Optimisation of Phosphorus Removal in Stormwater Biofiltration Systems

Bonnie J. Glaister

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Abstract

Biofiltration systems utilise natural attenuation and bioremediation processes intrinsic to plants, filter media and microbial communities to remove pollutants from urban stormwater. Previous research has demonstrated that stormwater biofilters can achieve pollutant reduction and flow regime objectives across a range of scales, yet outflow concentrations of many pollutants are still in excess of water quality targets for ecosystem protection. Phosphorus (P) is a critical pollutant in this regard given that many urban waterways are sensitive to excess concentrations of production-limiting nutrients. Poor removal of P, particularly phosphate, has been associated with the use of filter media with a high P content, addition of organic matter to the filter media, or use of media with a low affinity for P sorption. These issues reflect a limited understanding of P processing in biofilters which is partly due to the research approach applied to date being largely "black-box". P removal in biofilters is influenced by various competing biogeochemical processes including adsorption-desorption, precipitation-dissolution, ion exchange, complexation-dissociation, and redox reactions. These processes dictate the physicochemical speciation of P, which controls its bioavailability and capacity for retention within the system. Although these interactions have been studied extensively in natural and engineered soil-plant systems, the transferability of this knowledge to stormwater biofiltration systems is limited because of their unique design and the highly ephemeral conditions under which they operate.

To better understand P removal in biofilters, in particular the role of filter media, and investigate means to optimise biofilter design for P removal, this research was conducted in three experimental stages. The first stage investigated P-sorption properties of filter media with different physical and chemical properties, including natural iron-rich sand (known as "Skye sand"), using batch and through-flow column sorption tests. Sorption isotherms estimated the affinity and capacity for P removal of each filter media type and were used to predict the P-sorption capacity of the media in field scale applications. These experiments demonstrated that augmenting the standard loamy sand filter media with Skye sand could significantly enhance the P removal capacity of biofilters.

Further testing of Skye sand was undertaken in the second stage of research, which used 20 laboratory-scale study biofilter columns to study the influence of design characteristics (presence of vegetation, filter media type and inclusion of a saturated zone) on nutrient removal under

variable hydrologic conditions. The aim of this study was to design a biofilter which could co-optimise P and N removal, which has been shown to be highly variable and often where high rates are achieved it is to the detriment of P removal. Over twelve months of stormwater dosing, the nutrient removal performance of the biofilters was periodically monitored. Inflow dynamics and the presence of a saturated zone were found to significantly influence nutrient removal performance, although filter media type was not. Nevertheless, filter media is expected to play a greater role over time, particularly as plants reach maturity and their P uptake capacity is at least partially countered by senescence. Only the Skye sand biofilters that also contained a saturated zone maintained effluent at or below the target concentrations during the campaign. To investigate intra-event fluctuations in nutrient removal, and the influence of biofilter design on these, a high-volume sequential effluent sampling event was conducted using a sub-set of the biofilter columns. The ‘pollutograph’ revealed that vegetation and a saturated zone were critical to reducing fluctuations in N concentrations during an event. The saturated zone also played an important role in buffering against P-bound particle migration from the columns.

At the completion of the dosing period, the plants (*Carex appressa*) were harvested from each of the biofilter columns and analysed to investigate the influence of Skye sand and a saturated zone on plant growth and morphology. Growth of plants in Skye sand was comparable to loamy sand. However, root length, root surface area and root volume were significantly higher in the Skye sand columns, suggesting that their root architecture had adapted to maintain nutrient uptake in a filter media with a strong capacity to immobilise P. Inclusion of a saturated zone significantly increased plant biomass, but did not significantly affect root architecture. Plant biomass and root traits were negatively correlated with nutrient concentrations in biofilter effluent, suggesting that Skye sand biofilters can achieve greater nutrient removal than loamy sand when vegetated with *C. appressa*. Nutrient removal would be further enhanced through inclusion of a saturated zone.

The third stage of research analysed the form and distribution of P retained in filter media using filter media samples from the biofilter columns as well as existing field-scale systems. The P-sequential extraction analysis identified that P concentrations vary spatially (areally and with depth) in biofilters and that distribution between P-phases changes down the filter media profile. In the upper filter media layers P is mostly associated with organic and mineral phases, while at lower depths the percentage of adsorbed-P increases. These results provide insight into P removal processing and retention in biofilters and emphasises the importance of selecting filter media with a strong affinity for P sorption. The results also highlight the sensitivity of retention P to changes in physicochemical conditions.

This research provides comprehensive insights into the P removal processes that occur in biofilters and new evidence to support the effectiveness of biofilters to remove P from stormwater. Foremost, that incorporating Skye sand into filter media can ameliorate the P-sorption capacity of biofilters and, in conjunction with a saturated zone, enable biofilters to co-optimise N and P removal and satisfy water quality objectives for ecosystem protection.

Declaration

This statement is to certify that to the best of my knowledge and belief, this thesis contains no material which has been previously been submitted for the award of any other degree or diploma in any university or other institution and contains no material previously published or written by another person except where due reference is made in the thesis itself. The length of this thesis is less than 100,000 words, exclusive of figures, tables and references.

Bonnie J. Glaister

Department of Civil Engineering

Monash University

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I dedicate this thesis to the memory of Roger Pringle who always made me feel like I was destined for great things.

List of Publications

The following publications have resulted from the studies undertaken for this degree:

Journal Papers

GLAISTER B., FLETCHER T.D., COOK P.L.M., HATT B.E. 2017. Interactions between design, plant growth and the treatment performance of stormwater biofilters. *Ecological Engineering*. 105: 21-31.

GLAISTER B., FLETCHER T.D., COOK P.L.M., HATT B.E. 2014. Co-optimisation of Phosphorus and Nitrogen Removal in Stormwater Biofilters: the Role of Filter Media, Vegetation and Saturated Zone. *Water Science & Technology*. 69 (9): 1961-1969.

Conference Papers

GLAISTER B., FLETCHER T.D., COOK P.L.M., HATT B.E. 2016. Intra-event nutrient removal dynamics in stormwater biofilters: the influence of system design. *9th International Conference Novatech*, Lyon, France, June 28 – July 1.

GLAISTER B., FLETCHER T.D., COOK P.L.M., HATT B.E. 2013. Long-Term Phosphorus Accumulation in Stormwater Biofiltration Systems at the Field Scale. *8th International Conference Water Sensitive Urban Design*, Gold Coast, Australia, November 25-29, p1-10. *(Peer Reviewed)*

GLAISTER B., FLETCHER T.D., COOK P.L.M., HATT B.E. 2013. Co-optimisation of Phosphorus and Nitrogen Removal in Stormwater Biofilters: the Role of Filter Media, Vegetation and Saturated Zone. *8th International Conference Novatech*, Lyon, France, June 23-27. *(Peer Reviewed)*

GLAISTER B., FLETCHER T.D., COOK P.L.M., HATT B.E. 2012. Advancing Biofilter Design for Co-optimised Nitrogen and Phosphorus Removal. *7th International Conference Water Sensitive Urban Design*, Melbourne, Australia, February 21-23, p1-7. *(Peer Reviewed)*

GLAISTER B., FLETCHER T.D., COOK P.L.M., HATT B.E. 2011. Can Stormwater Biofilters Meet Receiving Water Phosphorus Targets? A Pilot Study Investigating Iron-rich Filter Media. *15th International Conference of the IWA Diffuse Pollution Specialist Group on: Diffuse Pollution and Eutrophication*, Rotorua, New Zealand, September 19-23, p1-9.

Declaration of Publications and Authorship

Thesis including published works declaration

This thesis includes 2 original papers published in peer reviewed journals. The core theme of the thesis is phospohrus removal from urban stormwater runoff using biofiltration. The ideas, development and writing of the papers in the thesis were the principal responsibility of myself, the student, working within the Department of Civil Engineering under the supervision of Dr Belinda Hatt, Prof Tim Fletcher and Assoc Prof Perran Cook.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research. In the case of published journal papers that have contributed to the thesis my contribution to the work involved the following:

Thesis Chapter	**Publication Title**	**Status** *(published, in press, accepted or returned for revision, submitted)*	**Nature and % of student contribution**	**Co-author name(s) Nature and % of Co-author's contribution***	**Co-author(s), Monash student Y/N***
4	Co-optimisation of Phosphorus and Nitrogen Removal in Stormwater Biofilters: the Role of Filter Media, Vegetation and Saturated Zone	Journal paper – published (based upon published peer-reviewed conference paper.)	75%: Experimental design and works, data collection, analysis and interpretation, write-up.	1) *Tim Fletcher: Ideas, data interpretation, manuscript revision and comments (10%)* 2) *Belinda Hatt: Experiment initiation, ideas, data interpretation, manuscript revision and comments (10%)* 3) *Perran Cook: Data interpretation, manuscript revision and comments (5%)*	No No No
5	Interactions between design, plant growth and the treatment performance of stormwater biofilters	Journal paper – published.	85%: Initiation, ideas, experimental design and works, data collection, analysis and interpretation, write-up.	1) *Tim Fletcher: Data interpretation, manuscript revision and comments (5%)* 2) *Belinda Hatt: Data interpretation, manuscript revision and comments (5%)* 3) *Perran Cook: Data interpretation, manuscript revision and comments (5%)*	No No No

**If no co-authors, leave fields blank*

I have renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

Student signature: **Date: 26/07/2018**

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author I have consulted with the responsible author to agree on the respective contributions of the authors.

Main Supervisor signature: **Date: 26/07/2018**

List of Abbreviations

ADWP	Antecedent Dry Weather Period
Al	Aluminium
ANZECC	Australian and New Zealand Environment and Conservation Council
Ca	Calcium
DO	Dissolved Oxygen
EDAX	Energy Dispersive X-ray Analysis
EMC	Event Mean Concentration
Fe	Iron
FIA	Flow injection analysis
FRP	Filterable Reactive Phosphorus
IOCS	Iron Oxide Coated Sand
LID	Low-Impact Development
LS-V-S	Loamy Sand/Vegetated/Saturated Zone
Mn	Manganese
NH_3	Ammonia
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_x	Oxidized nitrogen (NO_2^-/NO_3^-)
NOM	Natural Organic Matter
O_2	Oxygen
PO_4^{3-}	Phosphate
P_i	Bioavailable Inorganic phosphate
PON	Particulate organic nitrogen
SEM	Scanning Electron Microscope
SS-NV-S	Skye Sand/Non-Vegetated/Saturated Zone
SS-V-NS	Skye Sand/Vegetated/Non-Saturated
SS-V-S	Skye Sand/Vegetated/Saturated Zone
SUDS	Sustainable Urban Drainage Systems
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TSS	Total Suspended Solids
WSUD	Water Sensitive Urban Design
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Chapter 1: Introduction

1.1 Purpose

This thesis provides comprehensive insights into the phosphorus (P) removal processes that occur in stormwater biofilters and identifies ways to enhance the P removal performance of biofilters. By combining these outcomes with what is already understood about achieving high quality nitrogen (N) treatment, this research will investigate whether biofilters can co-optimise N and P removal and achieve all nutrient water quality targets for ecosystem protection. This research utilises a combination of laboratory- and field-scale studies to investigate P removal and retention processes in biofilters, and the influence of design characteristics on these (i.e. filter media type, vegetation, saturated zone and carbon source). The results of these studies are synthesised to make recommendations for improving the P removal capacity of biofilters, maintaining long-term P retention efficacy and achieving water quality objectives for protection of urban waterways and aquatic ecosystems.

1.2 Background

Anthropogenic distortion of catchment hydrology and nutrient cycling has significantly increased the concentration of nutrients (among a wide range of pollutants) present in urban stormwater (Hatt et al. 2004; Paul et al. 2001; Smith et al. 1999; Walsh 2000). Discharge of nutrient-rich stormwater into receiving waterways has been linked with excessive macrophyte growth, algal blooms, dissolved oxygen depletion, fish die-off, biodiversity loss and eutrophication (Paul et al. 2001; Sonneman et al. 2001; Taylor et al. 2004; Walsh et al. 2001). Recognition of the impacts associated with urban stormwater led to the emergence of concepts such as Water Sensitive Urban Design (WSUD) which aim to create synergies within and between urban landscapes and the water cycle at all stages and scales of planning (Mouritz et al. 2006; Wong 2001; 2006a).

Biofilters (also known as 'biofiltration systems', 'bioretention systems' and 'raingardens') use the natural attenuation and bioremediation processes intrinsic to plants, filter media and microbial communities to intercept and remove pollutants from stormwater and protect receiving waters against degradation (Davis et al. 2010; Fletcher et al. 2006). Biofilters provide additional benefits including wildlife habitat and improved landscape amenity (Victorian Stormwater Committee 1999; Wong et al. 2012). Over the past decade widespread implementation of stormwater biofilters has occurred internationally, and is expected to continue into the future as urban growth expands and WSUD becomes an increasingly critical sustainability objective (Wong 2006a; b).

Whilst previous research has demonstrated that biofilters are an effective technology for the removal of phosphorus (P) from stormwater (Bratieres et al. 2008; Davis et al. 2001; 2006; Henderson et al. 2007), knowledge gaps remain surrounding the role of filter media, in particular how physical and chemical properties of filter media influence P removal. Further, given that biofiltration is a relatively new technology, and most field-scale systems are still fairly young, understanding of P retention in biofilters is limited, thus little is understood about where and in what form P is retained in the filter media, and the effects this may have on the ability of biofilters to act as a long-term sink for P. A better understanding of the role of filter media in P removal may present opportunities to ameliorate the P removal performance of biofilters, improve estimates of long-term P retention capacity and design management strategies to maintain optimal performance.

