PSM amended FS treatments, with minimum removal efficiencies of 21.4 %. CG-O and WG-O showed statistically insignificant removal efficiencies over the RE RTPs.

Table 5.11. Differences in mean (n=5) orthophosphate removal efficiency (%) associated with the PSM amended FS treatments for the RTP storms investigated as compared with the non-PSM amended Compost (C) and Woodchip (W) FS treatments.

Treatment	5	18	41	75	126
C	N/A				
CPp	-7.3[a]	-10.1[a]	-7.6[a]	-5.6[a]	-4.7[a]
CFc-O	-28.9[a]	-24.5[a]	-24.8[a]	-27.3[a]	-26.4[a]
CG-O	-36.2[a]	-26.1[a]	-21.2[a]	-20.0[a]	-17.8[a]
W	N/A				
WPp	-34.2[a]	-6.1[a]	-5.3[a]	-4.0[a]	-4.0[a]
WFc-O	-34.0[a]	-29.9[a]	-24.3[a]	-21.9[a]	-21.4[a]
WG-O	-23.0[a]	-9.8[a]	-7.6[a]	-3.2[a]	-3.1[a]

For each RTP storm, values followed by the same letter are not significantly different following one-way ANOVA followed by post-hoc Fisher LSD analysis. Negative values indicate that PO_4^{3-} has been removed from the runoff, whilst positive values indicate PO_4^{3-} addition.

At the 5 yr RE RTP, CG-O had a removal efficiency of 36.2% which decreased throughout the 18, 41, 75, and 126 yr RTP to 17.8%. For WG-O, removal efficiency peaked at the 5 yr RTP (23.0%) and quickly decreased throughout 18, 41, 75, and 126 yr RTP to 3.1%. Lastly the CPp 5 yr RTP removal efficiency of 7.3% fluctuated throughout the 18, 41, 75 and 126 yr RTP, with no obvious trend. Conversely, WPp began with a high removal efficiency of 34.2% at the 5 yr RTP, but this rapidly decreased for the remaining RTPs.

Total P was determined by adding that which was within the soil, plus that which was in the FS fill media. The soluble orthophosphate was analysed from the runoff. These results were used to establish SB PO_4^{3-} (Equation 5.4). The results (Table 5.12) indicate that all treatments, across all RTPs significantly reduced SB PO_4^{3-} as compared to the control. However, the difference in SB PO_4^{3-} removal efficiency between any of the treatments is not statistically significant at any of the RE RTPs. The FS treatments removed between 59.2 – 78.0 % of the SB PO_4^{3-} from the runoff, which would otherwise discharge into waterbodies, so reducing water quality and increasing eutrophication risk. This is to be expected given that the FS treatments removed a significant amount of clay and silt from the runoff, with sediment removal efficiencies between 65.7 – 96.5%. This is a significant reduction and therefore could provide essential mitigation at the catchment scale. With the exception of CG-O and WPp, as RE RTP increased, so did the SB PO_4^{3-} removal efficiency, however this was not significant. As expected, the highest SB PO_4^{3-} removal efficiencies (although not significantly different to other treatments) were achieved by the C and W FS treatments, which also had the highest sediment removal efficiencies.

Table 5.12. Differences in mean (n=5) sediment bound PO_4^{3-} and sediment bound PO_4^{3-} removal efficiency (%) associated with FS treatments for the RTP storms investigated as compared with the non-FS control.

RTP	Sediment-bound PO_4^{3-}								
	Control	C	CPp	CFc-O	CG-O	W	WPp	WFc-O	WG-O
5	23.1^{a}	7.3^{b}	8.5^{b}	9.4^{b}	6.0^{b}	6.2^{b}	6.2^{b}	7.7^{b}	9.4^{b}
18	53.9^{a}	15.2^{b}	18.0^{b}	19.2^{b}	15.4^{b}	12.3^{b}	16.8^{b}	15.0^{b}	17.6^{b}
41	80.9^{a}	22.3^{b}	26.4^{b}	27.5^{b}	24.7^{b}	18.2^{b}	26.6^{b}	22.5^{b}	23.5^{b}
75	107.2^{a}	29.8^{b}	36.4^{b}	36.0^{b}	34.4^{b}	24.2^{b}	36.5^{b}	29.4^{b}	29.7^{b}
126	140.2^{a}	36.9^{b}	44.4^{b}	45.2^{b}	43.9^{b}	30.9^{b}	46.0^{b}	36.3^{b}	36.4^{b}
	Sediment-bound PO_4^{3-} removal efficiency (%)								
5	N/A	68.5^{a}	63.1^{a}	59.2^{a}	74.3^{a}	73.2^{a}	73.1^{a}	66.8^{a}	59.3^{a}
18		71.9^{a}	66.6^{a}	64.3^{a}	71.4^{a}	77.2^{a}	68.9^{a}	72.2^{a}	67.4^{a}
41		72.4^{a}	67.4^{a}	66.0^{a}	69.4^{a}	77.6^{a}	67.1^{a}	72.2^{a}	71.0^{a}
75		72.2^{a}	66.0^{a}	66.4^{a}	67.9^{a}	77.5^{a}	65.9^{a}	72.6^{a}	72.3^{a}
126		73.7^{a}	68.4^{a}	67.8^{a}	68.7^{a}	78.0^{a}	67.2^{a}	74.1^{a}	74.0^{a}
For each RTP storm, within RTP, values followed by the same letter are not significantly different following one-way ANOVA followed by post-hoc Fisher LSD analysis.									

5.4 Discussion

The FS have proven to be effective at reducing loads and concentrations of sediment, SB PO_4^{3-} and orthophosphate in experimental runoff representing agricultural conditions.

FS sediment removal efficiency is particularly effective (i.e. 65-97% of sediment removed compared to the control), which justifies the use of these products as a sediment control BMP within the USA. The matrix structure of the fill media is manufactured such that the particle size distribution allows runoff to pass through the matrix, demonstrated by the few statistical differences in runoff volume between treatments (Table 5.4). The friction that is created as runoff passes through the FS reduces the runoff velocity and associated flow transport capacity, allowing particles to deposit within or slightly upslope of the FS. Larger sand particles may be preferentially deposited upslope of the FS as it temporarily acts like a check dam. In this scenario, runoff may temporarily pond, allowing the relatively heavy sand particles to deposit. This range of sediment removal values is consistent with others reported in the literature (Filtrexx International 2005, Faucette et al. 2008, 2009a, 2009b, Shipitalo et al. 2010) and provides evidence that FS may be an effective in-field EOPS for sediment control.

SB PO_4^{3-} preferentially sorbs to clay fractions, and to some extent, silt fractions. Removing clays and silts from runoff before it enters a waterbody is important to remove associated SB PO_4^{3-} inputs. Results show that FS are effective at removing 59-78% of SB PO_4^{3-} from runoff (Table 5.12). Specifically, this can be attributed to the removal of clay (77-89% compared to the control) and therefore clay-bound PO_4^{3-}, as well as silt (72-82% compared to the control) and silt bound PO_4^{3-} (Table

5.6). Similar results reported in the literature are limited, however comparisons can still be drawn by using results of turbidity and suspended sediment studies (Faucette et al. 2009a). FS have been found to remove between 58-82% of suspended solids (Faucette and Tyler 2006, Faucette et al. 2008), and a reduction in turbidity of 53-78% compared to non-FS control (Faucette et al. 2008). Where specific readings have been taken, FS have been found to remove 65% of clay particles and 66% of silt particles (Faucette et al. 2009a), which is lower than the results reported in this study. Even so, clay and silt removal values for FS in the literature and in this study are far higher than those reported for other EOPS. SF have varying reported results, typically removing 0-20% of clay and silt particles (US EPA 1993a), 71-87% of suspended solids (Faucette et al. 2008), and reducing turbidity by 54-76% (Faucette et al. 2008). Discrepancies arise because the majority of studies are undertaken within laboratory environments, using simulators. In reality, SF installed in the field rarely obtain these high values (Cooke et al. 2015) due to their improper installation and maintenance, as well as their natural propensity to preferentially remove sand particles. The literature surrounding BS as EOPS indicates that their effectiveness at removing sediment from runoff decreases with decreasing particle size (Barling and Moore 1994; Newell Price et al. 2011). Performance is highly dependent on the vegetation species used and plant stem density (Pan et al. 2017), as well as slope, soil type and RE (Liu et al. 2008, Rickson 2014). This study indicates that FS are a reliable method for sediment removal of all particle size fractions, when trialled in a simulated laboratory environment.

Removal of clay, silt and sand particles simultaneously up to the 126 yr RE RTP is more efficient than with other EOPS; where the sand fraction is preferentially removed over silts and clays. Consequently, by removing clays and silts effectively from runoff, FS also remove associated SB PO_4^{3-} which could otherwise become soluble orthophosphate upon entering a watercourse (Logan 1982), thus impacting water quality. FS could therefore be an essential tool to help meet sediment and PO_4^{3-} water quality targets. Removal of silt and clay from runoff will also reduce water turbidity which can otherwise be detrimental to freshwater aquatic habitats. Specifically, highly turbid water decreases photosynthesis, thereby increasing eutrophication (Scholten et al. 2005), and increases the water temperature as the sediment is able to absorb and scatter solar energy (Paaijmans et al. 2008). Furthermore turbid water interferes with the habitats of freshwater fish, oysters and mussels which require clear water for feeding, growth and breeding (Engström-Öst and Candolin 2007, Österling et al. 2010). The Wye catchment has been identified as a priority habitat by the Habitats Directive (92/43/EEC), so it is imperative that water turbidity is reduced to maintain and improve the aquatic environment.