Knowledge gaps also exist surrounding co-optimisation of N and P removal in biofilters. Whilst water quality results from laboratory studies and monitoring of existing systems indicate that biofilters are generally capable of achieving nutrient load reduction targets (e.g. 45% load reductions of TP and TN in Victoria), effluent concentrations of TP and TN are still in excess of typical Australian water quality guidelines (e.g. ANZECC/ARMCANZ 2000). This matter is further complicated by the variability of N removal (Bratieres et al. 2008) and the fact that often where high rates of N removal are achieved it is to the detriment of P removal (Zinger et al. 2013). This is a critical issue given that ecosystems vary in terms of which nutrient limits their primary productivity. Further research is needed to ensure biofilters are co-optimised for N and P removal.

The existence of these knowledge gaps is due in part to the typical approach to biofilter assessment being largely “black-box” (Payne et al. 2014a). While this method of analysis is good for quantifying overall performance and optimising design in a relatively simple and efficient manner, it provides limited insight into the processes which facilitate P removal and how biofilter design affects these processes.

As biofiltration research advances from ‘proof of concept’ studies to design optimisation it is essential that these remaining knowledge gaps be addressed. While established soil-plant system science can provide valuable insight into understanding many of the processes that control P removal in biofilters, its applicability is often limited because of the unique hydrological conditions under which biofilters operate. Through a three-stage experimental research program the present research aims to open the “black box” and provide insights into the P removal processes and the fate of P in biofilters and identify ways to improve their P removal capacity.

1.3 Research objectives

Unlike N, which can theoretically undergo complete removal in biofilters through release of N_2 to the atmosphere via denitrification (Payne et al. 2014b), P removal relies on a biofilter's ability to retain P in the filter media or to transform P into a bioavailable form for plant acquisition, which can then be permanently removed via harvesting. As implementation of biofilters continues the need for empirical data to inform design optimisation and life-span models will become more critical. This thesis intends to offer data to assist with these pursuits whist providing new insights into enhancing the P removal capacity and retention longevity of biofilters.

The objectives of the present thesis are therefore to:

- review previous biofilter research and literature relevant to P retention in natural and engineered soil-plant systems to identify research limitations and knowledge gaps
- understand the role of filter media in facilitating P removal in biofilters, in particular the importance of Fe-P interactions, and investigate means of ameliorating the P removal capacity of filter media
- study the influence of biofilter design (i.e. filter media type, vegetation, inclusion of a saturated zone and carbon source) and variable hydrologic conditions on: inter- and intra-event P and N removal performance, plant growth characteristics and nutrient uptake capacity, and short-term P-partitioning in filter media
- investigate where and in what form P is retained in biofilter media and the implications this may have for long-term P retention in biofilters

1.4 Thesis structure

The structure of the thesis is illustrated in Figure 1.1. The introduction chapter describes the context of the research and the key research objectives. The literature review presented in **Chapter 2** provides background to the problem and outlines the current state of knowledge regarding P removal performance of biofilters and understanding of P removal processes; which form the key research areas of the thesis.

The results of experimental research are disseminated through chapters 3-6. **Chapter 3** presents the results of experiments investigating relationships between filter media properties and P-sorption; with a strong emphasis on how Fe and P interactions enhance P-sorption. **Chapter 4** presents the results of a biofilter column study which investigates the influence of design modifications (i.e. use of iron-rich filter media, vegetation, saturated zone and carbon source) and hydrologic variability on N and P removal performance, to determine which biofilter configuration best co-optimises N and P removal. Chapter 4 also describes the results of an intra-event study which sequentially monitored N and P concentrations in the column effluent to assess the influence of biofilter design on internal N and P processes and treatment fluctuations. **Chapter 5** analyses characteristics of plants established in the vegetated biofilter columns to quantify the influence of iron-rich filter media and inclusion of a saturated zone on plant growth and morphology. Relationships between plant characteristics and nutrient removal performance are also assessed and discussed with regard to plant-nutrient acquisition processes. **Chapter 6** presents the results of a P-sequential extraction analysis designed to elucidate where and in what form P is retained in biofilter media. Filter media samples from laboratory biofilter columns and existing field systems were analysed to compare P distribution and partitioning between biofilters of different design, size, age and catchment characteristics. The implications of the results in terms of long-term P-retention in biofilter media are discussed.

Chapter 7 synthesises the results from chapters 3-6 to draw out the key research findings and implications for practice. Strategies for enhancing P removal in biofilters, co-optimising N and P treatment, and maintaining long-term removal efficiency are outlined. Recommendations for further work are also discussed and final conclusions of the research.

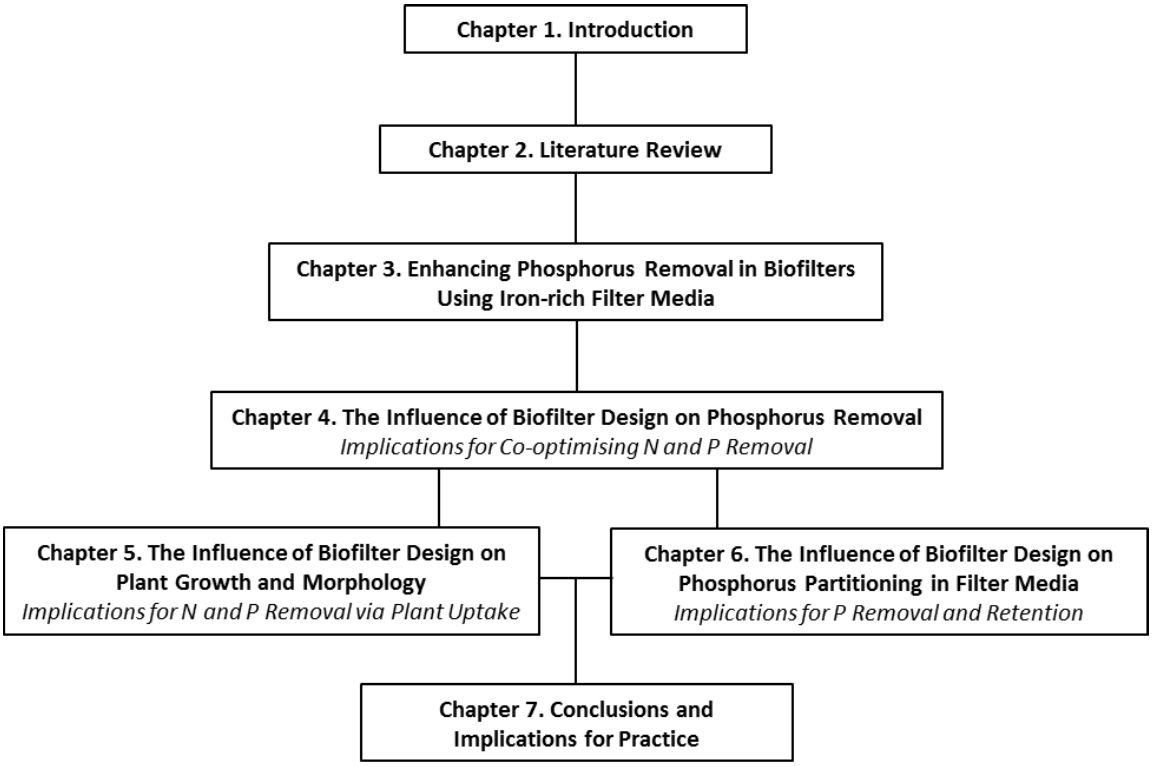

Figure 1.1 Flow chart depicting the thesis chapter structure

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Chapter 2: Literature Review

Foreword

The purpose of this literature review is to identify knowledge gaps surrounding phosphorus removal processes and performance in stormwater biofilters. To establish the research context the literature review first presents the background to the problem of urban stormwater pollution in surface waters and the need for treatment measures to mitigate this (Sections 2.2 and 2.3). Section 2.4 discusses the principles of stormwater treatment through biofiltration and processes driving P removal. Current knowledge pertaining to the P removal performance of biofilters is disseminated in section 2.5. In particular, this section discusses the limitations of previous research and identifies elements of biofilter design which are of concern to phosphorus removal. This section also includes a review of studies from a range of disciplines which investigate the use of novel materials to ameliorate phosphorus removal in plant-soil wastewater treatment systems. The final section of the literature review draws links between phosphorus removal processes and drivers, biofilter design characteristics and reported phosphorus removal performance to develop research hypotheses. The chapter concludes with a summary of the key knowledge gaps.

2.1 Phosphorus and urban stormwater

Conveyance of stormwater through conventional drainage systems has been recognised as a major cause of urban waterway pollution and degradation (Hatt et al. 2004; Paul et al. 2001; Walsh 2000). Phosphorus is a critical pollutant in stormwater runoff which, when present in excess concentrations, may contribute to eutrophication of receiving waters (Smith et al. 1999). Recognition of these impacts has led to increasing uptake of source-control technologies such as biofilters (also known as bioinfiltration systems, bioretention systems or rain gardens) to improve stormwater quality and hydrology and to protect aquatic ecosystems (Davis 2005; Wong 2006).

2.2 Biofilter design, operation and performance

2.2.1 Biofilter design and operation

Biofiltration systems are designed to improve the hydrology and water quality of urban stormwater. A typical biofilter generally incorporates a shallow excavated trench or basin filled with a porous filter medium and planted with vegetation (Hatt et al. 2007b; Henderson et al. 2007a). Stormwater flows over the vegetated surface and may be subject to temporary ponding, allowing suspended particles to settle. Stormwater then percolates through the media where pollutants are removed through physical, chemical and biological processes such as sedimentation, filtration, sorption and biological assimilation (Hatt et al. 2007b). The filtered effluent is then either collected for reuse, channelled into the drainage network and downstream waterways, or allowed to exfiltrate into the surrounding substrate and groundwater (Davis et al. 2001; FAWB 2009a; Hatt et al. 2007b). Through these processes biofilters reduce pollutant export and attenuate storm flows thereby improving the quality and quantity of stormwater. Biofilters also provide additional environmental benefits, such as micro-climate cooling, wildlife habitat and improved urban landscape amenity (FAWB 2009a).

Biofilters are flexible in design and can be installed at various scales to perform a range of functions. For example, linear biofiltration systems, also referred to as biofiltration swales, can provide both stormwater conveyance and treatment (Figure 2.1 left). Another common design approach is to install a series of discrete cells into the streetscape (Figure 2.1 right). Alternatively, bioretention basins can allow large volumes of stormwater to be captured at the base of the catchment or end of a swale. At the household scale, small raingardens can capture roof runoff from downpipes using an in-ground or above-ground approach (i.e. constructed or planter boxes). Biofilters can be modified in various ways to overcome site constraints or perform specific objectives, for instance removal of the underdrain or liner to promote exfiltration into the soil, or integration of a saturated zone to enhance denitrification.

Figure 2.1. Biofiltration swale (Lynbrook Estate) and cell example (Saturn Crescent) (Source: personal collection)

2.2.2 Overview of biofilter nutrient removal performance

Water quality results from laboratory studies and monitoring of field-scale systems indicate that biofilters are generally capable of meeting typical Australian pollutant load reduction targets for both N and P (e.g. 45% total nitrogen (TN) and 45% total phosphorus (TP) in Victoria) (Table 2.1). Generally, TN removal has been somewhat more variable than TP, ranging from as high as 80% removal to net export (Davis et al. 2006; Hatt et al. 2009; Hsieh et al. 2007b; Hunt et al. 2006). Nitrate in particular has proven very difficult to remove, and many cases of NO_3^- and oxidised nitrogen (NO_x) leaching have been reported in both vegetated (Bratieres et al. 2008) and unvegetated systems (Davis et al. 2006; Hsieh et al. 2007b; Lucas et al. 2008) (Table 2.1). Similarly, removal of dissolved P, in particular phosphate, has been highly variable, ranging from net export to more than 90% removal (Bratieres et al. 2008; Hatt et al. 2008). The variability in treatment of dissolved pollutants clearly presents an ongoing challenge. Further, even in instances where very high load reductions are reported, the concentration of nutrients in effluent still tends to exceed water quality guidelines for receiving waters (ANZECC/ARMCANZ 2000).

Although many studies have aimed to quantify the nutrient removal capacity of biofilters, most studies tend to report pollutant removal performance as a percentage reduction in pollutant loads and/or concentrations. Whilst this provides a useful measure of pollutant removal efficiency it does not necessarily consider the needs of the receiving water.

Table 2.1. Summary of biofiltration system nutrient removal performance (effluent concentration (mg/L); % concentration reduction in parentheses). Also shown are water quality guidelines for slightly disturbed lowland rivers in South-Eastern Australia (ANZECC/ARMCANZ 2000). Effluent concentrations shown in bold indicate results that complied with the guidelines. SZ: saturated zone, TP: total phosphorus, PO_4-P: phosphorus as phosphate, TN: total nitrogen, NH_3: ammonia, NO_x: oxidised nitrogen, TKN: total kjeldahl nitrogen.