The sorption capability of the PSMs used in this study was generally lower than that reported in the literature. The best performing PSM, Fc-O, adsorbed 21-34% of the orthophosphate from the runoff. It is postulated that adsorption occurs through the creation of monodentate or bidentate bonds with the Fe, O and OH^- groups (Parfitt 1989, Cornell and Schwertmann 2003, Wang et al. 2013), by coordination and ionic bonding, as well as some surface precipitation (Wang et al. 2013, Sundman et al. 2016). It is thought that these are also the adsorption mechanisms for the G-O PSM, which removed 3-36% of the orthophosphate. The Pp removed 4-10% orthophosphate, which was far lower than its reported values in the literature (Faucette et al. 2009a, Shipitalo et al. 2012). It is thought that the lower values are due to a first flush of soluble ions and fill media fines including orthophosphate, from the FS fill media. Reported results for FS in the literature typically span a season encompassing many REs, allowing the first flush period to finish and the impact of this to be masked over the total experimental time. It was thought that mixing PSMs with the FS fill media could allow the effects of this first flush to be mitigated. Fc-O was the most effective PSM trialled for both C and W fill media compared to the non-FS control as it consistently provided the highest levels of PO_4^{3-} removal across the RE RTPs (Table 5.10). However, when its impact was considered in relation to non-PSM amended FS (i.e. C or W filled FS), it did not necessarily always provide significant PO_4^{3-} removal. This is not consistent with the literature (Michel et al. 2010, Hiemstra 2013, Wang et al. 2013) where Fc-O tends to provide higher PO_4^{3-} removal than other PSMs. However, for all PSMs trialled within this study, the PO_4^{3-} removal for all FS treatments tends to be lower than that within the literature.

In the majority of studies, PSMs have not been mixed with fill media and often PO_4^{3-} removal is established using batch or column studies. These allow the runoff to spread and infiltrate evenly over the surface, allowing the PO_4^{3-} within the runoff to be exposed to the PSMs over a longer distance and time duration, thus allowing increased adsorption. This provides information on the maximum adsorption capability of the PSMs, but it is not particularly comparable to field conditions (further research is required whereby they are trialled in field) or the FS structure themselves. This could account for the lower values of PO_4^{3-} adsorption than those stated in the literature. Another reasoning is the pH of the incoming runoff which needs to be acidic for the highest PSE owing to more hydrogen atoms available for use in the binding of PO_4^{3-}(Fink et al. 2016, Ooi et al. 2017). Furthermore, one study (Sundman et al. 2016) has shown that OM limits PO_4^{3-} removal by Fc-O and G-O as PO_4^{3-} preferentially adsorbs to the OM, and contributes to increasing soluble orthophosphate. This may be one reason for the higher than expected orthophosphate concentration results of this study. Consequently it is believed that with more frequent and successive REs, and tailoring to the pH of the incoming runoff, the PO_4^{3-} removal results would increase. Further study is required into the interactions between OM and Fe-oxides for PO_4^{3-} removal. This may explain why there were few statistical differences in PO_4^{3-} removal between the FS treatments.

Conversely it may be beneficial for Fe-oxide PSMs, such as Fc-O and G-O, to be mixed with other PSMs, such as calcite or magnesium, allowing PO_4^{3-} removal to be maximised at both acidic and alkaline pH values (Perassi and Borgnino 2014, Xie et al. 2014, Xu et al. 2014b, 2014c). This would tailor the FS PO_4^{3-} control system to work across a wide pH range (pH 3-9), regardless of the pH of the soil and the incoming runoff. This would be particularly effective in a UK agricultural setting where there is a wide variety of soil types and amendments applied to agricultural land, which influence the runoff pH, and therefore the amount of adsorbed PO_4^{3-}.

PSMs with higher SA tend to have higher PO_4^{3-} removal efficiencies. SA was measured for the majority of the fill media and PSMs used within the study (Table

5.1). Fc-O had a lower SA than that of G-O (it was not possible to measure the SA of Pp), however Fc-O produced the highest PO_4^{3-} removal. This suggests that although SA is important, to maximise the benefit of having a high SA other conditions have to be favourable. Consequently, it is thought that favourable conditions would have increased the PO_4^{3-} removal effectiveness of G-O, as well as that of Fc-O. This also suggests why it may be preferable to tailor the FS PSM to a wide range of pH values to accommodate a variety of situations.

Specifically regarding Fc-O, SA and PSM particle size are effective indicators of whether the ferrihydrite is 2-line ferrihydrite (2LFh), or 6-line ferrihydrite (6LFh). The higher SA (Hiemstra and Van Riemsdijk 2009) and smaller particle size (Zhao et al. 1994, Janney et al. 2000) of 2LFh (~ 2.6 ± 0.1 nm), compared to 6LFh (5-6 nm) creates a greater number of reactive surface sites (Hiemstra and Van Riemsdijk 2009), resulting in a potentially higher PSE (Michel et al. 2010, Hiemstra 2013). The SA and particle size of the Fc-O used in this study (Table 5.1) suggests that it is 6LFh and therefore has less reactive surface sites available for PO_4^{3-} adsorption than if it was 2LFh. Consequently to maximise PO_4^{3-} removal and to help deal with the first flush effect, it is recommended that 2LFh is used as a PSM within FS.

The Pp treatment generally provided lower PO_4^{3-} removal efficiencies than the other treatments (Table 5.10), and so it is considered a less effective PSM. However due to the within treatment variation, it was not significantly worse performing than other treatments, other than at the 5 yr RE RTP. Given that it is currently not widely available within the UK, it is not practical or cost effective to use for PO_4^{3-} control. Fc-O and G-O provided generally higher PO_4^{3-} removal results (although not significantly so) and are more widely available within the UK (as remnants of the UKs mining history). The issue with their use as PSMs is that they are currently regarded as ‘waste’. This currently consigns them to being landfilled after they are dredged up from mine water treatment schemes, at cost to The Coal Authority. However with an annual production of 4500 t (Sapsford et al. 2015), if another use could be ensured, they could provide a reliable, accessible and economic PSM for PO_4^{3-} control on agricultural lands.

Overall, the results from the study suggest that FS mixed with PSMs, such as Fc-O, could provide effective and essential sediment, SB PO_4^{3-} and orthophosphate control. This would only be possible if such PSMs are affordable, reliable and easily available for wider uptake by enforcement agencies and farmers. Consequently this study confirms that the optimum PSM based on its reliability and accessibility is that of Fc-O. However more research is required in order to confirm their reliability and efficacy when placed within an agricultural field setting.

5.5 Conclusions

The ideal field practice for reducing sediment and PO_4^{3-} inputs to rivers from agricultural runoff is one which simultaneously reduces sediment, SB PO_4^{3-} and orthophosphate. A proof of concept study (Cooke et al. 2017) identified FS as a potential sediment control measure for use on UK agricultural lands. The literature indicates that the PSMs Fc-O and G-O are effective at controlling soluble orthophosphate. By combining FS and PSMs, this study has identified that even at extreme REs, such as those with a 126 yr RTP, FS are effective at controlling sediment and SB PO_4^{3-}. Furthermore the addition of PSMs, such as Fc-O, makes these products effective at reducing soluble orthophosphate by up to 34%, although this is far lower than that of previous laboratory based studies. The treatments trialled within this study indicate that the first flush of PO_4^{3-} and fines associated with the fill media is only effectively mitigated by the Fc-O and G-O PSMs. Although the results of this study show encouraging and effective results, it is believed that further studies are required to ascertain how successive REs affect the PO_4^{3-} removal efficiency of the PSMs within the FS. This would identify the maximum PSE as well as the longevity of the PSMs and the FS, providing significant evidence to underpin their wider adoption and uptake.

5.6 References

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CHAPTER 6: INTEGRATED DISCUSSION

The findings of this research have shown that removal of sediment, SB PO_4^{3-} and orthophosphate is optimised when FS are treated with PSMs. Furthermore their efficacy, reliability and longevity under a range of extreme REs has been assessed in simulated laboratory trials. This research suggests that FS could provide effective mitigation of both soil and PO_4^{3-} losses. In order for this to be verified, further laboratory trials are required into their efficacy and longevity, as well as the optimisation of the PSM fill media mix, assessment of the impact of pH and OM, all of which would eventually lead to more field trials to assess their real-world response and impact. If successful, a catchment scale assessment would be required with the understanding that catchment-scale uptake would limit the impact of cumulative diffuse pollution events on water quality.

The research has met its aims and objectives (Chapters 1 – 5), and confirmed that FS are a potential measure to mitigate sediment, SB PO_4^{3-} and orthophosphate losses from agricultural land. Their effectiveness under both current and extreme REs has been assessed within simulated laboratory conditions, and limited field trials. This chapter serves to discuss the wider application of FS for environmental protection within agricultural systems, as well as highlight further research required and recommendations for their adoption.

6.1 Filter sock costs and installation

6.1.1 Material costs

Utilising the methodology from Chapter 4 (Equations 4.5 - 4.8), the material cost results (Chapters 4 and 5), and the orthophosphate removal results (Chapters 4 and 5), Table 6.1 summarises the costs associated with the FS and PSM materials in terms of their sediment and orthophosphate removal. The costs associated with C and W for sediment control are nominal. Given their wide availability this could facilitate wider uptake of FS. Costs associated with orthophosphate removal are more variable. The Pp is particularly costly (£7.16 per mg of orthophosphate removed) owing to its lower PSE and low availability (only 1 UK distributor and the product needs to be shipped from the USA). The Fc-O and G-O have lower costs (£0.01 – £0.02 per mg of orthophosphate removed) owing to their higher PSE and the fact they are considered waste material. Their calculations used the current permitting, dredging, transport and landfill costs incurred by The Coal Authority.

Table 6.1. Material costs per mg of sediment and orthophosphate removed.

Material	Cost (£) per mg of removal
C	0.0000010†
W	0.0000011†
Fc-O	0.01*
G-O	0.02*
Pp	7.16*

†cost per mg of sediment removed associated with C or W fill media
*cost per mg of orthophosphate removed Fc-O, G-O and the Pp

Although these values indicate the variation in material costs, they are not helpful to the agricultural industry as they have been calculated using results from laboratory and simulation trials, based on conditions from one location (the case study catchment; the Lugg catchment). Furthermore the material costs associated with the C and W are not related to the FS dimensions (diameter, length). FS with larger dimensions are able to deal with larger amounts and velocities of runoff, and associated sediment.