Reference	Scale	Media	Vegetation	SZ	TP	PO_4-P	TN	NH_3	NO_x	TKN
ANZECC/ARMCANZ					**0.05**	**0.02**	**0.5**	**0.02**	**0.04**	**0.46**
Davis et al, 2006	Pilot-scale	Sandy Loam (0.9m)	Y	N	0.10 (81)	-	1.16 (37)	-	0.26 (24)	0.90 (68)
		Sandy Loam (0.6m)	Y	N	0.13 (71)	-	-	-	-	0.84 (76)
Dietz and Clausen	Lot-scale	Loamy sand	Y	N						
Henderson et al, 2007	Mesocosms	Loamy sand	Y	N	**0.03** (94)	**0.00** (100)	1.23 (77)	**0.02** (96)	0.15 (79)	1.08 (77)
		Sandy loam	Y	N	**0.05** (90)	**0.01** (97)	1.23 (77)	**0.03** (91)	0.05 (93)	1.18 (75)
		Loamy sand	N	N	**0.05** (90)	**0.00** (100)	4.91 (10)	0.13 (72)	2.54 (-268)	2.37 (50)
		Sandy loam	N	N	0.13 (74)	0.10 (74)	4.06 (25)	**0.02** (95)	2.59 (-291)	1.37 (71)
Davis et al, 2007	Field-scale	Sand/soil/mulch 50/30/20(%)	Y	N	0.17 (72)	-	-	-	**0.03** (79)	-
			Y	Y	0.15 (75)	-	-	-	**0.02** (86)	-
Lucas and Greenway, 2008	Mesocosms	Sandy Loam	Y	N	**0.03** (96)	-	3.69 (77)	-	0.37 (59)	
		Sand	Y	N	**0.04** (95)	-	2.83 (41)	-	0.63 (30)	
Bratieres, 2008	Large-Columns	Sandy loam	Y (*Carex*)	N	**0.02** (95)	**0.01** (90)	0.65 (71)	-	**0.03** (96)	
		Sandy loam	Y (*Melaleuca*)	N	0.07 (84)	0.03 (74)	1.19 (46)	-	0.38 (52)	

2.3 Phosphorus removal by biofiltration

Physical, chemical and biological processes interact within biofiltration systems to promote nutrient removal. Unlike N, P cycling does not result in the return of a gaseous form to the atmosphere. As such, the main objective for P is to secure long-term storage through retention in the filter media and biological pools. Optimising biofilters to facilitate processes that sequester P is fundamental to securing long-term P retention in biofilters. Figure 2.2 illustrates the pathways through which P may be sequestered and mobilised in water-soil-plant systems. The main processes responsible for facilitating P removal in biofilters include sedimentation, filtration, adsorption, precipitation, biological mineralisation and assimilation (Hatt et al. 2009; Henderson et al. 2007a).

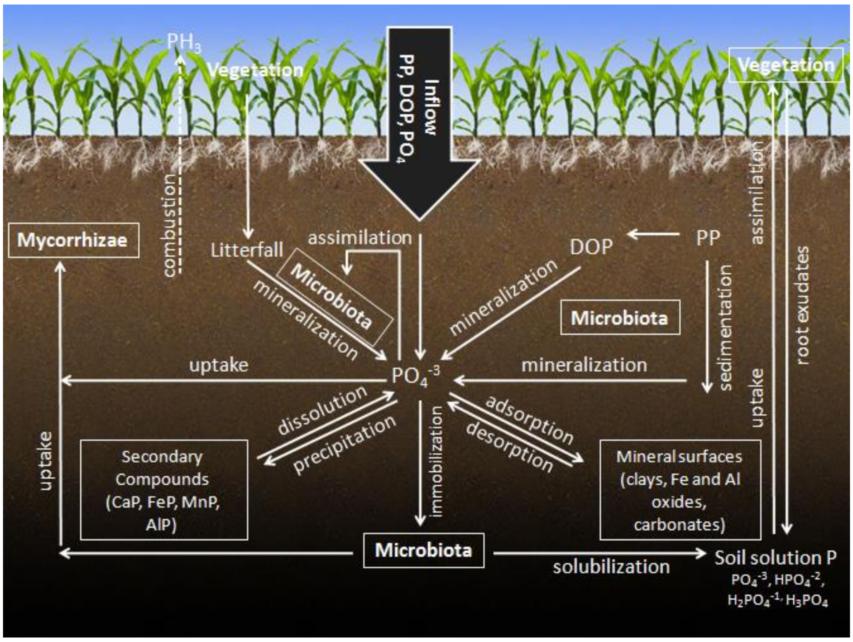

Figure 2.2. Phosphorus removal pathways in water-soil-plant systems. Storage pools are shown as text within a box. PP: particulate phosphorus, DOP: dissolved organic phosphorus, PO_4: phosphate.

2.3.1 The role of filter media

2.3.1.1 Removal of particulate associated nutrients

Particulate-associated P constitutes approximately 70% of TP in stormwater (Duncan 2006). Conversely, PON comprises approximately 25% of TN (Taylor et al. 2005). As such, removal of total suspended solids (TSS) is a critical element of P removal and to a lesser extent N. TSS removal is driven by sedimentation and mechanical straining (Hatt et al. 2007b). As stormwater moves over the biofilter surface vegetation and turbulent flow pathways reduce velocities and allow suspended solids to settle. Particulates not removed through sedimentation are mechanically filtered as stormwater percolates through the filter media. The extent to which biofilters capture TSS via filtration is determined by the particle size distribution (PSD) of the filter media. Australian biofiltration guidelines currently recommend the use of loamy sand filter media in biofilters (FAWB 2009b); although use of sandy loam and sand is also common. Loamy sand is a well graded medium which has a low native P and organic matter content, meaning the risk of P leaching from the filter media itself is minimised. Porosity, hydraulic conductivity and filter media depth and residence time have also been shown to affect TP removal in a number of field and laboratory experiments (Davis et al. 2006; Erickson et al. 2007; Fletcher et al. 2006; Hatt et al. 2007b; Le Coustumer et al. 2009). Including vegetation also improves capture of fine particulates, by enabling uniform flow distribution and increasing contact with plant roots, which bind and stabilise solids.

Testing of laboratory and field-scale systems using a range of filter media has demonstrated that biofilters are a very effective technology for the removal of TSS, with removal efficiencies of greater than 90% frequently reported (e.g. Bratieres et al. 2008; Hatt et al. 2007b; Hatt et al. 2008; Hsieh et al. 2005; Hsieh et al. 2007a). Because TP removal is largely dependent on the capture of particulates, poor TSS removal usually correlates with poor TP removal. Typically, poor TSS removal is observed when preferential flow paths have formed or following system construction; as the filter media settles, plants establish and a sedimentation layer builds on the biofilter surface (Hsieh et al. 2005; Hsieh et al. 2007a). Preferential flow pathways can develop after long periods of dry weather which, for example, can cause shrinking and cracking to occur. This has been observed in both laboratory and field scale experiments (Blecken et al. 2009; Brown et al. 2013).

Very good TSS and, in turn, TP removal usually occurs when biofilters are vegetated and designed with an appropriate filter medium (i.e. well graded, sand based and without a labile pool of P) (Blecken et al. 2010; Bratieres et al. 2008). For example, in a large-scale vegetated biofilter column study Bratieres et al. (2008) showed that sandy loam biofilters planted with *Carex appressa* achieved 99% TSS removal, which was correlated with more than 90% TP removal over a range of filter media depths (300-700mm). These same columns also achieved relatively high TN removal (~70%). However, in isolated testing of sandy loam filter media (i.e. no vegetation) using laboratory-scale columns, good TSS removal coincided with net TP production (Hatt et al. 2008). This was attributed to leaching of dissolved P either from the filter media itself or from P accumulated during the experiment. This hypothesis was validated through the analysis of water samples collected along the filter media profile, which revealed that TP concentrations decreased by 70% in the top 10cm of the filter media (indicating removal of particulate P through sedimentation and filtration) then increased over the next 90cm to concentrations in excess of the inflow (>0.3mg/L), which was made up almost entirely of dissolved P (Hatt et al. 2008). TN production was also observed in this study, which was also almost entirely dissolved (NO_x) and had a similar concentration profile to TP through the media. Filter media analysis following the experiment revealed that TP and TN were concentrated in the top few centimetres of the filter media, highlighting the removal of particulates facilitated in this zone by sedimentation and filtration (Hatt et al. 2008). This finding emphasised that in order to provide good overall nutrient removal the filter medium must be able to capture nutrients in both particulate and dissolved forms. Biofilter media analyses have also shown that carbon accumulation (TOC) is greatest at the surface where sediment is deposited (Blecken et al. 2009; Hatt et al. 2007b). Sediment may play an important role in the ongoing removal of P, by providing a carbon source to support microorganism growth and a P sorption sink.

2.3.1.2 Removal of dissolved nutrients

P sorption

While biofilters have been shown to effectively facilitate removal of P associated with suspended solids, removal of dissolved P has been more variable, ranging from net production to greater than 90% removal. Even when high concentration reduction rates were reported, effluent concentrations still tended to exceed water quality guidelines for PO_4-P (Bratieres et al., 2008, Davis et al., 2001, Hsieh et al., 2007). As such there is a need to improve removal of dissolved forms of P in biofilters. Sorption is regarded as the dominant mechanism for dissolved pollutant removal from wastewater in constructed wetlands (Kadlec et al. 1996). Given both wetlands and biofilters water-plant-soil systems, it can be inferred that the P-sorption capacity of filter media plays a critical role in optimising P removal in biofilters. However, since studies of biofilter treatment performance have been largely “black box”, our knowledge of the role of filter media with regard to P-sorption and retention is limited and somewhat contradictory. Henderson et al. (2007b) argue that filter media is unlikely to retain P in the long term though it may play an important role by extending the residence time of P to allow plant and microbial assimilation to occur. Others have suggested that filter media could enable complex sorption and precipitation processes which are able to bind phosphorus strongly (and possibly even permanently) (Arias et al. 2001; Brix et al. 2001; Lucas et al. 2008).

Sorption can be defined as the removal of a compound from solution by either concentrating it in (absorption) or on (adsorption) a solid phase (Henderson 2008). Mechanisms of sorption include electrostatic ion-exchange and ligand exchange (chemisorption) (Stumm 1992), whereby hydroxyl groups on the adsorbate surface are replaced by phosphate ion (Borggaard et al. 1990). Inner-sphere complexes formed through ligand exchanges are coordinated by monodentate or bidentate chemical bonds, which are highly specific and quite strong (Barber 2002); although bidentate ligands have a relatively greater stability and are less reversible than monodentate bonds (Stumm et al. 1996). Conversely, electrostatic ion-exchanges occur when localised charge imbalances attract PO_4-P to surface hydroxyls to form non-specific outer-sphere complexes (Barber 2002); this is a rapid process and the complexes formed are highly reversible (Lucas et al. 2008). The P sorption capacity of a filter media is largely dependent on its physical and elemental composition (Hsieh et al., 2007). Phosphate ions react strongly in filter media with clay minerals (which have a high surface area and abundance of surface sorption sites), iron (Fe) and aluminium (Al) oxides and hydroxides, and calcium carbonates; as well as the corresponding metal ions in soluble form (Beek et al. 1979). P-sorption occurs predominately with Fe, Al and manganese (Mn) in acidic soils and with calcium (Ca) and magnesium (Mg) in alkaline soils (Beek et al. 1979; Wild 1950). The abundance of these elements will therefore have a considerable influence on the P-sorption capacity of filter media, which will eventually become exhausted. P-saturation of filter media is therefore a critical issue when optimising biofilters for P removal. Release of P-sorbed from readily reversible sorption sites also poses a challenge (Henderson et al., 2007b). Optimising conditions for slow sorption processes such as deposition of P into the mineral structure of Fe and Al oxides or precipitation of calcium phosphates to occur is likely to provide a less-reversible, more permanent, P-storage pool in biofilters. However, retention times on the order of several days are necessary for these reactions to occur (Søvik et al. 2005).

Precipitation occurs when two or more soluble substances combine to form a solid phase (Stumm et al. 1996). In order for precipitation to occur each solute must be present in concentrations high enough to exceed the critical concentration for seed crystal nucleation (Henderson 2008). In filter media containing calcite or calcium sulphate (gypsum) phosphate may react with Ca to form insoluble calcium phosphates (Reddy et al. 1999). However, the solubility of these crystalline solids is highly pH dependent, and below pH 8 are likely to be re-solubilized (Diaz et al. 1994). In non-calcareous filter media, PO_4-P precipitation and co-precipitation may occur following adsorption to Fe and Al oxides (Clark et al. 2012). Both forms of iron (Fe^{2+} and Fe^{3+}) can combine with PO_4-P in solution to form solids. Precipitation with ferric iron (Fe^{3+}) forms the mineral strengite (FePO4), while precipitation with ferrous (Fe^{2+}) ions can form the mineral vivianite (hydrated iron(II) phosphate) ($Fe_3(PO_4)_2 \cdot 8H_2O$) (de Haas et al. 2000). However, precipitation is only likely to be an important process for P removal in biofilters if (1) the filter media has a high Ca or Fe content, (2) the electrical conductivity (EC), pH, and temperature of the soil solution are appropriate (3) and if PO_4-P concentrations in stormwater are relatively high (Henderson 2008).

Because the P-removal capacity of filter media is ultimately finite, it is of interest to elucidate the P-sorption capacity of filter media to assess the suitability and long-term P removal potential of different media. Various methods exist for determining the P-sorption capacity of filter media. Agronomy studies use soil-P index tests to estimate the amount of P available to plants in soils. Similarly, batch-tests have been used to investigate the P-sorption capacity of filter media for use in wastewater treatment systems. Arias et al. (2001) found that a simple batch isotherm study, using water of a similar chemical composition to the target wastewater, offers a simple and quick method for testing and comparing the P removal potential of filter media. Column studies are also recognised as suitable method for measuring P-removal under operating conditions representative of field systems. Both these methods have been utilised to investigate P-sorption to filter media in natural wastewater treatment systems (Del Bubba et al. 2003; Hatt et al. 2007c; Hsieh et al. 2007a).

Hsieh et al. (2007a) used batch-tests and small-column experiments to study P-removal from an aqueous solution. The short-term phosphorus sorption capacity of the media was determined using the Langmuir isotherm equation. The P-sorption capacities of the two sands tested were 20μg/g and 89μg/g, the latter of which was attributed to the formation of calcium-phosphates due to the presence of higher Ca and Mg concentrations in the medium. They also tested three different soils and these showed little variability ranging from 128-137μg/g, while mulch sorbed less than 5μg/g P. The small-columns tested by Hsieh et al. (2007a) examined P removal in three columns containing different ratios of soil and sand (70/30; 50/50; 30/70). The columns were continuously dosed with a 3mg/L solution of P (Na_2HPO_4) at a constant flow-rate of 3.1 mL/min (0.97 mm/min loading) for 29 days. Effluent P concentrations were similar from all three columns for the first six days, after which the P_{in}/P_{out} ratio began to gradually increase. The 70% sand columns were exhausted most quickly and the 70% soil least quickly. After 100 bed volumes, all columns had become P saturated. The total mass of the input P (391mg) retained in each of the columns was 184 mg (70/30), 139 mg (50/50) and 92 mg (30/70). These values were greater than that estimated using the batch-test data, which suggests that under these conditions additional removal through slow-reactions had occurred. Clearly, the columns which contained the most soil had the highest P-sorption capacity. This is not surprising given that the soil contained higher concentrations of P attracting ions and a larger portion of fine particles.

Arias et al. (2001) and Del Bubba et al. (2003) used short-term isotherm batch-experiments to study the P-sorption properties of 13, mostly calcareous, Danish sands for use in constructed reed beds. Using the Langmuir model to describe P-sorption, Del Bubba et al. (2003) calculated the maximum P-adsorption capacities and P-binding energy constants of the sands and investigated relationships between these and physico-chemical characteristics of the media. This analysis determined that for these sands Ca and Mg content, grain size, porosity, bulk density and hydraulic conductivity were significantly related to the estimated maximum P-adsorption capacity. In addition to batch tests Arias et al. (2001) examined P-removal of the 13 Danish sands using column experiments under saturated conditions, where 1000g of media were dosed continuously for 12 weeks with 240 mL day of 10mg P/L solution.

Similar to the findings of Hsieh et al. (2007a), Arias et al. (2001) found that the maximum P-adsorption capacities measured by the batch-tests underestimated the removal achieved in the column-tests, thus may infer that slow-sorption reactions are occurring. However, this may simply be an artefact of scaling-up the results of a bench-scale test to pilot-scale systems. Nonetheless, as suggested by Arias et al., batch-tests provide a simple and efficient method to estimate and compare the P-sorption capacity of filter media. The column study showed that the sands exhibited varying rates of P removal, which was significantly correlated to calcium content and the 0.6-2.0mm grain size fraction. The use of rather hard tap water (90mg Ca/L) and sands containing high concentrations of Ca (including an exchangeable fraction) suggests that chemical precipitation of calcium phosphates is likely to have been one of the main processes responsible for P removal. The relationship between P-sorption and particle size is not surprising, since this has been previously established in the literature (Viklander 1998). However, since specific guidelines exist for the particle size distribution of biofilter media to maintain hydraulic conductivity (Payne 2015), P-removal capacity cannot simply be increased by altering the PSD of the media. The studies undertaken by Arias et al. (2001) and Del Bubba et al. (2003) determined that the calcium content of media is of greater importance for P removal than Fe and Al. This is a suitable conclusion for the treatment of domestic sewerage, which typically has a high pH and so will favour the precipitation of calcium-phosphates that are sparingly soluble at pH below 8. However, since stormwater is typically slightly acidic, precipitation of calcium-phosphates is not likely to have a significant bearing on P removal. The Fe and Al content of media is more likely to be of significance. Strong sorption of P to Fe and Al occurs at a pH 5-6, thus is likely to be the dominant sorption process in biofilters. Sorption capacity is dynamic and can be altered by changes to soil environment, inflow P concentrations, and biological processes.

Large-scale columns have often been used to investigate pollutant removal and test filter media for use in stormwater treatment systems. These experiments typically apply an influent mixture with a chemical composition representative of stormwater to the columns. In doing so, P-removal is tested in an environment where multiple processes and competition between pollutants can be simulated under various hydrologic conditions.

Several studies have used methods of accelerated dosing to attempt to measure the P sorption capacity or P-removal lifespan of biofilters (Hsieh et al. 2007a; Lucas et al. 2011). However, most of these have been conducted under isolated laboratory conditions, without the influence of vegetation or the additional microbial activity which is stimulated by the presence of plants. This may mean that the P sorption capacity is somewhat underestimated. Others have applied P at concentrations far in excess of typical stormwater which overestimates the P-sorption capacity of filter media and promote precipitation that would otherwise not occur at typical stormwater influent concentrations.

N sorption

Dissolved organic N and ammonium are retained during events through rapid chemical reactions, including adsorption to negatively charged clays and organic matter in soils (Chen et al. 2013; Hsieh et al. 2007b). However, adsorption would be considered a transient removal process prior to biological uptake or transformation. Conversely, nitrate and nitrite (NO_x) anions adsorb poorly to filter media and are very mobile in soils. Therefore, if NO_x is not transformed via denitrification or assimilated by plants and microbes it is unlikely to be retained in the system. This may explain the frequent reporting of instances of NO_x leaching from biofilters. The production of NO_x via ammonification and nitrification of retained org-N and NH_4^+ during events which results in NO_x washing out in subsequent events further exacerbates the challenge of removing NO_x (Henderson et al. 2007a; Kim et al. 2003).

2.3.1.3 The influence of organic matter

Organic materials, such as mulch or compost, are sometimes added to biofilters as a filter media ameliorant or cover layer to provide a source of nutrients to boost plant establishment and/or provide additional capacity for dissolved pollutant removal. However, the use of easily biodegradable organic matter, or filter media containing a labile pool of P, can result in P losses; meaning the system acts as a source of P rather than a sink (Hatt et al. 2008). This has been observed in several studies, and is also applicable to high N content materials. Bratieres et al. (2008) and Hatt et al. (2007b) examined nutrient removal performance of vegetated and non-vegetated biofilters containing sandy loam media amended with compost/mulch. In both instances net TP production occurred, where the effluent TP was made up almost entirely of dissolved P. Since TP export was not observed in sandy loam only controls the authors concluded that the leaching was associated with biodegradation of embedded organic materials. Other studies of non-vegetated biofilters have also shown that barren systems tend to leach nutrients, particularly when the filter media is soil based (Henderson et al. 2007a; Hsieh et al. 2007b). Over two years of monitoring, Dietz et al. (2006) observed substantial TP export from raingardens which contained native loamy sand with less than 2% organic matter but covered with a layer of shredded hardwood bark mulch approximately 5 cm thick. A mass balance of P associated with various biofilter components showed that the TP concentration of the mulch increased by 8% during the experiment. However, this did not distinguish between P captured or released; thus if P was released from the mulch it was not monitored. The authors suggest that P leaching occurred due to disturbance of the soil during system construction, which mobilised P-bound particulates and caused breakdown of P associated with organic debris (e.g. plant roots). These findings suggest that, in order to minimise the risk of P leaching, care must be taken to avoid materials with a high P content and ensure filter media stability in newly constructed systems.

An assessment of pollutant removal in six field-scale biofilters demonstrated considerable variability in TP removal (37-99%) (Hsieh et al. 2005). Interestingly, the three best performing systems (greater than 90% TP removal) were those with the highest organic matter content. Rustige et al. (2003) also found that TP removal in subsurface flow constructed wetlands was highly correlated with organic matter content. As carbon accumulates within biofilters the rate of microorganism growth will increase. This is because microorganism growth is dictated by the C:N:P ratio of the soil (Reddy et al. 1999). If labile carbon is abundant relative to N and P (i.e. ratio is high), the surplus energy for microbial growth drives the demand for N and P, causing immobilisation to occur. However, under circumstances where N and P are not growth limiting (i.e. at lower ratios), mineralised nutrients will be released back into the soil solution (Henderson 2008). In vegetated biofiltration systems where carbon is abundant, immobilisation of nutrients is likely to be the dominant process. Microbial immobilisation may become an increasingly important reservoir for P storage as biofilters mature and organic matter accumulates in the system. This may provide an explanation for the P removal exhibited by biofilters with a high organic matter content. Sorption of P to cations bound to the surface of natural organic matter may also provide an explanation for the correlation between P removal and organic matter content.

In summary, the evidence of P leaching from systems which have incorporated an organic matter component (i.e. compost) suggests this may not be replicated by adding organic materials. Allowing organic material to build naturally in biofilters may be preferable if a low P content carbon source cannot be identified.

2.3.2 The role of plants and microorganisms

Plants have been shown to support the hydrologic function of biofilters by improving soil structure and porosity, reducing the risk of clogging and maintaining hydraulic conductivity (K_s) (Le Coustumer et al. 2012) and promoting evapotranspiration, which can reduce outflow volumes and benefit micro-climate cooling. Establishing plants in biofilters also creates a vibrant biological environment in which soil microbes, plant roots, and fungi interact to enhance nutrient uptake (Curl et al. 1986). Plants assimilate P in the form of phosphate (PO_4-P) at a neutral pH (i.e. as HPO_4^{2-} and $H_2PO_4^-$). Microorganisms (bacteria, fungi) are largely responsible for transforming organic-P into bioavailable forms via mineralisation (Reddy et al. 1999). Although mineralisation is not a removal process per se, it is an essential step in the immobilisation of P in biological systems.

Mineralisation is enzymatically driven by catabolic processes which break down organic-P compounds (e.g. phosphate esters and nucleic acids) into monomer units (e.g. nucleotides), which are either used by microbes for metabolic function or respiration, then degraded into energy and inorganic P waste products (mineralisation) (Henderson 2008; Reddy et al. 1999) or assimilated to serve as building blocks for cell and tissue growth (immobilisation) (Vymazal 2007).

Inorganic P is very reactive and may therefore be quickly sequestered via sorption to filter media following microbial mineralisation (Frossard et al. 1995; Tiessen 2008). To overcome the challenges of P availability in soils, plants have developed special biochemical techniques to liberate P from sorption sites, including root zone acidification, organic acid exudation and phosphatase enzyme secretion (Geelhoed et al. 1999; Lambers et al. 1998; Shane et al. 2006). Once assimilated by plants P plays a critical role in the storage and transfer of energy. P is an essential component of adenosine triphosphate (ATP), the linchpin for metabolism in biological systems, DNA (deoxyribonucleic acid), RNA (ribonucleic acid), and phospholipids, which are the building blocks for cell wall membranes (Filipelli 2008). The importance of vegetation in facilitating nutrient removal in biofilters has been demonstrated by several studies using large-scale vegetated biofilter columns and mesocosms (Bratieres et al. 2008; Henderson et al. 2007b; Lucas et al. 2008; Read et al. 2008).

2.3.2.1 Nutrient removal in vegetated biofilters

Henderson et al. (2007a) compared nutrient removal performance in biofilter mesocosms with and without vegetation. They found that vegetated loamy sand/sandy loam mesocosms reduced TP concentrations by 90–94% and TN by 77%, which was substantially more TN than removed in the non-vegetated treatments (10-25%) and slightly more TP (74-90% in non-vegetated). Although vegetation improved PO_4-P removal in the sandy loam systems (74% non-vegetated; 94% vegetated), no difference in PO_4-P removal was evident between the vegetated and non-vegetated loamy sand mesocosms, inferring PO_4-P was either released from or less well retained in the sandy loam, as previously indicated by Hatt et al. (2008). Bratieres et al. (2008) showed that adding vegetation to sandy loam biofilter columns increased PO_4-P removal by up to 40% and Read et al. (2008) determined that vegetation had a significant effect on the removal on PO_4-P in sandy loam media. These studies also emphasised the effect which vegetation had on removal of nitrates. Read et al. (2008) measured nutrient removal performance across twenty plant species and found that vegetated systems reduced NO_x concentrations by ~80%, compared to only 6% in soil-only systems.

Similarly, Bratieres et al. (2008) reported up to 96% NO_x removal in vegetated biofilters and net export from soil only systems. Lucas et al. (2008) investigated nutrient removal in biofilter mesocosms established three years prior by Henderson et al. (2007a). This study again demonstrated higher nutrient removal in the vegetated (V) compared with non-vegetated (NV) mesocosms: TP (96% V, 71% NV), TN (79% V, 45% NV), and NO_x (30% V, 15% NV). These results were similar to those reported by Henderson et al. (2007a), implying that the mesocosms could maintain nutrient removal even after plants were fully established. However, TN removal in the barren sandy loam systems had improved substantially (from 25 to 45%), which was attributed to the growth of microbial communities in the media over time. Nitrate removal is facilitated by biological assimilation and transformations.

Studies of vegetated biofilters have confirmed that vegetation plays a critical role in nutrient removal, in particular nitrate (NO_x), thus is an essential biofilter design component for the co-optimisation of N and P removal. However, not all plant species are suited to performing nutrient removal; indeed selection of an inappropriate species may be detrimental to system performance (Read et al. 2008).

2.3.2.2 The importance of plant species selection

The rate at which plants assimilate P is dependent on the P loading and P uptake capacity of the plant, which varies between species (Reddy et al. 1999). If the latter is similar to the nutrient loading rate then P accumulation in the plant tissues may be responsible for a large portion of overall P removal. However, if the P loading rate far exceeds the P uptake capacity of the vegetation, then plants are unlikely to significantly contribute to P removal (Henderson 2008). Previous biofilter research has focussed on validating nutrient removal variation among plant species. For example, Read et al. (2008) and Bratieres et al. (2008) conducted large-scale column studies and showed that nutrient removal performance is highly sensitive to plant species selection, and significantly influenced by plant characteristics such as relative growth rate, root architecture and root density (Read et al., 2010). These studies identified species that are effective for targeting nutrient removal in biofilters (e.g. *Carex appressa*, *Melaleuca ericifolia*) and species which are ineffective (e.g. *Microlaena stipoides, Dianella revolute, Lomandra longifolia).* These findings challenged the concept that biofilters simply need to be 'vegetated' to be effective and suggested that variation in performance could be due to physiological, chemical and morphological variations among species.