For comparison with other EOPS, Table 6.2 details the costs associated with using a 100 m length of 8-inch FS. Cost of the materials includes the materials themselves, as well as installation costs (including transport where applicable), but do not include maintenance costs as no information on this could be found in the literature.

Table 6.2. Total costs per 100 m length of 8-inch FS

Materials	**Cost (£)**	
	100 m length of 8 inch diameter FS	**1 m length of 8 inch diameter filled FS**
Filter sock outer material	1000	10
Compost fill mediaϕ	171	N/A
Woodchip fill mediaϕ	199	
Pp†	479.4	
Fc-O†	6.80	
G-O†	6.80	
Filled FS options trialled in research		
C filled FS	1171	11.7
CFc-O filled FS†	1177.7	11.8
CG-O filled FS†	1177.7	11.8
CPp filled FS†	1650.2	16.5
W filled FS	1199	12.0
WFc-O filled FS†	1206.1	12.1
WG-O filled FS†	1206.1	12.1
WPp filled FS†	1678.7	16.8
ϕ Assuming a bulk density of 0.7 g cm3 † Assuming an application rate of 20 kg per m^3 of fill media (equates to 0.1 t of PSM for a 100 m length, 8 inch diameter FS).		

Table 6.2 shows that a standard compost or woodchip filled FS costs £11.70 – £12.00 per metre (8-inch diameter), using the methodology from Chapter 4 (Equations 4.5 - 4.8) and the material results from Chapters 4 and 5. However wider adoption as a sediment control BMP would reduce bulk shipping, and therefore overall costs. Further cost reductions would occur if farmers used non-PAS100 compost, or began to use their own composted material for the fill media (compost would still need to meet the specifications for PSD, organic matter and water content). Table 6.2 also shows that when PSMs are added for orthophosphate control, FS costs increase to £11.80 - £16.80 per metre of FS (8-inch diameter). This assumes an application rate of 20 kg of PSM per m^3 of fill media, (trialled within Chapters 3 – 5).

Table 6.3. Sediment and orthophosphate removal by FS

FS options	Sediment removal (kg) ϕ	Orthophosphate removal (mg)†
C filled FS	179.2	N/A
CFc-O filled FS	179.2	514.9
CG-O filled FS	179.2	375.9
CPp filled FS	179.2	66.9
W filled FS	180.9	N/A
WFc-O filled FS	180.9	514.9
WG-O filled FS	180.9	375.9
WPp filled FS	180.9	66.9

Φ Assuming a 100m length, 8-inch diameter FS
† Assuming a PSM application rate of 20 kg per m3 of compost or woodchip fill media, in a 100m length 8-inch diameter FS

Using the sediment and orthophosphate removal results from Chapters 4 and 5 and scaling them up to a 100 length of FS, Table 6.3 details the sediment and orthophosphate removal of various FS options (with and without PSMs). This shows that a CFc-O filled FS would remove 179.2 kg of sediment, as well as 514.9 mg of orthophosphate. This is far more than would normally be required in typical agricultural conditions, and therefore a lower PSM application rate may suffice in locations where smaller decreases are required to meet water quality targets. This would reduce the total cost. Furthermore, a 100 m length FS of 8 inch diameter is able to filter 4922 – 13124 litres min^{-1} of runoff, accounting for low – high overland flow scenarios (Alexander Associates 2006). This capacity is far larger than is typically required for individual agricultural fields and so it is thought that strategic placement of FS of shorter lengths and/or smaller diameters would allow water quality targets to be met at lower costs.

The longevity of the FS and fill media, for both sediment and orthophosphate control, is currently unknown. This was not researched within this 3-year study. Naturally, FS will have a maximum sediment retention capability, and likewise, PSMs will only be able to adsorb a certain amount of orthophosphate before all the reactive exchange sites are filled. Research into the longevity of these materials in the field is essential before FS can be used widely. Research is also required into whether the fill media can be replaced in-situ, such that the FS can be used for long-term sediment and orthophosphate control.

6.1.2 Installation

FS installation is currently undertaken by 1 UK supplier, Scotbark, based in Glasgow, Scotland. For this they use a blower from an articulated lorry to blow C into the FS (at the approved standards) on site. The FS is laid by hand into position on the ground as it is filled (Figure 6.1).

This is inappropriate for an agricultural system as an articulated lorry would often not be able to access the site. Furthermore the additional installation costs (included within the FS cost) may be suitable for areas where large tracts of FS are required; however for smaller field-scale FS positioning, the installation costs may be

[redacted]

prohibitive to a farmer. Consequently this research has looked into alternative installation methods that are more applicable to farm-scale uptake.

If only a few short lengths of FS are required (< 1.2 m), one option is to mix the fill media and pack the FS by hand. This was the method utilised by the trials detailed in Chapters 3, 4 and 5. For this, an appropriate diameter mould is required (this study used an open ended waste drain pipe at the correct diameter) to allow the FS to be packed to the correct bulk density whilst minimising material slumping. Fill media treated with PSMs were pre-mixed in buckets to the correct application rate to meet a bulk density of 0.7g cm^3. The FS material was placed surrounding the mould and the media was added by hand into the mould using buckets and scoops. After every bucket load, material was packed down in the mould using a press in order to maintain the correct bulk density. FS were then tied off and positioned in field by hand. This method worked very well for short lengths of FS (<1.2 m), in applications such as surface field drains or check dams, or where there are in-field concentrated flow paths. However this method would not be suitable for larger lengths and FS diameters (unless they could be positioned with machinery) due to the weight of a filled FS. Furthermore, it is unlikely that farmers would use this option as it is quite labour intensive.

An alternative option for filling the larger sized FS would be the use of a hopper, such as those already commonly used in the agricultural industry for grain, C, granular fertiliser, mulch, or drainage materials. This would allow FS to be filled at the required rate on site and, depending on the type of hopper used, laid as the hopper is pulled along by a tractor, or moved into place post-filling. A smaller tube composter hopper would allow FS to be concurrently filled and laid (Figure 6.2). This would be more suitable for agricultural applications where long lengths of FS are required, such as in lining riparian areas for wider catchment installations.

[redacted]

Due to the cost of this equipment - the large tube composter hopper of Figure 6.2 costs €30,000 (Murska 2017) - this may be more suitable if environmental protection / enforcement agencies / water companies found benefit in their installation and were therefore installing large numbers of them across a catchment(s), or if the equipment could be hired out to growers.

However, as has been proven in Chapters 3 and 5, in reality expensive equipment is not required in order to successfully install smaller lengths of FS (<1.2 m), as farmers already have easy access to the equipment required.

6.1.3 Placement

This research suggests that the placement of FS at the bottom of slopes may be effective at mitigating sediment movement and PO_4^{3-} losses from agricultural lands. To verify this, further research needs undertaking on their effectiveness within a field environment. This research has assumed FS are best placed as EOPS at the bottom of slopes, as this is the common practice in the USA on construction sites (Faucette et al. 2009, Shipitalo et al. 2012, US EPA 2017). Their use in agricultural lands in the USA and the UK is uncommon, and therefore the existing literature regarding their use and alternative location is limited (Shipitalo et al. 2010, 2012).

Placing FS at the bottom of slopes does not prevent the detachment phase of erosion from occurring, however it disrupts the transport phase and encourages deposition, thereby preventing the removal of sediment and PO_4^{3-} off-site, and subsequent water quality degradation. Consequently, when placed at the bottom of slopes it is recommended that they are used in conjunction with a wider erosion control management plan for the site.

However the assumption that they are best placed at the bottom of slopes comes from the perspective of their use as sediment control only. There is research to suggest that they could equally be used for erosion control if placed within the field (Nyssen et al. 2007, Wei et al. 2016, Chen et al. 2017, Lenka et al. 2017).

If FS were placed within field, it is postulated that they would act as berms, terraces or check dams as they reduce the slope length. Soil loss per unit area, *E*, is related to the slope angle, *θ*, and the slope length, *L*:

$$E \propto tan^{1.4}\theta L^{0.6}$$

Equation 6.1. The relationship between erosion and slope (Morgan 2005).

As detailed in Equation 6.1 (Morgan 2005), the erosion rate is reduced at certain slope lengths. Consequently if FS are placed on the contour / across slope within a field and the effective slope length is reduced, overall soil loss decreases, as the smaller length segments are not long enough to generate erosive overland flow. Theoretical critical slope length (*Lc*) at which runoff becomes erosive can be calculated (Equation 6.2) using the maximum permissible velocity of the overland flow (*vcr*), the Manning's roughness coefficient (*n*), the rainfall intensity (*R*), the infiltration capacity of the soil (*i*), and the slope (*S*):

$$Lc = \frac{vcr^{5/2}\, n^{3/2}}{(R-i)sin^{\frac{3}{4}}\, S\; cosS}$$

Equation 6.2. The theoretical critical slope length at which overland flow becomes erosive (Morgan and Rickson 2005).

This theory applies in many Mediterranean countries (Bevan and Conolly 2011, Stanchi et al. 2012, Arnáez et al. 2015) where terraces are used to break the slope into smaller, less erodible lengths. Establishing the critical slope length at which erosive overland flow is generated for a given rainfall intensity allows slopes to be broken up into smaller lengths e.g. for terrace spacing. This decreases the velocity of the overland flow, thereby limiting its ability to detach, entrain and transport sediment. Consequently the overall agricultural production potential of the parcel of land is increased, as soil losses are controlled. Consequently the method stated in Equation 6.2 for calculating terrace spacing can also be used to identify placement of FS (Morgan and Rickson 2005). This would allow FS to be used to prevent soil erosion at source, as they would reduce runoff velocity, and therefore limit the ability of runoff to detach and transport soil.

In the UK, although FS used this way could be a potential erosion control measure, they would likely only be applicable for high value crops, such as asparagus. The higher turnover obtained from farming such crops allows a larger uptake of more innovative measures to combat environmental and agricultural issues. Consequently, this may provide an initial target market for the initial uptake of FS as an erosion control measure.