In both studies *C. appressa* performed best for TP and TN removal. By maturation, sandy loam based biofilters planted with *Carex* were achieving 70 and 95% TN and TP removal respectively, and 90% PO_4-P. The excellent performance of this sedge can be explained by its extensive root system and the presence of root hairs; traits which are recognised for effective nutrient uptake (Read 2010). These architectural traits aid plants to overcome the low diffusion coefficient of PO_4-P in soils (Gahoonia et al. 1998; Lambers et al. 1998; Lynch 1995). Using a radioactive tracer Gahoonia et al. (1998) showed that PO_4-P uptake via root hairs satisfied 60% of the plant's P demand. Very high rates of P removal are also exhibited by species which produce root clusters, including *C. appressa* and more broadly, *Cyperaceae* (Lambers et al. 2006; Shane et al. 2006).

Bratieres et al. (2008) also found *M. ericifolia* to be a reliable species for nutrient removal (46% TN, 52% NO_x, 84% TP, 74% PO_4-P) and noted that mycorrhizal fungi had colonised on the roots of these trees. Plants develop symbiotic relationships with fungi *mycorrhizae* to enhance acquisition and rapid diffusion of PO_4-P to the root surface (Bolan 1991; Bucher 2007; Van Tichelen et al. 2000). Van Tichelen et al. (2000) showed that plants with arbuscular mycorrhizal (AM) fungi associations were able to assimilate 75% of TP from a 4.8mg-P/L solution within two hours. This association may explain the very good P uptake demonstrated by *M. ericifolia*. Both *M. ericifolia* and *C. appressa* have been used extensively in biofilters around Australia (Dalrymple 2012).

A study of the effects of competition between plant species showed that the nutrient removal performance of biofilter columns planted with *C. appressa* increased when planted in combination with *L. longifolia* (Ellerton et al. 2012), an average performing species for nutrient removal (Read et al. 2008). As such, a mix of very good and average performing plant species may provide optimal outcomes for nutrient removal and offer practitioners more options in terms of landscape design. This finding may be of further benefit seeing as plant species are not universally effective at removing pollutants, so a mix of species may be needed when targeting several pollutants (Read et al. 2008).

2.3.2.3 Contribution of biological uptake to P-removal

Uptake by plants is an important consideration when quantifying P retained in the biofilters and estimating the P removal longevity of systems. As shown in the previous section, the inclusion of appropriate plant species can substantially increase their P removal performance. However, reported measurements of plant contribution to P removal have found that plant P uptake represents only a small fraction of overall P removal. For instance, Dietz et al. (2006) determined that over two years of operation that plant uptake contributed to only 3% of TP removal in a rain garden treating roof runoff. Similarly, Lucas et al. (2008) determined that only 6% of TP removal in biofilter mesocosms with well-established plants was attributed to plant uptake.

Immobilisation of P by microorganisms may provide an explanation for the enhanced P removal exhibited by vegetated biofiltration systems. Over time, as natural organic matter builds in biofilters the rate of microbial growth and nutrient immobilisation will increase. Microbial immobilisation occurs at a much faster rate than plant uptake. Therefore, in biofiltration systems where contact time between plants and stormwater is limited, rapid microbial uptake is likely to contribute more to P removal than plant uptake. Microbial uptake is likely to be highest in filter media with a high surface area and well-established microbial community (Henderson et al. 2007a). Microbes are especially active in the rhizosphere where they are nourished by root exudates and debris, thus plants play an essential role in supporting microbial activity (Curl et al. 1986). Rapid microbial uptake may be particularly important in circumstances where influent PO_4-P concentrations are at or below the P equilibrium concentration and P removal via sorption is prevented (Henderson 2008). However, because microorganisms are vulnerable to disturbances such as predation and desiccation, plants will eventually capture and retain more P than microbial biomass (Henderson 2008). Upon cell lysis and decomposition, organically bound N and P are returned to soil solution where they can be acquired by plants or undergo further microbial degradation (Filipelli 2008).

Microbes are essentially a transient sink for nutrients. However, P stored in the form of refractory organic compounds, may not be degraded during microbial decomposition (Gächter et al. 1993). Over time these compounds may accumulate in biofiltration systems, becoming a long-term storage sink for nutrients (Henderson 2008). Nonetheless, uptake by plants provides a more secure and long-term retention pool. P storage in plants can range from short- to long-term, depending on vegetation type, growth characteristics, rates of litter decomposition, P leaching from detrital tissue, and transient storage mechanisms. For example, prior to autumn senescence, P may be translocated between above-ground and below-ground biomass stores to reduce nutrient losses (Reddy et al. 1999). Periodic pruning of plants may present a permanent P removal pathway that would also reduce the quantity of P returning to the soil through plant die-off.

This suggests that while plants may provide an important long term storage pool for P in biofilters, retention in the filter media and microbial immobilisation may play a more essential role in the removal and retention of P in biofilters.

2.3.3 Influences of climate and water dynamics

Biofilters experience a high level of variability in the frequency of inundation and length of intervening dry periods. These wetting and drying cycles significantly alter conditions within the biofilter (e.g. temperature, pH, soil moisture, EC, DO) and affect nutrient removal processes. Hatt et al. (2007a) assessed the treatment performance of non-vegetated stormwater filters under varying periods of wetting and drying and found that P removal was unaffected. Hsieh et al. (2007a) found that TP removal recovers quickly following long dry weather periods. Other studies which used repetitive events to test P removal by soils also showed that the soil regains some capacity to remove P after drying and wetting cycles (Hatt et al. 2009). This renewal could be attributed to slow-sorption reactions which occur between events and free sorption sites on the surface of particles, for instance, diffusion of sorbed P into the media matrix, or precipitation of P with ions in solution (Brix et al. 2001; Torrent et al. 1992).

Release of bioavailable nutrients from soils and sediments after long antecedent dry periods has been observed in various soil environments (e.g. floodplains, ephemeral rivers) (Baldwin et al. 2000) as well as in biofilters (Zinger et al. 2007a). The flush of nutrients from these systems upon rewetting has been associated with lysis of soil microorganisms and release of nutrients from dead plant tissues (Baldwin et al. 2000). In addition to this initial nutrient pulse, the death of soil microbes may continue to have an impact on nutrient removal during successive events, since these biota play an essential role in nutrient removal processes (e.g. mineralisation, immobilisation, acquisition of nutrients from sorption sites).

Increased cycling between oxic and anoxic conditions has been associated with a high abundance bacteria (Chen et al. 2013). Concentrations of dissolved oxygen within the saturated zone have been shown to be oxic immediately following inundation but rapidly decline towards anoxia within 24 hours (Payne et al. 2014b). As such, it could be expected that biofilters that incorporate a saturated zone would release higher amounts of nutrients following extended dry periods. On the other hand, saturated zones have been shown to improve plant growth and sustain health during dry periods.

Therefore, losses due to plant tissue decomposition during dry spells may contribute less to nutrient release than the standard design.

2.4 Phosphorus cycling and retention in biofilters

2.4.1 Forms of P retained in biofilters

Once sequestered within filter media, phosphate falls into one of four categories: labile or non-labile sorbed phases, phosphate minerals, or organic phosphate (Org-P) (Barber 2002). Depending on the chemical nature of the filter media, labile and non-labile sorbed phases may be classified as Ca-bound or Fe- and Al-bound phosphate (Barber 2002). Non-labile P is usually incorporated within the matrices of Fe and Al minerals which are quite insoluble, while labile, or more bioavailable, P_i is loosely-sorbed to the surface of silica, calcium carbonate, or other soil minerals (Barber 2002). In acidic soils, Fe- and Al-phosphates and complexes dominate the mineral phase, while in alkaline environments the mineral fraction mainly comprises Ca-phosphates (Barber 2002). The term "occluded" is often used to describe non-labile P phases, including phosphate minerals, Fe- and Al-sorbed phosphate and various organic phosphate compounds (Beek et al. 1979). Org-P represents the P bound in organic biomass (i.e. plant tissue, root debris, microorganisms). However, within the biofilter environment P is subject to further transformation through both biotic and abiotic processes, which are strongly influenced by physical and chemical conditions within the system (e.g. temperature, pH, soil moisture, EC, DO) (Reddy et al. 1999). Thus, the fraction of P retained in various mineral and biological pools is dynamic and can in principle be mobilised (Beek et al. 1979).

Biofilter studies to date have focussed mainly on quantifying P removal performance on an event basis. Consequently, little attention has been paid to monitoring P once it has entered the system. Further, laboratory scale biofilter studies are typically "black box", so while we may have an overall estimate of the P removal capacity of a system, we have a limited understanding regarding the form(s) in which P is retained in filter media. The form in which P is retained influences the potential for P to become re-mobilised or exported from the system thus is an important measure when estimating the capacity of biofilters to retain P in the long term. Elucidating the concentration of P stored in various pools can also provide important information about transformations occurring within the filter media and the relative contribution of each phase to P retention. Several studies have used P-extraction methods to determine the form in which P is retained in constructed wetlands following short-term laboratory scale testing (Arias et al. 2001; Del Bubba et al. 2003). Such approaches have also been applied to understanding P sorption in stormwater biofilters (Komlos et al. 2012), although in a limited capacity to date.

2.4.2 Long-term retention of P in biofilters

Although biofiltration systems have been widely adopted in Australia and abroad, our understanding of long-term P removal and retention processes in biofilters is limited. This is an essential area of research given that biofilters have a finite capacity for P removal. At the time of writing only one study had examined the long-term retention of P in biofilters (Komlos et al. 2012). This study examined P concentrations along the filter media profile of a nine year old biofilter located in a car-park at the University of Villanova (PA, USA). The authors concluded that while the top 10cm of the infiltration bed was saturated with PO_4^3-P saturation at deeper depths would not occur for >20 years. This research provided new insight into the long-term P removal capacity of biofilters. However, this study did not quantify the contribution of different P-pools to P retention. More detailed quantification of P-partitioning in biofilters is needed to improve knowledge of P-cycling and improve the accuracy of P-removal longevity estimates.

2.5 Optimising filter media for P removal

2.5.1 Modifications to enhance P removal

Augmenting the sorption capacity of the soil using materials with a high P sorption capacity may provide a means to increase P removal in biofilters and satisfy receiving water guidelines. A similar approach has been taken to target removal of heavy metals by ameliorating the filter media with a high cation exchange material (vermiculite/perlite) (e.g. Hatt et al., 2007b, Zinger et al., 2007b). In the natural environment, phosphorus cycling is closely related to that of iron, and interactions between iron and phosphorus have been identified as important mechanisms for sequestering phosphorus in sediments (Smolders et al., 2001). Utilising iron-phosphorus interactions to improve the binding capacity of filter media may provide a means to enable strong binding of phosphorus in biofilters.

2.5.1.1 Using Fe to enhance P retention

The importance of iron in formation of amorphous ferric oxyhydroxides, which have a high adsorption capacity for phosphorus, is often stressed in terrestrial and aquatic sedimentary studies (e.g. Baldwin, 1996a, Baldwin and Mitchell, 2000, Boström et al., 1988, Mortimer, 1941). Iron (III) adsorbs and precipitates phosphorus in sediments, providing a potentially long-term sequestration site. Sperber (1958) described how the addition of iron oxide (Fe_2O_3) could reduce the mobility of phosphates in water logged siliceous soils. Since then a number of investigations into the application of iron compounds to control phosphate release from sediments have been conducted. Boers (1991) found that the addition of iron (III) chloride to the upper sediment of a shallow lake resulted in a significant improvement of water quality for the next three months. More recently Smolders et al (2001) undertook a laboratory experiment to test whether adding various iron compounds to a phosphate-enriched sandy loam sediment could control the release of phosphate to overlying water. The results of this study suggested that the application of some iron compounds resulted in a strong decrease of phosphate release to the sediment pore water (PO_4-P<100μmol.l-1). This work built upon previous research by Smolders et al (1995) which demonstrated that adding iron (II) chloride to the sediment of a eutrophic ditch could prevent eutrophication of the overlying water layer.

These findings suggest that the addition of iron compounds to sediments is a potentially valuable technique for controlling phosphate mobilisation and release. Application of this technique to biofiltration systems could increase the phosphorus sorption capacity of filter media, improving phosphorus removal and retention time while also providing a site for microbial assimilation or plant uptake (Schachtman et al., 1998, Petersen and Bottger, 1991, Miyasaka and Habte, 2001).

2.6 Co-optimising N and P removal in biofilters

When optimising biofilters for P removal it is essential to consider the effect of design on the removal of other pollutants, in particular N, since co-optimisation of N and P removal is a key design objective for biofilters and fundamental to achieving environmental protection targets. Nitrogen removal is governed primarily by biological processes. Bioavailable N species are removed directly through plant uptake or via transformation of N into a gaseous form through microbially mediated processes.

2.6.1 The importance of plant uptake

The role of plant uptake has already been discussed extensively. Recent insights from Payne et al. (2014b) reaffirm the importance of plant uptake for N removal in biofilters and question the role of denitrification. Using a stable NO_3^- isotope tracer Payne et al. (2014b) investigated nitrogen processing in biofilters and reported that, for biofilters containing effective plant species, assimilation was the primary fate for NO_3^-, contributing an average 89-99% on NO_3^- processing, while only 0-3% was denitrified. Optimising opportunity for biological assimilation will therefore form a key part of co-optimising biofilters for N and P removal.

2.6.2 Inclusion of a saturated zone

Vegetation significantly improves TN removal in biofilters, in particular NO_x. However, concentrations of TN and dissolved N species in biofilter effluent are typically in excess of water quality guidelines. Enhancing denitrification is therefore regarded as a potential solution to improving N removal in biofilters. Further, it may be crucial for ensuring ongoing removal of N in the long term, for example, after plants reach maturity, at which point assimilation rates may be negated by equivalent release rates due to senescence. However, complete denitrification requires anaerobic environments (Kadlec et al. 1996).

Modifying biofilters to include a permanently submerged zone in the base of the system could increase retention time and limit oxygen diffusion to provide suitable redox conditions for denitrification to occur, provided a carbon source is available (Hsieh et al. 2007b). The inclusion of a saturated zone reduces oxygen diffusion into the filter media creating redox conditions under which nitrate is reduced (Eh=+350 to +100 mV) (Vymazal 2007). Addition of a carbon source to the saturated zone filter media provides energy for the nitrifying and denitrifying bacteria that facilitate the denitrification processes. However, it should be noted that dissimilatory nitrate reduction to ammonium (DNRA) may occur under these conditions if nitrate-reducing bacteria are present. This is an undesirable process which may occur if nitrate availability is high relative to carbon. Using a carbon source with a high carbon/nitrogen ratio may therefore reduce the risk of DNRA occurring (Kim et al. 2003).

It has been argued that due to the through-flow structure of biofilters, and the regular wetting and drying cycles which they experience, the saturated zone may not become fully anoxic(Payne et al.

2014b). This is unlikely to be a significant concern since environments with high oxic/anoxic site heterogeneity are considered optimal conditions for denitrification to occur. Moreover, anoxic microsites may also develop in biofilters within localised zones of high microbial respiration; even when overall saturated conditions do not occur (Davis et al. 2006; Robertson et al. 1988).

Experimental research has demonstrated that inclusion of a SZ and a carbon source enhances nitrogen removal in biofilters, in particular nitrate (Zinger 2007, Kim 2003)(Payne et al. 2014a). Laboratory testing has also shown the inclusion of a SZ to be beneficial for removing metals (Blecken 2009) and maintaining nutrient removal resilience following long dry spells (Blecken et al. 2009; Zinger et al. 2007a). Instances of improved TP removal have also been reported (Zinger 2012). However, testing of SZ inclusive biofilters at the field scale has had mixed results. Hsieh and Davis (2005) observed improved nitrate removal with a saturated zone, while Dietz and Clausen (2006) measured a decrease in effluent total nitrogen but no effect on nitrate. Hunt et al. (2006), by contrast, did not see a significant improvement in nitrogen removal due to a saturation zone in a paired-site study.

Zinger (2012) demonstrated that the inclusion of a saturated zone could dramatically improve NO_x removal in biofilters even when configured with plants with poor nitrogen removal capabilities. Likewise, Payne et al. (2014a) reported that the saturated zone reduced performance differences between plant species. The saturated zone therefore acts as an "insurance policy" against sub-optimal plant selection. In unsaturated conditions biofilter columns planted with the species *Dianella revoluta* and *Microleana stipoides* demonstrated poor nitrogen removal performance (TN leaching of up to 200% and NO_x leaching of up to 500% for both plants). Following retrofit with a saturated zone, mean NO_x removal increased by 370% for *D. revoluta* and 180% for *M. stipoides* (n=5), although the latter still showed a net production of TN (~10%). Including the SZ reduced NH_4^+ removal performance by ~50% for both plants. This is not surprising given that nitrification is driven by aerobic bacteria which would be less abundant under saturated conditions. Given that these species have been shown to be relatively ineffective in the removal of NO_x these results lead to the conclusion that the reduction in NO_x must be associated with denitrification. The outcome of Zinger's study suggests that the inclusion of a SZ enhances N removal and makes the influence of plant selection less critical. In practice this may improve biodiversity outcomes by allowing a variety of species to be used.

2.6.2.1 Addition of a carbon source

Addition of a readily biodegradable organic material can provide denitrifying bacteria with an easily accessible source of carbon. However, if the carbon source has a high nutrient concentration, its decomposition may result in the release of nutrients from the system (Dietz et al. 2006; Kim et al. 2003). Zinger et al. (2007b) studied pea straw and red-gum woodchips as a carbon source and found that the woodchips did not cause nutrient leaching. Zinger (2012) also tested nutrient removal performance of biofilter columns retrofitted with a SZ but without the addition of a carbon source. Contrary to the findings of Kim et al. (2003) who concluded that efficient NO_x removal depended on the addition of organic carbon, Zinger demonstrated that its omission did not diminish denitrification and subsequent N removal. Zinger (2012) hypothesised that organic carbon in the filter material itself (sandy loam, ~4%), and that which had accumulated in the biofilter from stormwater and turnover of root and microbial biomass, provided sufficient carbon to facilitate denitrification. This hypothesis is based on the assumption that the N removal observed was facilitated by denitrification. However, the reliability of this assumption has recently been called into questioned by Payne et al. (2014b), who proposes that the reason the carbon source provided no additional benefit was because N removal was not being driven by denitrification. Rather, the saturated zone benefits plant health such that more plant assimilation can occur.

Nevertheless, these results suggest that addition of a carbon source may only be required to support denitrification during system establishment, after which biofilters become carbon self-sufficient enough to sustain denitrification. This may have benefits in terms of reducing the risk of nutrient leaching associated with organic matter addition, particularly if a low nutrient content carbon source can be identified.

2.6.2.2 Effect of SZ on P retention in filter media

While including a SZ has been shown to enhance TN and NO_x removal, there have been instances reported of P leaching, mostly PO_4-P, associated with the modification. The inclusion of a SZ creates an environment in which P may become mobilised (e.g. through desorption from sorption sites, dissolution of phosphate precipitates or decomposition of organic matter)

Zinger 2012 noted a mean reduction in TP removal performance of 45% between unsaturated and saturated conditions, which was mostly associated with FRP (-102% in the *M. stipoides* and -45% in the *D. revoluta* vegetated columns respectively). In this experiment the biofilter columns had operated under freely draining conditions for a year prior to SZ retrofit. Under freely draining conditions it is likely that P sorption to clay minerals and amorphous iron and aluminium oxides in the sandy loam media would have occurred. Zinger suggests that the onset of anaerobic conditions may have induced dissimilatory iron reduction which caused PO_4-P to desorb and subsequently be washed out of the biofilters. Interestingly, the columns planted with *C. appressa* maintained PO_4-P removal of approximately 85% before and after the SZ retrofit. The authors suggested that *C. appressa* species was able to overcome the effect of PO_4-P leaching in the SZ due to the effective uptake of P by its deep dense root system, which after a year of growth should have penetrated the saturated zone. In comparison, *D. revoluta* and *M. stipoides* have a shallow root network which would be unable to access bioavailable P in the SZ.

2.6.2.3 Use of iron ameliorated substrates under anaerobic conditions

It is well known and generally accepted that oxic sediments retain phosphorus more efficiently than anoxic sediment; that is, formerly oxic sediments release large amounts of phosphate when they become anoxic (Pratt, 2006, Gächter and Müller, 2003). With increasing interest in the use of saturated zone to enhance N removal it is important to consider that implementation of a saturated zone may result in release of phosphorus from the biofilter, unless P can be retained in the top, unsaturated section of the biofilter. As redox potential becomes sufficiently low, dissimilatory reduction of insoluble iron(III) to soluble iron(II) occurs thus releasing previously sorbed P into the soil solution (Baldwin, 1996a). Breakdown and release of nutrients from organic matter may also result in P release.

2.7 Research Priorities

Performance results from existing systems and laboratory research supports biofiltration as an effective treatment measure for the removal of phosphorus from stormwater. However, the literature review has identified some significant knowledge gaps and areas in need of further research in order to improve our understanding of phosphorus removal, particularly in relation to long-term performance, which can then be translated into design and performance outcomes. The research priorities of the present thesis will therefore be to:

+ investigate means of ameliorating the P removal capacity of filter media using iron-based filter media amendments to harness processes that occur in the natural P cycle

+ improve understanding of the form(s) in which P is retained in biofilters
+ determine whether a saturated zone can be configured such that N removal can be facilitated without creating the risk of P leaching – i.e. co-optimising N and P removal
+ study the influence of biofilter design (i.e. filter media type, vegetation, inclusion of a saturated zone and carbon source) and variable hydrologic conditions on N and P removal performance, plant growth and nutrient uptake and short-term P-partitioning in filter media
+ investigate where and in what form P is retained in biofilter media and the implications this may have for long-term P retention in biofilters

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Chapter 3: Enhancing Phosphorus Removal in Biofilters Using Iron-rich Filter Media

Foreword

Iron-phosphorus interactions are an important mechanism for phosphorus sequestration in aquatic and terrestrial environments. Applying this knowledge in the context of biofilters may provide a means to enhance the effectiveness and longevity of phosphorus removal. The present chapter describes experimental work undertaken to investigate the phosphorus sorption properties of various biofilter media. This investigation focuses primarily on determining whether the use of an iron-oxide coated sand (Skye sand) can ameliorate the phosphorus removal capacity of biofilters. More broadly, this chapter aims to improve understanding of the role of filter media in facilitating phosphorus removal in stormwater biofilters.

This chapter is presented in the format of a journal paper and contains content from a published conference paper:

Glaister, B., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (unpublished). Enhancing phosphorus removal in stormwater biofilters using natural iron-oxide coated sand.

Glaister, B., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (2011). Can stormwater biofilters meet receiving water phosphorus targets? A pilot study investing metal-oxide enriched filter media. 15th International Conference of the IWA Diffuse Pollution Specialist Group on: Diffuse Pollution and Eutrophication. Rotorua, New Zealand, IWA.

This conference paper and supplementary information for this chapter can be found in the Chapter 3 Appendix.

Objectives and hypotheses

This chapter presents experimental research designed to investigate the use of novel filter media to ameliorate the phosphorus removal performance of biofilters. The experimentation includes tests to examine the physical and chemical properties of the filter media as well as batch- and through flow column-tests to examine the phosphorus sorption properties of the filter media. The present chapter aims to answer the following questions:

- what physical and chemical properties of filter media most influence their phosphorus removal effectiveness?
- does blending Skye sand and loamy sand filter media have the potential to improve the phosphorus removal performance (i.e. efficacy, longevity) of biofilters?
- does using Skye sand enhance the ability of biofilters to remove P at very low concentrations?
- could Skye sand filter media provide biofilters with the potential to achieve water quality targets for ecosystem protection (i.e. ANZECC water quality guidelines)?

The main hypotheses tested are as follows:

- phosphorus has a strong affinity for iron. Therefore, incorporating an iron-rich filter media into biofilters could ameliorate the effectiveness of phosphorus removal
- being an iron-rich filter media, ‘Skye sand’ should demonstrate a greater capacity to remove and retain phosphorus than typical loamy sand filter media

Abstract

Biofiltration systems have been shown to be an effective technology for the removal of phosphorus from stormwater. However, dissolved phosphorus concentrations in biofilter effluent, mainly in the form of phosphate, are typically in excess of receiving water guidelines for ecosystem protection. This study investigated phosphorus sorption properties of different filter media, including a naturally occurring iron-coated sand, known as Skye sand. Batch-sorption tests demonstrated that Skye sand had a higher phosphate sorption capacity than standard loamy sand filter media, particularly at low equilibrium concentrations, and therefore could be used to enhance phosphate removal in stormwater biofilters. The Freundlich and Langmuir adsorption-isotherm equations both described the batch-test data well and indicated that Skye sand had a stronger affinity for phosphate sorption than loamy sand, which may improve the long-term retention and removal capacity of phosphate in biofilters. This was attributed to the high surface area and Fe and Al content of Skye sand, each of which correlated strongly with phosphate removal.

Column studies showed that blending Skye sand with loamy sand at a ratio of approximately 2:1 extended the 'useful' phosphate removal life-span of the filter media (i.e. the period during which effluent concentrations remained below water quality guideline trigger values, <0.02mg/L) by almost 2 years, representing a six-fold increase in the amount of phosphate removed from the standard loamy sand filter media. However, due to the gap-grading and high fraction of very fine particles in Skye sand, blending Skye sand with loamy sand at a ratio of 1:2 or 1:3 would be recommended to enhance phosphate sorption capacity whilst maintaining hydraulic integrity.

This study highlights the important role that filter media, and its composition, play in reducing phosphate concentrations in stormwater through biofiltration. Nevertheless, these findings showed that filter media alone is unlikely to facilitate adequate phosphorus removal across the entire lifespan of a biofilter, thus highlighting the importance of biological assimilation for effective long-term operation.

3.1 Introduction

Conveyance of stormwater through conventional drainage systems has been recognised as a major cause of urban waterway pollution and degradation (Hatt et al. 2004; Paul et al. 2001; Walsh 2000). Phosphorus (P) is a critical pollutant in stormwater runoff which, when present in excess concentrations, may contribute to the eutrophication of receiving waters (Smith et al. 1999). Recognition of these impacts has led to increasing uptake of source-control technologies such as biofilters (also known as bioinfiltration systems, bioretention systems or rain gardens) to improve stormwater quality and hydrology and to protect aquatic ecosystems (Davis 2005; Wong 2006).

Biofilters typically consist of an excavated trench filled with a vegetated porous medium (usually loamy sand). Particulate associated P, which accounts for approximately 70% of total phosphorus (TP) (Duncan 2003), is removed primarily through sedimentation and filtration, as stormwater moves across the biofilter surface and percolates through the filter media (Davis et al. 2001; Fletcher et al. 2006). Dissolved forms of P, including inorganic phosphate (P_i), are removed within biofilters via adsorption, chemical precipitation plant uptake and microbial immobilisation (Hatt et al. 2008; Hsieh et al. 2007; Kadlec et al. 1996; Reddy et al. 1999).