Another target market for consideration are fields where there are either tramlines or wheelings; especially those where there is an additional contributing area. Wheelings and tramlines are areas of high erosion and runoff owing to their typically compacted soil, and concentrated flow path. Row crops such as asparagus, potatoes and maize typically have deep and compacted wheelings, whilst tramlines are commonplace throughout many agricultural lands. Short lengths of FS may be placed within the wheelings or tramlines, either at the bottom of the slope or spaced at strategic points within field. This could provide effective sediment and pollution control in these high-risk areas in field. Research into their use within wheelings and tramlines is required before wide uptake.

The effectiveness of FS field placement within a catchment for the mitigation of soil erosion, sediment movement and PO_4^{3-} losses can then be quantified through existing prediction models, such as SCIMAP (SCIMAP 2018). SCIMAP is already used to model and map the risk of potential sources of diffuse pollution at the catchment scale by environmental agencies, catchment partnerships and agricultural advisors. Strategic placement of FS, with or without PSMs, in areas identified by SCIMAP as likely to be sources of diffuse pollution, would be the most cost-effective option, and would limit the impacts associated with erosion and diffuse pollution from these areas. SCIMAP utilises data on topography, land cover, erodibility and soil moisture, to create a map of surface hydrological connectivity (to the nearest watercourse). Utilising this data, SCIMAP establishes surface flow paths, and identifies where in the landscape there are risks of diffuse pollution.

6.2 Wider impacts

6.2.1 Water and wastewater industry

Diffuse pollution and poor water quality are a global problem, accentuated by poor agricultural practices, and are likely to worsen under climate-induced extreme events (Woznicki et al. 2011, IPCC 2014).

The 11 billion litres of wastewater collected every day (DEFRA 2012a) need to be treated to a maximum permissible concentration of 0.1 mg l^{-1}, for both sediments and PO_4^{3-}. However for PO_4^{3-} in aquatic environments, the target concentration is often set at <0.025 mg P l^{-1} (Shepherd et al. 2016, Ye et al. 2017) to limit eutrophication and aquatic degradation. In 2014-2015, the UK water industry spent £1104.1 million on upstream water treatment (Water UK 2015). Specific costs attributed to PO_4^{3-} and sediment removal are old and vary widely, with estimates ranging from between £15 - £90 million per annum (D'Arcy et al. 2000, Pretty et al. 2000). Although current equivalent figures cannot be confirmed due to a lack of freely available information, given the updated 2010 WFD permissible limits for PO_4^{3-} it is likely that these costs have increased in the years since.

Consequently, if traditional treatment is unable to meet these environmental targets, additional measures are required to prevent sediment and PO_4^{3-} entering waterbodies, in order to decrease their concentrations on a catchment scale. Many water companies which have an economic interest (i.e. abstraction) in a water body's water quality are investigating additional catchment management and field-based measures to reduce sediment, nutrient and pesticide losses upstream. This catchment based approach often involves collaboration with other stakeholders to achieve the common goal of improving and preserving water quality (DEFRA 2013), addressing sediment and PO_4^{3-} removal close to or at source. The Severn Trent Environmental Protection Scheme (STEPS) is one such initiative whereby capital grants are made to farmers and landowners for undertaking infrastructure improvement and land management changes, which exceed good agricultural practice, for the purpose of improving and protecting water quality (Severn Trent Water 2018). Measures include installation of BS, cover cropping, fencing, pesticide wash down areas, culverting, wetland creation, and precision agriculture amongst others. Making these changes at the field level alongside maintaining good agricultural practice, helps to limit runoff and nutrient losses, and the detachment and transport of sediment, close to or at the source. This reduces the need for additional treatment downstream to meet water quality targets.

Due to the lack of information freely available by the water industry, direct economic impacts of the placement of FS-based sediment and PO_4^{3-} control, at source as a catchment based measure, cannot be quantified. However it can be assumed that their strategic placement within agricultural landscapes (e.g. by using SCIMAP) would, at the very least, reduce sediment movement to watercourses and supplement traditional water and wastewater treatment to help meet water quality targets. At the most, their use would reduce the need for conventional sediment and PO_4^{3-} treatment. In either case, total overall costs of sediment and PO_4^{3-} removal are reduced, however this is dependent on appropriate management of the ‘flush’ phenomenon that was experienced (Chapter 3). This initial flush from the FS fill media after installation can temporarily result in delivery of more fines and nutrients to the receiving waterbodies, unless measures are undertaken to limit this. The addition of PSMs into FS fill media goes some way to mitigating this impact (up to 34% for Fc-O; Chapter 5), although more research is required to identify the appropriate PSM application rate, such that sediment, SB PO_4^{3-} and orthophosphate are continually removed, not just in the first flush phase (Chapters 3 and 5). The flush of fines and nutrients from the FS fill media was experienced from all of the treatments trialled (Chapters 3 – 5). However the treatments which were amended with Fc-O or G-O PSM reduced the impacts of the flush to the receiving waters.

6.2.2 Habitats

Additional savings can be made in relation to the benefit of FS in contributing to cleaner and clearer water for aquatic ecosystems. Currently the Wye catchment is not only failing to meet its WFD water quality targets, but due to orthophosphate levels, is also failing its conservation targets to maintain its SAC status under the Habitats Directive (Environment Agency and Natural England 2014).

The catchment’s designation as a SAC is due to the *Ranunculion fluitantis* and *Callitricho-Batrachion* species found there (Joint Nature Conservation Committee 2018). This provides habitat for the white-clawed crayfish (*Austropotamobius pallipes*), the brook lamprey (*Lampeta planeri*), the river lamprey (*Lampetra fluviatilis*), the thwaite shad (*Alosa fallax*), the Atlantic salmon (*Salmo salar*), the bullhead (*Cottus gobio*) and the otter (*Lutra lutra*).

By exceeding its orthophosphate concentration targets, detrimental changes may occur to these habitats and primary species. These include stress; reduced oxygen availability due to algal blooms associated with the waters' nutrient enrichment; production of toxins; and adverse effects on species growth, development and stoichiometry (Hering et al. 2006, Cai et al. 2016, Glibert 2017). Furthermore salmon and trout juveniles depend on good water quality so that they are able to grow and develop. Specifically, excessive sediment (>0.1 mg l^{-1}) can limit embryo development to the larvae stage as it smothers spawning grounds and can reduce growth in the juvenile stage (Robertson et al. 2006). In addition, excessive sediment loads can produce gill damage by scouring, particularly at the juvenile stage, often causing fatalities (Henley et al. 2000, Robertson et al. 2006). Furthermore suspended sediment reduces the visibility for fish to avoid predators and detect prey, and forage for food (Robertson et al. 2006). Lastly, as these impacts also apply to species of mollusc, zooplankton and insects, excessive sediment can impact the food web whereby even if fish survive, there is little left for them to eat, which then impacts on their breeding potential (Henley et al. 2000).

FS have proven to meet sediment water quality targets (Chapters 3 and 5) in both field and laboratory studies, and therefore can help to provide the cleaner, clearer water that these species require. It is postulated here that the strategic placement of FS will assist the Wye catchment in meeting conservation targets to maintain its SAC status, as well as other SAC catchments across the UK, if applied elsewhere. There are 620 land-based SACs within the UK, totalling 8,777,221 ha (Joint Nature Conservation Committee 2017). Of these, 37 are failing their Habitats Directive conservation targets (Natural England 2017, Natural Resources Wales 2017, Scottish Natural Heritage 2017) due to inputs of sediment and orthophosphate (3 in Wales, 17 in Scotland, 17 in England). If PSM-enhanced FS are strategically placed to protect these SACs, along with other measures, they can help to meet the orthophosphate targets associated with these catchments, thereby helping maintain their SAC status.

6.2.3 Agricultural industry

Based on the current FS application costs (Chapter 6, Section 6.1), it is unlikely they will be widely taken up by the agricultural industry. FS are not currently listed as an approved method for which farmers would receive a BPS payment, and it is unlikely that FS would be applicable under the BPS in the future, thus they are unlikely to be a cost-effective EOPS when compared to measures in which farmers would receive such payments.

FS are more suitable to other farmer support grant systems, such as the Catchment Sensitive Farming (CSF) and Countryside Stewardship grants. These mechanisms provide farmers with capital grants to undertake improvement measures on their farm or farmland, which would have an environmental benefit that goes above and beyond basic good agricultural practice. These grants are only available in high priority areas where water quality and the WFD would benefit the most from farmland improvements. The applicability of FS under these schemes would require further research into their efficacy in different landscapes, soil types and farming systems.

The current costing model also does not account for the likelihood of farmers receiving a penalty from the Environment Agency for unauthorised inputs to water bodies by diffuse pollutants. These penalties can amount to 100% of the payment received for repeat offenders, regardless of whether erosion control measures have been applied. Many of the approved methods, such as BS, are less effective under extreme REs and particularly for concentrated flow paths (Dosskey et al. 2002, Rickson et al. 2010, Newell Price et al. 2011). Consequently, if exposed to these conditions, these measures are more likely to fail, allowing the release of pollutants to waterbodies. FS have been proven in laboratory studies to be as effective in controlling sediment movement at the 5 yr RE as the 126 yr RE (Chapter 5). In theory, if FS were applied to agricultural lands, penalties for unauthorised diffuse pollution inputs are less likely, although this needs confirming through further field research.

England, Wales, Scotland and Northern Ireland are able to decide which measures they recommend to the farming industry as soil erosion control for grants, in order to meet the EU WFD and Habitats Directive. This is funded by the EU CAP and associated agri-environment schemes administered by the Rural Payments Agency (RPA). It is not known how payments to farmers will be funded after the UK has exited the EU and consequently the CAP (House of Lords EU Committee 2017). Realistically in the short term, the impact of Brexit is unlikely to change current policies and practices, as all current EU law should be transposed into UK legislation, especially that associated with agriculture and the environment (House of Lords EU Committee 2017). The UK exiting the EU provides an opportunity to update the legislation to that which is more effective, applicable and/or representative for the diverse farming and environmental systems of the UK. This presents the opportunity for the inclusion of more innovative solutions and stricter environmental rules. However there is a chance that the resultant final legislation may not be as extensive as it currently is, owing to the fact that the UK will no longer be required to meet EU Directives. Brexit may significantly impact the uptake of FS which, for their wide uptake, are largely reliant on their inclusion as an approved measure within the various farmer support mechanisms.

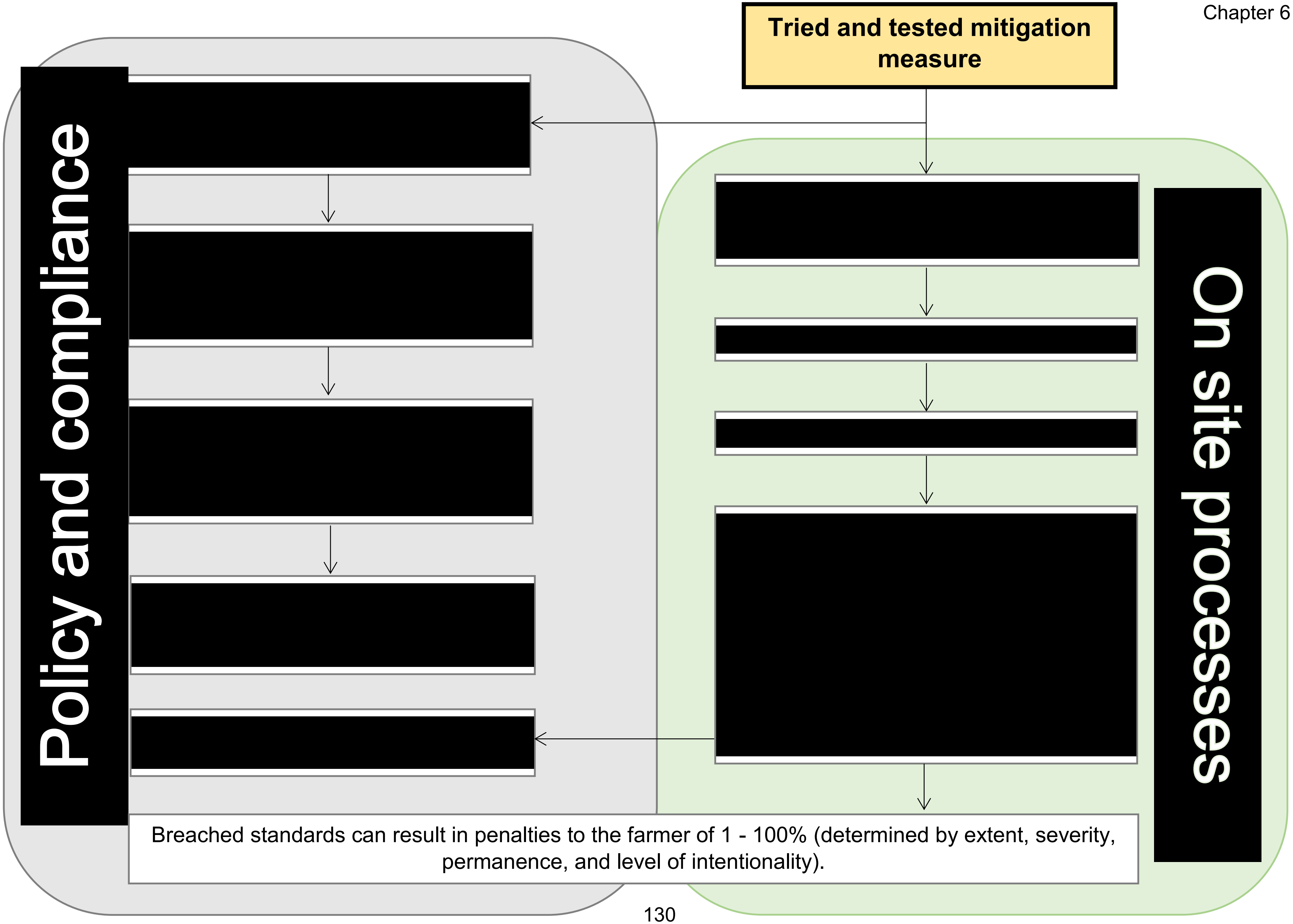
Figure 6.3 details the process by which new measures are integrated into the current compliance and policy system for resource protection. This details the stakeholders that would require involvement, the site implementation and verification, as well as the policy development and compliance monitoring. This shows that the process by which FS could be integrated is very detailed and requires much stakeholder engagement. Consequently it is unlikely to happen in the near future given that we are unsure how Brexit will impact environmental and agricultural policies, especially as there are other widely used mitigation options available (e.g. BS and cover crops). However, Britain exiting the EU, provides the opportunity to integrate more innovative measures providing there is a robust scientific evidence base behind their effectiveness. The current research has attempted to contribute to this.

This opportunity has also been identified within the governments recently published 25 year Environment Plan (DEFRA 2018b). FS, with and without PSM amendments, positively contribute to the goals that the plan outlines. Specifically, FS contribute to achieving '*clean and plentiful water'* for a minimum of 75% of our waterbodies; through the objectives set within the River Basin Management Plans. FS proactively control sediment and PO_4^{3-} inputs to these waterbodies and therefore, positively contribute to achieving the water quality and SAC habitat targets of these waterbodies. The new 'Farming rules for Water' (DEFRA 2017) will also contribute to achieving this goal . These came into force on 2nd April 2018 and have been specifically created to tackle diffuse pollution.

FS specifically contribute to the rule that farmers are to take all reasonable precautions to reduce soil erosion and runoff from their lands, to prevent sediment, nutrient and bacterial inputs to waterbodies. These new rules will be enforced and monitored by the EA.

FS also contribute to the goal '*mitigating and adapting to climate change*' which will in part be achieved through the implementation of a National Adaption Programme (DEFRA 2018b). FS have proven capability up to the 126 year RE RTP in the control of sediment and PO_4^{3-} inputs, and therefore provide a reliable measure which is important for mitigating the impacts of climate change to waterbodies.

This research suggests that FS are applicable to the current and future direction of the UK's environmental strategy surrounding soil erosion and diffuse pollution. However wider uptake will only be possible with further research into their applicability, and the inclusion of more innovate mitigation measures within policy.



Breached standards can result in penalties to the farmer of 1 - 100% (determined by extent, severity, permanence, and level of intentionality).

Figure 6.3. RPA Process by which mitigation measures are decided upon, and implemented.

6.3 Research recommendations

Further field-based research is needed into the longevity and effectiveness of FS when placed in field (different soil types, slopes, crops, farming systems, rainfall). Furthermore, field-based research is required into the strategic placement of FS. Both research strands are essential before FS can be included in any of the various farmer support mechanisms e.g. capital items through CSF.

Also, more performance data on the PSMs themselves is required (both in the laboratory and in the field) if PSM-enhanced FS are to be used for concurrent sediment, SB PO_4^{3-} and orthophosphate control. This research strand should also include field-based research into the different types of PSMs, to identify those which are applicable for different site conditions (e.g. pH of soil and runoff, or concentrated vs sheet runoff).

Of particular importance is establishing the most effective application rates of the PSMs when used to amend FS fill media. Chapters 3, 4 and 5 used PSMs at an application rate of 20 kg m^3, as was standard for the Pp and therefore allowed direct comparisons between treatments. However, the PSE of the ochres tested indicates that similar levels of orthophosphate removal could be achieved by the ochres at a lower application rate. Alternatively, instead of providing a standard application rate for the ochre, it could be tailored to the site conditions based on the required level of orthophosphate removal. A replicated batch experiment would identify the optimum orthophosphate removal across a variety of concentrations and therefore allow tailoring of PSM application rate to the orthophosphate removal required based on site conditions, and water quality targets. Furthermore, as identified in Chapter 2, to accommodate the diverse farming and environmental systems (soils, slopes, rainfall etc) found in the UK, research needs to be undertaken into PSE when different PSMs are mixed together (e.g. ochre with calcite) and used within FS. This would tailor the PSMs to site conditions, in particular accommodating the varying pH of the incoming runoff, owing to different soil types and soil amendments.

In addition to this, the PSM configuration for optimum orthophosphate sorption needs to be established, i.e. powdered or pelletised form. The majority of commonly used PSMs are either in nano or micro form (5nm - 2µm) or pelletised. Apart from the Pp, which was pelletised, this study trialled PSMs which were in powder form. Research needs to be undertaken to establish the configuration for these PSMs for optimum PSE without changing the FS fill media particle size distribution (Alexander Associates 2006) which maximises sediment removal.

It is essential that the PSM supply is secured and price-competitive, such that they can be widely accessed and used by the farming industry. Part of securing the supply involves establishing an approved use which allows the ochre to no longer be classified as a waste, such that it is able to be reused (as a PSM), rather than landfilled, or spread to land under permitting. The process for this involves identifying whether it has or can be transformed into a '*distinct and marketable product'*, where it presents no harm to human or environmental health as per the EU End of Waste Regulations, and the UKs Legal Definition of Waste Guidance (DEFRA 2012b).

Lastly, wider adoption of FS might be possible if research was undertaken into the incorporation of a seed bank within the product. Seeding the socks with an appropriate seed mixture, e.g. one that is beneficial to pollinators, would mineralise some of the orthophosphate that is captured and aid in meeting environmental targets.

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CHAPTER 7: CONCLUSIONS

This research was undertaken to address the paucity of measures available to concurrently remove sediment, SB PO_4^{3-} and orthophosphate from agricultural runoff in order to meet WFD water quality targets. The literature review identified FS as being significantly better at removing sediment from runoff than other more widely used measures. PSMs are commonly used within the wastewater treatment industries to remove excess levels of orthophosphate. The ability to combine PSMs with FS would in theory address diffuse pollution in failing catchments, helping them meet their water quality targets.