Previous research has demonstrated that biofilters are an effective technology for removing phosphorus from stormwater (Davis et al. 2001; 2006). However, if filter media contains a labile pool of phosphorus, biofilters have been shown to behave as a source of phosphorus rather than a sink (Dietz et al. 2005; Hatt et al. 2009; Hunt et al. 2006). Conversely, when designed with an appropriate filter media and suitable plant species, biofilters have demonstrated greater than 90% reductions in the concentrations of TP and P_i (Bratieres et al. 2008; Henderson et al. 2007). Despite this, reported concentrations of P_i and TP in biofilter effluent typically exceed water quality guidelines for the protection of receiving waters (e.g. ANZECC & ARMCANZ, 2000). To ensure that biofilters achieve ecosystem protection objectives and maintain effective phosphorus removal throughout the system lifespan, the P_i removal capacity of filter media needs to be increased.

Sorption is regarded as the dominant process for dissolved pollutant removal in soil-plant wastewater treatment systems (Kadlec et al. 1996; Reddy et al. 1999). The term sorption is used broadly to describe the removal of a solute from solution through adsorption, absorption or precipitation. These studies have tested a range of materials, including sands, soils, clays (Arias et al. 2001; Del Bubba et al. 2003) and other natural materials (Arias et al. 2005; Brix et al. 2001; Drizo et al. 1997; Forbes et al. 2004; Molle 2011; Ray et al. 2005). Processed and modified minerals (Beck et al. 2011; Dao 2003; Robb et al. 2003; Zhu et al. 2003) and a range of industrial waste products have also been tested (Babatunde et al. 2009; Bird et al. 2010; Bryant et al. 2012; Miller et al. 2011; Sakadevan et al. 1998; Zhang et al. 2008).

This research has typically concluded that filter media and/or amendments that are fine textured with a high surface area are well suited to enhancing phosphorus removal from polluted water. Materials with a high metal-oxide content, especially materials with a high iron (Fe) content or iron-oxide coating have also been shown to be particularly effective at removing phosphorus via adsorption (Boujelben et al. 2008; Erickson et al. 2010; Liu et al. 2012; Oguz 2004; Van Riemsdijk et al. 1984). This is perhaps not surprising given that sorption to Fe plays an important function in the cycling of phosphorus in the natural environment (Reddy et al. 1999). However, many of these materials, in particular those derived from industrial waste by-products, present potential contamination hazards. Therefore, in the interest of satisfying sustainability objectives and minimising the risk of further stormwater contamination, materials used to ameliorate phosphorus removal in biofilters should be non-hazardous. Further, although these studies provide sound evidence to support the use of materials to ameliorate phosphorus removal in stormwater biofilters, most were conducted within the context of treating agricultural runoff or wastewater, the phosphorus concentration and inflow dynamics of which are very different to stormwater. Therefore, more stormwater-centric research should be conducted before conclusive recommendations can be made with regard to these ameliorants. Through a series of laboratory-scale tests this study investigates the P_i sorption properties of 'Skye sand', quartz sand with a natural coating of very fine amorphous iron particulates, and evaluates its potential for enhancing the P_i removal capacity of stormwater biofilters.

3.2 Materials and methods

3.2.1 Summary of methods

Experimental work was undertaken in three stages (Figure 3.1). First, the physical and chemical characteristics of the filter media were analysed. Following this a series of batch-sorption tests were conducted to investigate the rate and capacity of P-sorption to filter media. Column experiments were then used to investigate filter media P-sorption properties in a through-flow operational environment.

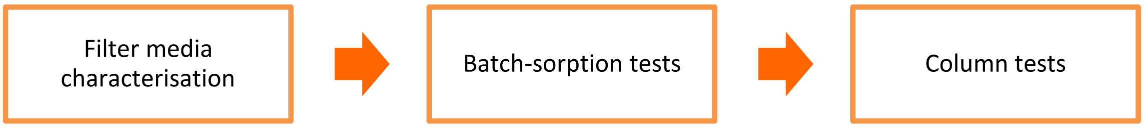

Figure 3.1. Flowchart of experimental methods

3.2.2 Filter media characterisation

Three filter media were tested in this study: an engineered loamy sand currently recommended for use in biofilters (FAWB 2009a), a natural iron-coated sand, 'Skye sand' (Figure 3.2), and coarse washed sand, typically used as a transition medium in biofilters. All filter media were obtained from local suppliers in Melbourne, Australia. Skye sand was procured directly from the sand quarry in Skye, Victoria. Prior to analysis all materials were oven dried for 24 hours at 60˚C and sieved through a 2mm sieve to remove deleterious material. The particle size distribution (PSD) of the filter media was analysed on a volume basis using a particle size analyser (Malvern Mastersizer 2000). Surface area was also determined where N_2 was the absorbate (Micromeritics Gemini 2390). The density of the filter media was evaluated using standard test methods (ASTM 2009).

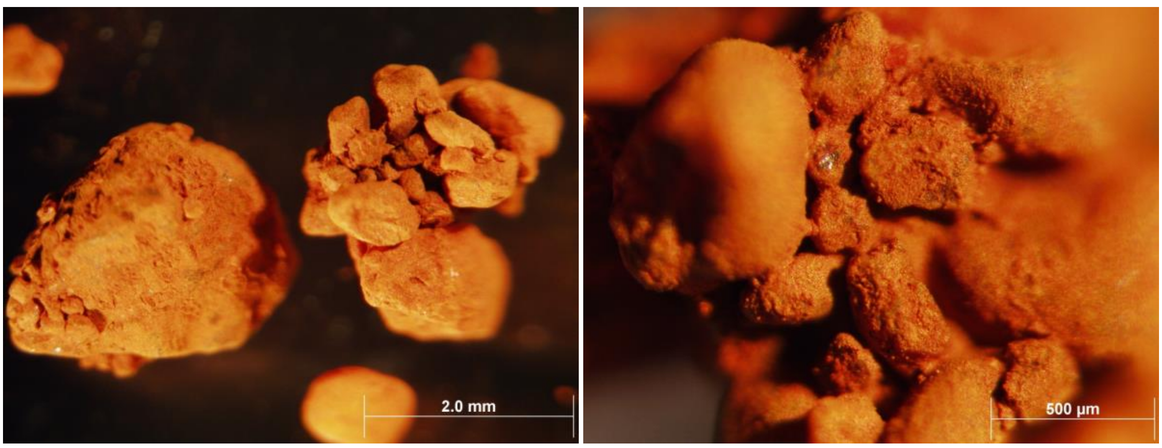

Figure 3.2. Optical microscope image of Skye sand showing fine coating of amorphous iron particles.

To investigate the influence of the very fine amorphous iron particles which coat the surface of Skye sand, a sample was washed in a 1M NaOH solution and rinsed in a wet sieve to remove particles less than 100µm. Figure 3.3 shows the Skye sand before and after washing. The effect of the washing on the morphology of the particles was qualitatively analysed with a scanning electron microscope (SEM) (FEI Quanta 3D FEG). Further SEM imaging of the different filter media was conducted for qualitative purposes, see the Chapter 3 Appendix section A3.2. The concentration of Fe, Al, Ca, Mg and reactive P_i in each filter media was analysed using an inductively-coupled plasma mass spectrometer/optical emission spectrometer ICP-MS/OES (n=2). The atomic mass percentage of iron-oxide in Skye sand and loamy sand was determined using X-ray fluorescence (XRF) and the major iron types characterised using X-ray diffraction (XRD). The distribution of elements in the Skye sand were also visualised qualitatively under SEM using Energy Dispersive X-ray analysis (EDAX), these images are presented in Chapter 3 Appendix section A3.3. All assays were undertaken by NATA (National Association for Testing Authorities) certified laboratories.

Figure 3.3. Skye sand before (left) and after (right) washing with a 0.1M NaOH solution and rinsing through a 100µm sieve (wet).

3.2.3 Batch sorption experiments

Batch-sorption tests were conducted to investigate P_i removal in filter media with different physical and chemical properties. Samples of Skye sand (SS), loamy sand (LS), coarse washed sand (CWS), washed Skye sand (SSW) were analysed. In addition, <75µm diameter fractions of Skye sand (SS<75µm) and loamy sand (LS<75µm) were tested. These very fine samples, obtained using a 75µm sieve, were included to quantify the P_i removal associated with this fraction of filter media, and investigate the influence of the presence Fe on P_i removal in this range. Overall 6 filter media types were tested.

To determine the exchangeable concentrations of Fe, Al, Ca, Mg and P_i, 1g samples of each filter medium was agitated in 50mL 0.1M KNO_3 for 20 hours using an orbital shaker (250RPM) (Del Bubba et al. 2003). The KNO_3 solution maintained the electrical conductivity of the solution at approximately 10,000µS/cm. Blank tubes containing no filter media were included to monitor incubation P_i concentrations (C_i). The samples were centrifuged for 10mins (4000RPM) before a 30mL aliquot of supernatant was drawn off and passed through a 0.45µm filter (Bonnet scientific) then analysed for Fe, Al, Ca and Mg using ICP-MS/OES, and P_i, measured as filterable reactive phosphorus (FRP), via flow injection analysis (FIA) (Molybdenum-blue ascorbic acid method) (APHA/AWWA/WPCF 2001). A second unfiltered aliquot (20mL) was used to measure the equilibrium pH and conductivity of the filter media.

A kinetic batch-sorption test was then conducted to measure the rate at which P_i is sorbed by the filter media. This test would also reveal any desorption of P_i from the filter media over a 24 hour period. Samples of each filter media (1g) were placed into 11 separate centrifuge tubes (50mL, Falcon TM), 66 samples in total. A 40mL solution representing typical P_i concentrations in stormwater (0.1mg-P/L) (Duncan 2006; Taylor et al. 2005) was prepared by adding 39.6mL of 0.1M KNO_3 and 0.4mL KH_2PO_4 (10mg-P/L) to the tubes. The tubes were then sealed, placed in test tube racks, and strapped horizontally to an orbital shaker agitating at 250RPM. Once again, blank samples containing no filter media were included to monitor incubation P_i concentrations. One tube per filter media type was retrieved at the following intervals: 1, 2, 5, 10, 20, and 40min, and 1, 2, 4, 8, and 24 hours. The samples were centrifuged for 10mins (4000RPM) before the supernatant was drawn-off, filtered (0.45µm) and analysed for FRP using FIA. A second batch-sorption test investigated P_i removal at different solid/solution ratios. Different quantities of each filter media (0.05g, 0.1g, 0.25g, 0.5g and 1.0g) were agitated for 2 hours in a 40mL solution of 0.1M KNO_3 and KH_2PO_4 (0.1mg-P/L), then analysed for P_i as per the previous batch-test.

3.2.3.1 Adsorption models

The Freundlich and Langmuir adsorption-isotherm equations are commonly used to model P_i removal and equilibrium P_i concentration relationships (Arias et al. 2001; Boujelben et al. 2008; Del Bubba et al. 2003). In this study both the Langmuir and Freundlich adsorption-isotherm equations were applied to the batch-test data to determine which best describes the P_i removal by different filter media types.

The Langmuir model was first used to describe P_i sorption on mineral surfaces by Olsen et al. (1957) and since then has been widely used for this purpose (e.g. Del Bubba et al. 2003; Parfitt 1978; Sposito et al. 1977; Syers et al. 1973). The Langmuir equation can be written in non-linear form as:

$$\frac{q}{Q} = \frac{bC}{1+bC} \tag{1}$$

where C is the equilibrium concentration (mg/L), q is the mass of adsorbate per unit mass of adsorbent at equilibrium (µg/g), Q is the maximum mass of adsorbate adsorbed at saturation per unit mass of adsorbent (µg/g), and b is an empirical constant with units inverse to concentration C (l/mg) which is a measure of the adsorbent's affinity for the adsorbate (Barrow 1978; Del Bubba et al. 2003). In linear form, Equation (1) becomes:

$$\frac{C}{q} = \frac{C}{Q} + \frac{1}{bQ} \tag{2}$$

which describes a straight line with the slope $1/Q$ and intercept $1/bQ$ (Olsen et al. 1957). This equation theoretically allows for estimating the sorption maximum, Q, and the constant b, which represents the inverse of the equilibrium concentration of adsorbate at one-half saturation and therefore gives a measure of the affinity of the adsorbate for the adsorbent (Del Bubba et al. 2003). As the value of this constant increases, the bonding energy of the soil for phosphorus increases (Olsen et al. 1957).

The Freundlich adsorption-isotherm equation can also be used to describe phosphorus adsorption by soils (Barrow 1978). This isotherm can be written as

$$q = aC^b \tag{3}$$

where C and q have the same aforementioned meanings, and a and b are constants. All constants were derived using the solver tool in Microsoft excel by optimising for the minimum residual sum of squares.

3.2.4 Column experiments

3.2.4.1 Experimental apparatus

A time-accelerated dosing column experiment was conducted to compare the P_i removal capacity of loamy sand filter media with a blended filter media comprising Skye sand and loamy sand. Two additional filter media configurations: loamy sand blended with iron ore and loamy sand blended with goethite, were also tested, however, these materials were neither effective nor suitable for ameliorating phosphorus removal in biofilters and thus were omitted from the present chapter for brevity. The iron ore and goethite column results were reported in a conference paper (Glaister et al. 2011) (see Chapter 3 Appendix section A3.1).

Six columns (Chromaflex, Multi-Lambda Scientific, 25 x 150mm, Figure 3.4) tested three replicates of the alternate filter media configurations under vertical through-flow conditions simulating stormwater contact with filter media in biofilters. The control columns contained 120g of loamy sand, whilst the blended filter media columns contained 40g of loamy sand and 70g of Skye sand, which were blended ex-situ until homogeneous. The target concentration of Fe in the blended loamy sand and Skye sand columns (as well as the other columns configurations tested) was 800 mg-Fe, compared with 160 mg-Fe in the control columns. Achieving this Fe content target meant the mass of filter media used varied slightly between the configurations (~10g).