The aim of this thesis was therefore to:

Critically evaluate whether FS can be combined with PSMs to facilitate the concurrent removal of sediment, sediment-bound PO_4^{3-} and orthophosphate from runoff.

In order to meet this aim, a number of objectives were set:

- **Objective 1**: Critically evaluate existing sediment control measures regarding their capability to remove sediment from runoff. This was undertaken through an extensive literature review (Chapter 2);

- **Objective 2**: Critically evaluate the effectiveness of FS to remove sediment from runoff. This was undertaken through field trials (Chapter 3) and rainfall simulation experiments (Chapter 5);

- **Objective 3**: Identify PSMs, and critically evaluate their effectiveness in removing soluble orthophosphate from runoff. This was undertaken through an extensive review of existing literature (Chapter 2), laboratory column trials (Chapter 4) and rainfall simulation experiments (Chapter 5);

- **Objective 4**: Critically evaluate the effectiveness of FS amended with PSMs in removing sediment, SB PO_4^{3-} and orthophosphate from runoff. This was undertaken through rainfall simulation trials (Chapter 5) at a range of RE RTPs;

- **Objective 5**: Carry out a cost-benefit analysis (CBA) of FS application for the reduction of sediment, SB PO_4^{3-}, and soluble orthophosphate losses from agricultural land. This involved a suitability assessment of these materials and solutions for the agricultural sector. This was undertaken using the results of the laboratory column trials (Chapter 4) and the rainfall simulation experiments (Chapter 5). Additional discussion is made on this in Chapter 6.

7.1 Research achievements in relation to research objectives

7.1.1 Objective 1

'Identify and critically evaluate existing sediment control measures regarding their capability to remove sediment from runoff'

The literature was critically reviewed to investigate a range of EOPS which are currently used for sediment control (Chapter 2). The key outcomes of this review were as follows:

- Silt fences are the most widely used form of sediment control in an engineering/construction context, however they are not as reliable, cost-effective or environmentally beneficial as other methods. Furthermore, their efficacy has been exaggerated by laboratory results which do not compare to the conditions which are experienced in field scenarios.

- Buffer strips are the most widely used form of sediment control in an agricultural context due to their inclusion in the BPS and cross-compliance (Rural Payments Agency 2017). However, their efficacy is highly dependent on vegetation species and habit, slope gradient, soil type, runoff event, age, and the nature of the pollutants within the runoff. Their long term effectiveness can be limited as they can remobilise both sediment and PO_4^{3-} previously deposited within the strip (Habibiandehkordi et al. 2014, Allaire et al. 2015).

- Filter berms are an effective form of sediment control, however they are not widely used within the UK, especially within the agricultural sector. As they are only effective for minor unconcentrated runoff flows (<15 l min^{-1}), and slopes $<15^o$ (Idaho Department of Environmental Quality 2005; Morgan et al. 2003), they are not suitable for wide application within the agricultural sector.

- Filter socks are generally the most effective form of sediment control, and can be used on a range of slope gradients (up to 45^o), where both minor and major concentrated or unconcentrated runoff flows occur, i.e. up to 38 l min^{-1} per linear foot of FS (Alexander Associates 2006). However, currently they are not widely used in an agricultural context, or within the UK. Furthermore, their compost/woodchip fill media has the potential to release soluble nutrient forms into the runoff (such as orthophosphate). However, prior to the present research, the conditions and processes which influence this were not widely understood.

- Based on this literature, FS were chosen as the optimum sediment control for these experimental trials. They were selected due to their applicability in a wide variety of conditions and landscapes; the lack of experimental work undertaken on their suitability for a UK agricultural context; and the potential for introducing PSMs into their current form.

7.1.2 Objective 2

'Critically evaluate the effectiveness of FS to remove sediment from runoff'

This objective was achieved through a set of replicated field trials (Chapter 3) and simulation experiments (Chapter 5) which demonstrated that FS are effective forms of sediment control. Treatments included traditional C FS, W FS, and C/W FS which were all amended with a commercial Pp used as a PSM. These were compared to the non-FS control, representing the business-as-usual scenario. The following conclusions were drawn in meeting this objective:

- When applied in a series of replicated field trials (Chapter 3), in an erosive environment, FS treatments are able to trap significant amounts of sediment (up to 69% removal) when compared to the non-FS control.

- When applied within an erosive laboratory based simulation experiment (Chapter 5), FS treatments are able to trap significant amounts of sediment (66 - 97%), when compared to the non-FS control.

- Overall, FS provide significant sediment control compared to the non-FS control, in both laboratory and in-field research trials. This is important as it shows that FS have the potential to be used as an effective measure to prevent sediment inputs to waterbodies, and therefore help these waterbodies meet their water quality targets. However, more field-based research is required to understand their efficacy within different field conditions (soils, slopes, crops types etc).

7.1.3 Objective 3

'Identify PSMs and critically evaluate their effectiveness to remove soluble orthophosphate from runoff'

This was undertaken through an extensive review of existing literature (Chapter 2), replicated field trials (Chapter 3), laboratory column trials (Chapter 4) and rainfall simulation experiments (Chapter 5).

The literature was critically reviewed to select PSMs (Chapter 2) that have potential applicability in the context of this research. This identified that:

- PSMs are typically clay sized (<2 μm) and have high specific surface area. PSE is a function of the PSM surface structure, specific surface area and ionic groups. Best performing PSMs also tend to contain a metal oxide (such as Fe, Ca, and Mg). There was some evidence to suggest that performance of the metal oxides for orthophosphate removal (and therefore PSM performance) was influenced by pH, although this was not investigated specifically within this research. For example, Fe-rich PSMs have higher orthophosphate removal efficiency in acidic environments, whereas Ca-rich PSMs have higher efficiency in neutral - alkaline environments.

- Highest PSE has been reported for Fe-oxides such as goethite and ferrihydrite (Torrent et al. 1992, Cornell and Schwertmann 2003). Ferrihydrite typically has higher specific surface areas and therefore there are more reactive surface sites for PO_4^{3-} adsorption. PO_4^{3-} replaces Fe-OH, forming either $Fe\text{-}OPO_3H^-$ or $(Fe\text{-}O)_2PO_2^-$. Ochre is a natural source of ferrihydrite and goethite, and is currently treated as a waste material.

- Using the information presented by this literature review, K, FE, Fc-O and G-O were selected for research into their PSE, and applicability for inclusion within FS. A commercial Pp was also selected in order to compare the efficiency of these materials for orthophosphate removal against a current market leader.

The PSE of the selected PSMs was investigated through a series of field trials (Chapter 3), column trials (Chapter 4), and rainfall simulation laboratory experiments (Chapter 5). The following conclusions were drawn in meeting this objective:

- The widely used commercial Pp, used as a PSM to adsorb orthophosphate, is not effective for use as a PSM within a UK agricultural context. This is due to its varying ability to adsorb orthophosphate from runoff where, on occasions, it acts as an orthophosphate source. In the replicated field trials (Chapter 3) performance varied. Some treatments added up to 67% orthophosphate to the leachate, whilst others removed up to 59% orthophosphate, compared to the non-FS control. This variation results from an initial release of fines and orthophosphate from the FS after their installation, originating from their fill media. This can initially increase levels of orthophosphate from FS treatments in receiving waters, as seen across the sampling events.

- When applied to FS fill media within a column trial (Chapter 4), under a variety of orthophosphate concentrations (0.08 – 1.30 mg P l^{-1}), there were appreciable variations in orthophosphate removal between PSMs. Fc-O and G-O both provided significant amounts of orthophosphate removal. Fc-O was the most effective, removing between 51 - 99% orthophosphate compared to that from the non-PSM control, and was the only PSM to meet the water quality target (0.05 mg P l^{-1}). G-O removed between 32 – 94% compared to the non-PSM control, but this performance did not meet the water quality target. The Pp, FE and K varied between acting as orthophosphate sources (i.e. adding orthophosphate to the runoff), and removing significantly less orthophosphate compared to the other PSMs. For these reasons, K and FE were not used later in the present study, however the Pp was used in the simulator trials (Chapter 5) to compare PSM performance to the current widely used market product.

- When PSMs were used as FS amendments and trialled under the rainfall simulation experiments (Chapter 5), their PSE was significantly less than that measured in the column trials (Chapter 4). Once again, Fc-O was the most effective PSM, removing between 14 – 31% orthophosphate from the runoff compared to the non-FS control. G-O was also effective, removing between 11 – 27% orthophosphate from the runoff compared to the non-FS control. Once again, the Pp varied between acting as an orthophosphate source (adding up to 6% of orthophosphate to the runoff), and removing up to 26% of the orthophosphate from the runoff compared to the non-FS control. In these rainfall simulation experiments, where orthophosphate was removed, no significant differences were observed between PSM treatments. Furthermore, the water quality target (0.05 mg P l^{-1}) was not met by any of the treatments.

7.1.4 Objective 4

'Critically evaluate the effectiveness of PSM-amended FS to simultaneously remove sediment, sediment-bound PO_4^{3-} and orthophosphate from runoff'

This objective was addressed through a series of replicated laboratory trials using a rainfall simulator and erosion/runoff rigs (Chapter 5) under a range of RE RTPs. FS were scaled down and packed with C/W as fill media, amended with Fc-O, G-O or a commercial Pp. Treatments were tested under an 80mm hr^{-1} intensity RE, for five different durations, equating to five RTP storm events; 5 yr, 18 yr, 41 yr, 75 yr and 126 yr. The following conclusions were drawn in meeting this objective:

- PSM and non-PSM amended FS gave 66 - 97% reductions in sediment movement compared to the non-FS control. FS are able to trap significant amounts of clay, silt and sand (up to 89%; 82%; and 75% compared to the non FS control respectively). All of the FS treatments met the sediment water quality target (0.1 mg l^{-1}).

- PO_4^{3-} preferentially adsorbs to fine sediments. FS treatments removed between 59% - 78% of SB PO_4^{3-} compared to the non-FS control.

- PSM-amended FS were able to remove between 11 - 31% of orthophosphate compared to the non-FS control, however the water quality target (0.05 mg P l^{-1}) was never met. Highest removal of orthophosphate was associated with the Fc-O. The Pp was sometimes found to act as a source of orthophosphate (adding up to 6% compared to the non-FS control).

- The efficacy of PSM-amended FS to concurrently remove sediment, SB PO_4^{3-} and orthophosphate is maintained, even with increasing RE severity in laboratory conditions. The addition of PSMs into the FS fill media does not diminish the FS ability to remove sediment.

7.1.5 Objective 5

'Carry out a CBA of the application of PSM-amended FS for the reduction of sediment, SB PO_4^{3-}, and orthophosphate losses from agricultural lands'

This involved a suitability assessment of PSMs, FS, and PSM-amended FS for the agricultural sector. This objective was fulfilled by undertaking a CBA (Chapter 6, using results from Chapters 4 and 5) of the PSM-amended FS evaluated in this study. Costs of FS were also put into the context of the environmental benefits they provide. The following conclusions were drawn in meeting this objective:

- The financial costs associated with construction and installation of the PSM-amended FS are not comparable to more widely used sediment control measures. This is mainly because FS are not currently included within any of the farmer support mechanisms e.g. CSF or Countryside Stewardship, which would provide capital grants to farmers for their installation. Specifically, FS costs equate to £11.80 – £16.80 per linear metre of FS, amended with either Fc-O or G-O PSM.

7.1.6 Other findings

- There is evidence to suggest that FS could be used for in-field soil erosion control, as well as sediment control, through manipulation of slope length. Research is required into their strategic placement within fields (e.g. along the contour, down the slope, within wheelings or along tramlines), and within catchments (e.g. high-risk priority fields). If successful, their strategic placement could help to meet water quality targets, for sediment, SB PO_4^{3-}, and orthophosphate.

- For wide uptake by the agricultural industry, FS need to be included within the approved list of measuresunder the agri-environment schemes. This would allow farmers to obtain capital grants for their installation and maintenance, to make environmental improvements on their farmlands specifically targeting diffuse pollution, which is above and beyond good agricultural practice.

7.2 Contribution to knowledge

A summary of the principal novel aspects of this research are detailed below:

- The detailed literature review collated, for the first time, research demonstrating the efficacy of FS as sediment control measures and iron-oxides, such as ferrihydrite and goethite, for orthophosphate removal in water treatment. This identified the potential for PSM-amended FS to concurrently mitigate sediment, SB PO_4^{3-} and orthophosphate from agricultural runoff.

- The research describes and quantifies performance for the first time application of PSM-amended FS within a UK agricultural context (Chapter 3).

- This research demonstrated the successful application of Fc-O, a PSM that is currently considered a waste material.

This research demonstrated that PSM-amended FS can be used for concurrent sediment, SB PO_4^{3-} and orthophosphate removal in a simulated laboratory environment, with efficacy demonstrated under a range of REs.

7.3 Concluding remarks

The Lugg river catchment, a tributary of the River Wye, is failing its EU WFD water quality targets for sediment and orthophosphate. In turn, this is causing the Wye catchment to fail to qualify as an EU Habitats Directive SAC. Sediment and orthophosphate losses have to be reduced from the catchment's agricultural lands for the sustainable delivery of a range of ecosystem goods and services. As a result, the Lugg catchment was used as a case study site for the application of FS to control delivery of sediment and orthophosphate to its receiving waters.

This research has investigated sediment control and orthophosphate mitigation measures (Chapter 2) and how they can be combined to effectively reduce diffuse pollution arising from agricultural lands (Chapters 3 and 4). Part of this research looked into FS applicability under extreme REs likely to arise from climate change (Chapter 5). Chapter 6 assessed the costs, implementation and benefits associated with the wider uptake of FS (with and without PSMs) within the agricultural and water industries.

Analysis suggests that FS are effective in controlling sediment, with sediment trapping efficiencies of up to 97% (Chapters 3 and 5). However, as the highest efficiencies were seen within a simulated laboratory environment (Chapter 5), more research is required into their applicability in-field. Their trapping of up to 88% of clay and 82% of silt particles (Chapter 5) has a profound influence on the resultant removal of SB PO_4^{3-}. This is important as SB PO_4^{3-} can remobilise and become soluble in the water environment. This analysis needs to be undertaken on a field-based trial to ensure that the trapping efficiencies of clay and silt are not only seen within a laboratory environment

FS efficiency can be increased by the addition of PSMs (e.g. Fc-O, G-O) which specifically remove orthophosphate from the runoff (Chapters 3, 4 and 5). The efficacy of FS, with and without PSMs, has been proven under current and extremeREs (Chapters 3 and 5), including the 126 year RTP storm for the Lugg catchment. This is important as it ensures they will remain viable mitigation options in the future as extreme REs become more prevalent.

The research has generated empirical evidence that FS, with and without PSMs, are important measures that, could help water bodies meet their water quality and conservation targets, especially if used in conjunction with other measures.

Future research should initially focus on further in-field testing of FS efficacy in relation to their costings. In-field testing also needs to be undertaken into types of PSMs used, and their optimisation to maximise orthophosphate removal from runoff, without diminishing the performance in controlling sediment and SB PO_4^{3-}. This includes optimising application rates, as well as the configuration of the materials, e.g. powder or pelletised. Following this, security of PSM supply should be a priority.

Research should also focus on the seeding of the FS (both with and without PSMs) with an appropriate seed bank mixture e.g. that which is beneficial to pollinators. Nutrient cycling and uptake by the plants would mineralise the absorbed orthophosphate and give the FS an additional ecological benefit.

It is essential that the next stages establish the efficacy of FS in-field in a variety of environmental and agricultural conditions. This should include the cost, installation and maintenance measures farmers would need to undertake to ensure their applicability for the agricultural sector – the key target market.

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APPENDIX 1: Chapter 3 as conference proceedings of the World Conference on Soil and Water Conservation (CONSOWA) in Lleida, Spain, June 2017

FILTER SOCKS TO MITIGATE RUNOFF, SOIL AND PHOSPHATE LOSSES FROM ARABLE LANDS UNDER CURRENT AND EXTREME RAINFALL EVENTS

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Introduction

Filter socks (FS) are widely used in the USA as a best management practice (BMP) to control sediment on construction sites. They are little known within the UK, but with water quality widely declining due to diffuse pollution from arable lands, FS may be one solution to help to control sediment and phosphate (PO_4^{3-}) inputs to vulnerable watercourses. Controlling these inputs will satisfy water quality targets (prescribed by the EU Water Framework Directive; WFD), decrease sedimentation and mitigate flooding and eutrophication processes. As a result, aquatic ecosystems will be better protected. The main focus of this research was to trial filter socks within an agricultural setting, and to enhance the efficacy of FS in the control of sediment and PO_4^{3-} using a range of fill media and phosphorus sorbing materials (PSMs).

PSMs are used within the wastewater industry for P adsorption from sewage sludge. They usually consist of P-sorbing resins or membranes, which are rarely used by the agricultural industry due to cost and upscaling constraints. Consequently, there is a need for alternative PSMs that can be used in agricultural settings. Appropriate field placement of FS will allow sediment capture as well as PO_4^{3-} adsorption from the runoff before it enters the drainage network. The PSM initially trialled in this study was chosen from a literature review and project based assessment criteria (ability to reduce PO_4^{3-} to meet the WFD water quality target; 0.05 mg P l^{-1}).

Climate change is projected to increase the number of extreme weather events, including higher rainfall intensities, which will ultimately increase the frequency and magnitude of runoff and soil erosion (IPCC 2014). For the UK, it is predicted that only a 10% increase in winter rainfall could result in a 150% increase in arable soil erosion (Favis-Mortlock & Boardman 1995), with associated delivery of sediment and PO_4^{3-} load to watercourses. Therefore, it is essential that PSMs and FS fill media are effective in mitigating the effects under current and extreme rainfall events (RE's).

Methods

The experiment consisted of monitoring soil erosion and runoff in a fully replicated field trial which ran for 36 weeks from July 2015 – March 2016. The field site was located at 52.095354, -2.7217984 (Lat/Long) near Hereford, UK. It was chosen for its high erosion risk, fine silty soils (Cranfield University 2016); commonly steep slope gradients (11-17°); susceptibility to soil compaction and surface capping; relatively high annual rainfall (665 mm yr^{-1}) and increasingly extreme storm events; and erosive land use (maize with rows running up/down slope, perpendicular to the contour). These conditions meant the tenant farmer had regularly experienced soil erosion issues.

Table 1. Sampling occasions	
Sample period	**Date**
1	09/07/15 – 14/10/15
2	15/10/15 – 14/01/16
3	15/01/16 – 17/02/16
4	18/02/16 – 09/03/16

Twenty hydrologically isolated erosion plots (1.5 m wide x 15 m long) were set-up, oriented downslope; parallel to the maize rows. The plots allowed the collection and monitoring of runoff and eroded sediment in plastic tanks (capacity 227 litres each), using pre-calibrated Liquid Vertical Continuous Series (LVCS) sensors located in each of the runoff collection tanks. Each sensor was connected to a data logger (Delta-T DT80/2), and together they monitored the levels of runoff in the tanks, as well as site precipitation, temperature and humidity as recorded by a linked on-site weather station. The data logger began logging immediately after the onset of 0.2 mm of rainfall and continued for 1 hr post-rainfall cessation. Baseline soil sampling was undertaken on each erosion plot, and sampling of the runoff in the tanks took place on 4 occasions (Table 1).

Table 2. Treatment codes	
Treatment	**Code**
Control (no FS)	Control
Compost FS	C FS
Woodchip FS	W FS
Compost + proprietary product FS	CPp FS
Woodchip + proprietary product FS	WPp FS

The field trial investigated 5 treatments (Table 2), each with 4 replicates, which were randomly distributed across the erosion plots. As the Control did not have a FS treatment it represented 'business-as-usual'. The trials used 8-inch diameter FS with PAS100 compost or fine woodchip used as fill media. This met the FS fill media specifications (Alexander Associates, 2006). A branded proprietary product (Pp) was used as the PSM, applied at the required application rate of 20 kg m^3 within the CPp FS and WPp FS treatments, providing an industry 'standard' with which to compare alternate PSM treatments.

Treatment performance criteria included total runoff volume (l $plot^{-1}$), runoff sediment concentration (g l^{-1}), sediment load (g $plot^{-1}$), and runoff PO_4^{3-} concentration (mg P l^{-1}) which were sampled for in four sampling occasions throughout the experiment.

Results and discussion

Baseline sampling showed plot soil properties (texture, pH, organic matter, Total P) were not significantly different, confirming the trials were a fair test. Weather data indicated 214.8 mm of rain fell during the trial, with a maximum RE intensity of 228 mm^{-1} hr^{-1} over a 7 minute duration (22/08/15), and maximum RE duration of 41 minutes (12 mm^{-1} hr^{-1} intensity, 21/09/15). The majority of REs were 1 in 1 year storms; however a 1 in 30-year and 1 in 400-year RE were also recorded.

The results show an initial release of sediment and nutrients from the FS, and high runoff volume in the early stages (July-October 2015) of FS application. This is consistent with results of other FS and compost studies (Al-Bataina et al. 2016; Glanville et al. 2003; Nguyen & Marschner 2013; Waters 2010). This first 'flush' of runoff is shown in Table 3, where no statistical differences were observed between the FS treatments and the Control. After this initial period, the C FS and W FS FS produced statistically less runoff than the Control plots. By the end of the trial (Sampling Period 4), the majority of the FS treatments were associated with a consistent reduction in runoff volume, compared to the Control.

Regarding sediment concentrations, initially, the FS treatments gave statistically higher values than the Control (Table 3). However a robust trend of lower sediment concentrations was identified by Sampling Periods 3 and 4 (not significant) suggesting that FS efficiency increases over time. By sampling period 4, the W FS was meeting the water quality target for sediment (0.1 mg l^{-1}). The WPp FS treatment did not perform as efficiently, with runoff and sediment concentrations being no different or even higher than the Control (not significantly) (Table 3). This is due to plot spatial variability (e.g. microtopography, soil compaction levels), and noise in the data. This could have been

Table 3. Mean runoff volume (l plot^{-1}) compared to the control (%), and sediment concentration (g l^{-1}) for each treatment and sample period.

Treatment	Runoff Volume (l plot^{-1}) and change from the control (%)					Sediment concentration (g l^{-1})			
	Sample period	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Control	Mean ±S.E	23.6^{a} ±0.0	59.1^{a} ±6.4	19.9^{a,b} ±4.7	12.6^{b} ±2.2	0.6^{a}	0.2^{a,b}	0.6^{a}	0.3^{a}
	Change (%)	-	-	-	-				
C FS	Mean ±S.E	14.8^{a} ±3.8	31.8^{b} ±3.7	11.8^{a} ±1.7	5.9^{a} ±1.2	0.7^{a,b}	0.2^{a}	0.4^{a}	0.2^{a}
	Change (%)	-37.5	-46.3	-40.7	-52.9				
W FS	Mean ±S.E	17.0^{a} ±4.1	32.5^{b} ±3.0	17.0^{a,b} ±3.9	5.2^{a} ±0.7	1.2^{a,b}	0.2^{a}	0.2^{a}	0.1^{a}
	Change (%)	-28.1	-45.0	-14.8	-58.8				
CPp FS	Mean ±S.E	16.2^{a} ±1.5	34.7^{a,b} ±12.4	27.2^{b} ±5.2	7.9^{a,b} ±2.6	2.3^{b}	0.3^{a,b}	0.3^{a}	0.2^{a}
	Change (%)	-31.3	-41.3	+36.3	-37.3				
WPp FS	Mean ±S.E	20.7^{a} ±3.8	56.1^{a,b} ±7.8	24.8^{a,b} ±4.9	13.8^{b} ±2.0	1.2^{a,b}	0.3^{b}	0.3^{a}	0.2^{a}
	Change (%)	-12.5	-5.0	+24.4	+9.8				

Sample period 3; plot 14 not included in analysis
Sample period 4 ; plots 1 and 14 not included in analysis
N.B. Within each sample period, values for litres plot^{-1}, followed by the same letter are not statistically different ($p \leq 0.05$) following one-way ANOVA and post-hoc Fisher LSD.

due to a lack of replicates in Sample Periods 3 and 4, where movement of the plot boundaries only allowed 3 replicates for WPp FS and CPp FS treatments.

Regarding sediment loads (Figure 1), there was a distinct first flush in Sample Period 1 whereby the majority of FS treatments displayed higher sediment loads than the Control, however by Sample Periods 2-4 the FS treatments had consistently lower sediment loads than the Control, although these were not always statistically significant.

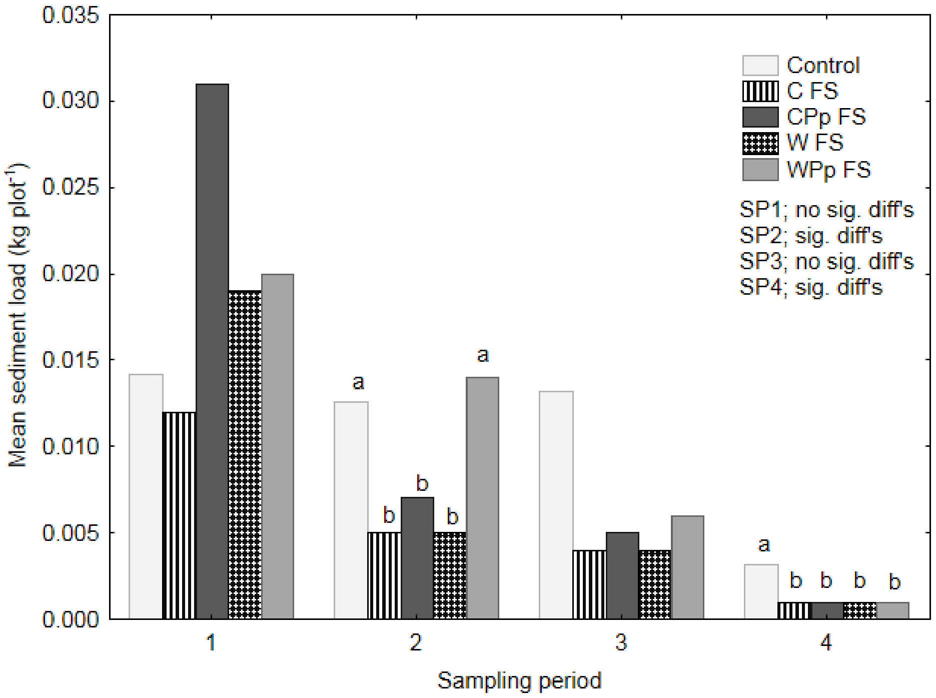

Figure 1. Mean sediment load (kg plot^{-1}) between treatments and sampling periods. Significant results between treatments indicated by different lettering.

PO_4^{3-} concentrations in the runoff varied significantly between treatments (Figure 2). Runoff from the Control plots had statistically lower PO_4^{3-} concentrations than the FS plots in Sampling Period 1. In Sampling Periods 2 and 3, there were no statistical differences between treatments. A similar result was observed for Sampling Period 4 with the exception of the C FS and WPp FS treatments, which were associated with statistically higher PO_4^{3-}concentrations in the runoff.

It is suggested that the weather conditions impacted on the variability and lack of results between Sample Periods, especially when comparing Sample Period 1 to Sample Periods 2-4. Rainfall intensity during sampling period 1 may have increased the first flush phenomenon. A longer monitoring period might have captured more statistically robust differences between the FS treatments and the Control, as the current results suggest a prolonged first 'flush' period, which has masked treatment efficiency. Variability between same treatment replicates, both within and between sampling periods, highlights the challenges associated with fieldwork.

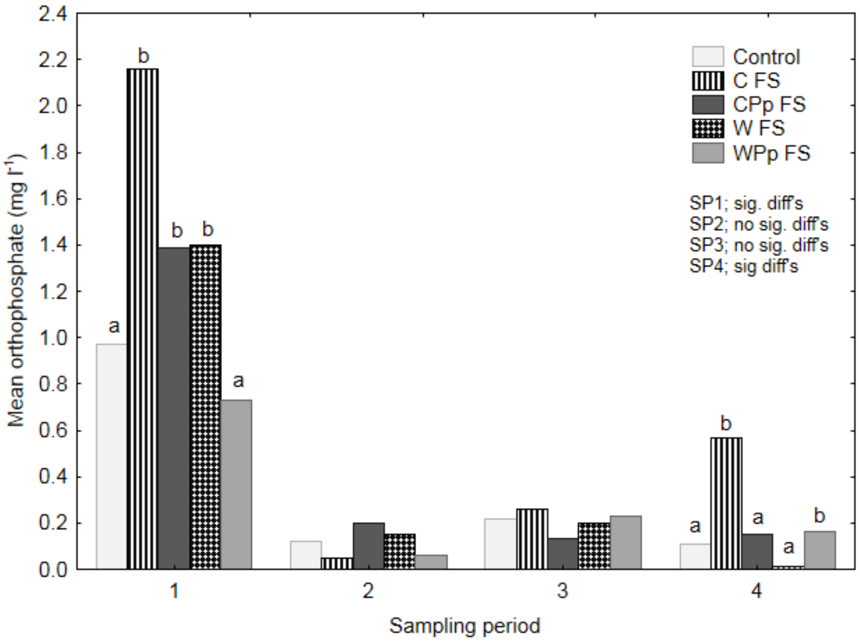

Figure 2. Mean orthophosphate (mg l^{-1}) between treatments and sampling periods. Significant results between treatments indicated by different lettering.

Conclusions

Initial results show that FS could be an effective end-of-pipe solution for the control of soil erosion and runoff, however more research is required into the phenomenon of the 'first flush' of runoff, sediment and P. Furthermore more research is required into the efficiency of various PSMs for agricultural settings.

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