To reduce disparity between the replicates and satisfy soil guidelines for biofilter media, equal mass portions of filter media across three particle size fractions were added based on the following percentages of total mass: 7%<106μm, 106μm<50%<400μm, 400μm<43%<1700μm (FAWB 2009b). The columns were filled manually using a funnel then flushed with 2L of deionised water to fill voids, flush free particles and minimise preferential flow paths; wetting the soil also reduced the filter media hydrophobicity.

3.2.4.2 Inflow characteristics

A synthetic solution of dissolved phosphorus (0.1mg-P/L) was prepared using KH_2PO_4. To account for the presence of organic matter or natural polymeric compounds in stormwater, which may compete with P_i for sorption sites, dissolved humic acid (3.0mg/L) was also added to the inflow solution (Hongve 1997). This target concentration was based on typical concentrations of dissolved organic carbon (DOC) in stormwater (Hatt et al. 2004).

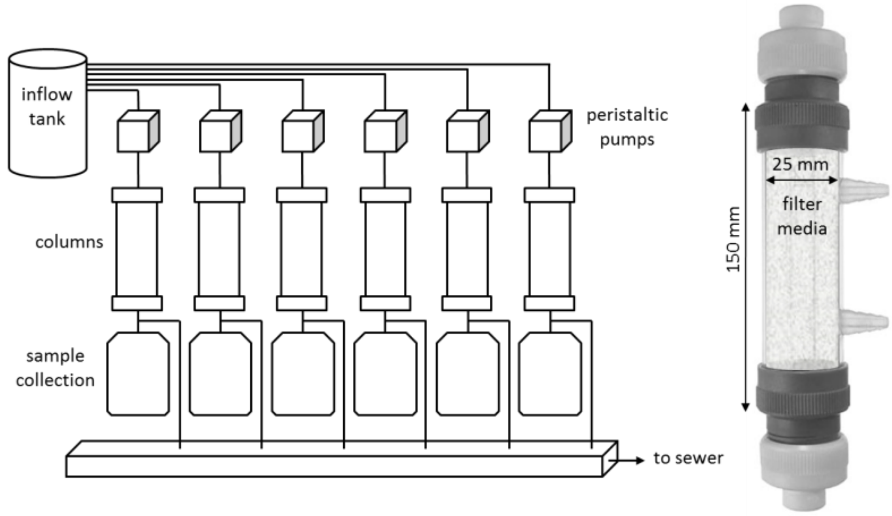

Figure 3.4. Apparatus for column experiment

3.2.4.3 Column dosing regimen

Peristaltic pumps conveyed the inflow solution from a 20L tank (replenished periodically) to the columns at a constant infiltration rate of 820mm/hr. This is substantially higher than the recommended infiltration rate for biofilters (200-400mm/hr) (FAWB 2008) and thus represents a short-term retention (i.e. worst-case scenario testing). To distribute flow evenly and minimise particle migration the inlet and outlet of the columns contained a 20μm nylon mesh. The equivalent of 2.5 years of rainfall (reflecting a 6 month average recurrence interval (ARI) storm for a biofilter sized to 2% of its contributing catchment area) was passed through each column (approx. 32L) over seven days. Inflow operated in 12 hour intervals to reflect the cyclic wetting and drying conditions which biofilters experience. Flow operated continuously during dosing intervals.

3.2.4.4 Data collection

Effluent samples were collected to monitor P_i removal at the beginning of the experiment (t=0) and at intervals corresponding to volumes equivalent to 6 months of rainfall passing through the columns (i.e. 6.3L) until 2.5 years were completed. Six effluent sampling events occurred in total. Inflow samples were collected at the same intervals to monitor influent P_i concentrations (C_i). The samples were analysed for total phosphorus (TP), filterable reactive phosphorus (FRP), total organic carbon (TOC), and total iron (Fe) (to monitor leaching from the Skye sand amended columns) using standard methods (APHA/AWWA/WPCF 2001). Prior to analysis for FRP, the samples were filtered through a 0.45μm filter (Bonnet Scientific). The detection limits of TP, FRP, Fe and TOC were 0.01, 0.001, 0.02, and 0.2 mg/L, respectively. Where water quality results were below the detection limits a value equivalent to half of the detection limit was assigned. Approximately 20% of Fe results and 30% of TP results were under detection limits. No FRP or TOC results recorded were under the detection limit. Following the experiment, the filter media was removed from the columns and partitioned into 30mm segments to analyse P_i accumulation in the filter media. After the samples were homogenised, sub-samples were collected and analysed for FRP using the alkaline persulphate digestion method (APHA/AWWA/WPCF 2001).

3.2.4.5 *Calculating phosphorus removal in columns*

The amount of P_i removed by the columns (q) was calculated using the following formula

$$q = \frac{\int_0^V C_i - C_o \; dV}{M} \qquad (4)$$

where C_i represents the inflow P_i concentration, C_o the effluent FRP concentrations, V the cumulative volume treated, and M the mass of filter media in the column (Davis et al. 2001).

3.2.5 Statistical analysis

A bivariate correlation analysis was performed on the results of the sorption batch-tests to investigate relationships between P_i removal and filter media properties. Significance was quantified by the Pearson correlation coefficient and two-tailed significance tests. Independent sample t-tests compared P_i removal between filter media groups (SS<75 vs. LS<75; SS vs. LS; and SSW vs. CWS).

3.3 Results and Discussion

3.3.1 Filter media characterisation

3.3.1.1 *Physical and chemical assay*

The particle size distribution analysis (PSD) revealed that Skye sand has a far higher volume of fine particles than loamy sand and coarse washed sand. The volume of particles 2µm or less constitutes approximately 25% of Skye sand, whilst in loamy sand this range represents only 2% of total volume (Table 3.1) (see Chapter 3 Appendix section A3.4 for particle size distribution charts). Consequently, Skye sand has a substantially higher surface area than the other sands, upon which P_i sorption is largely dependent (Wild 1950). The coefficient of uniformity (d_{60}/d_{10}) indicates that both loamy sand and coarse washed sand are relatively well graded compared to Skye sand which is gap-graded.

Table 3.1. Filter media physical analysis results. Coefficient of uniformity (d_{60}/d_{10}) represents the ratio between the particle diameter at 60% passing (d_{60}) and the particle diameter at 10% passing (d_{10}). Specific surface area was measured using the Brunauer–Emmett–Teller (BET) method (Brunauer et al. 1938).

Filter Media	Particle size fraction (µm)					d_{10} (µm)	d_{60} (µm)	d_{60}/d_{10}	BET surface area (m^2/g)	Density (g/cm^3)
	Clay <2	Silt 2-63	Fine sand 63-200	Med sand 200-630	Coarse sand 630-2000					
	%									
Skye sand	25	9	10	52	4	0.6	290	480	4.8	1.9
Loamy sand	2	5	20	55	18	100	390	3.9	1.0	2.2
Coarse washed sand	0	6	59	28	7	220	640	2.9	0.4	2.6

The chemical assay determined that all filter media contained <50mg/kg TP and <0.2mg/kg P_i, measured as FRP (Table 3.2). The Fe content of the filter media differed markedly between the filter media types. Skye sand had the highest Fe concentrations, equivalent to approximately 20 times the Fe content of loamy sand. The concentration of Fe and Al in the filter media suggests that P_i removal will occur predominately through sorption to these minerals. Phosphorus precipitation with Ca may also occur, however, the solubility of these solids is highly pH dependent, and below pH 8 phosphorus is likely to be re-solubilized (Diaz et al. 1994). Washing Skye sand in NaOH reduced Fe and Al concentrations by approximately half.

Table 3.2. Filter media chemical analysis results

Media	Fe[a]	Al[a]	Mn[a]	Ca[b]	Mg[b]	Fe_2O_3[d]	Al_2O_3[d]	SiO_2[d]	Organic matter
	(mg/g)					(%w/w)			%
Loamy sand	1.0	0.9	<0.005	0.07	<0.05	0.21	0.58	99	0.2
Skye sand	21	1.0	0.005	<0.05	0.1	1.8	2.2	94	<0.1
Skye sand (washed)[c]	10	0.5	<0.005	<0.05	<0.05	-	-	-	<0.1
Coarse washed sand	0.2	0.2	<0.008	<0.05	<0.05	-	-	-	<0.1

[a] Analysed using ICP-MS (n=2), [b] Analysed using ICP-OES (n=2), [c] Skye sand washed in 1M NaOH, [d] Analysed using XRF

The scanning electron microscope (SEM) images show that after washing the surface of the Skye sand, particles appear smooth (Figure 3.5). After washing in 0.1M NaOH, the concentration of Fe in Skye sand remained an order of magnitude greater than Fe in loamy sand (Table 3.2). Conversely, the Al content of the washed Skye sand was approximately half that of loamy sand. These concentrations are associated with Fe and Al minerals not extracted by the 0.1M NaOH solution. X-ray diffraction identified Fe(III) oxide and Fe(III) oxide-hydroxide as the major iron types in Skye sand and loamy sand. Magnetite was also identified as a minor iron type in Skye sand. Evidence from a range of studies suggests that iron-oxide minerals such as magnetite, goethite, hematite and ferrihydrite can form binuclear complexes with P_i and therefore may provide a long-term storage pool for P_i in filter media (Arai et al. 2001; Borggaard et al. 2005; Goldberg et al. 1985; Khare et al. 2007).

3.3.1.2 Exchangeable ions

The exchangeable ions batch-test detected no P_i in solution (<0.001mg/L) from the filter media tested after 24 hours, indicating that P_i associated with the filter media is not extracted in the 0.1M KNO_3 solution (data omitted for brevity, see Chapter 3 Appendix section A3.5 for details). Dissolution of Fe and Al from loamy sand (0.07mg/L and 0.12mg/L, respectively) suggests that these ions are not bound as strongly to loamy sand as to Skye sand, which did not release measurable quantities of Fe or Al. This may account for the equilibrium pH of the loamy sand solution (~5.4) being marginally lower than the Skye sand solution (~6.0). The exchangeable concentrations of Ca and Mg were higher than the other cations, suggesting that a fraction of these macro-minerals are loosely-sorbed or labile. The concentration of Ca released from loamy sand (1.0mg/L) was considerably higher than from Skye sand (0.3mg/L). In instances where Ca and Mg were released, but not Fe and Al (i.e. Skye sand), pH in solution increased slightly (pH 5.9-6.0). Overall, this test found that minor dissolution of Fe, Al, Ca and Mg ions occurs in solution. These ions may bind with P_i in solution to form solid precipitates, however, these labile cations are more likely to be re-sequestered through sorption to clay minerals and natural organic matter in the filter media (Beek et al. 1979; Goldberg et al. 1985; Wild 1950).

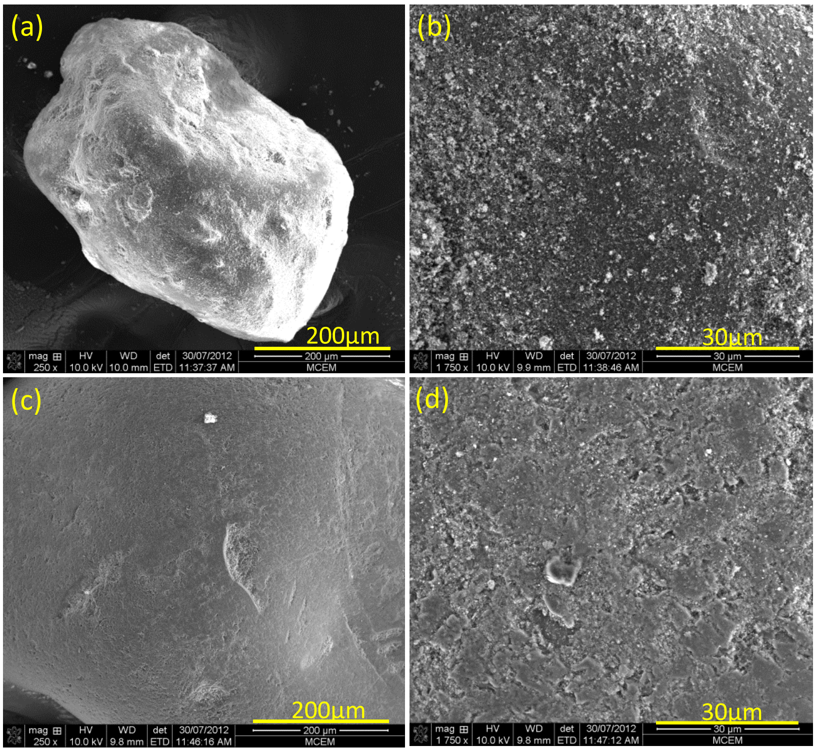

Figure 3.5. SEM images of Skye sand particles before washing (a, b) and after washing (c, d). Note: particles are of different sizes but scale is uniform.

3.3.2 Phosphate removal isotherms

The kinetic batch-sorption test indicated that all filter media samples either removed >90% of P_i from solution, or reached their maximum P_i sorption capacity within 2 hours (Figure 3.6). The <75µm Skye sand sample demonstrated the most rapid P_i sorption, achieving >99% removal after 1 minute of agitation. P_i removal by the <75 µm loamy sand sample also occurred very quickly (90% within 10 minutes). Skye sand removed 90% of P_i after 10 minutes, and washed Skye sand after 1 hour. Loamy sand exhibited a similar P_i removal rate to washed Skye sand, and coarse washed sand reached its maximum P_i sorption capacity (~70% removal) after 20 minutes. The results of the kinetic batch-test indicate that no P_i desorption occurred over the 24 hour period. The mechanism of contact between filter media and stormwater in biofilters differs considerably to that of a batch-test; in practice contact with individual particles is limited to a few seconds. Nonetheless, these results suggest that stormwater retention time, which for a biofilter with an infiltration rate of 200mm/hr and depth of 500mm is approximately 2.5 hours, far exceeds the time needed for P_i to sorb to filter media.

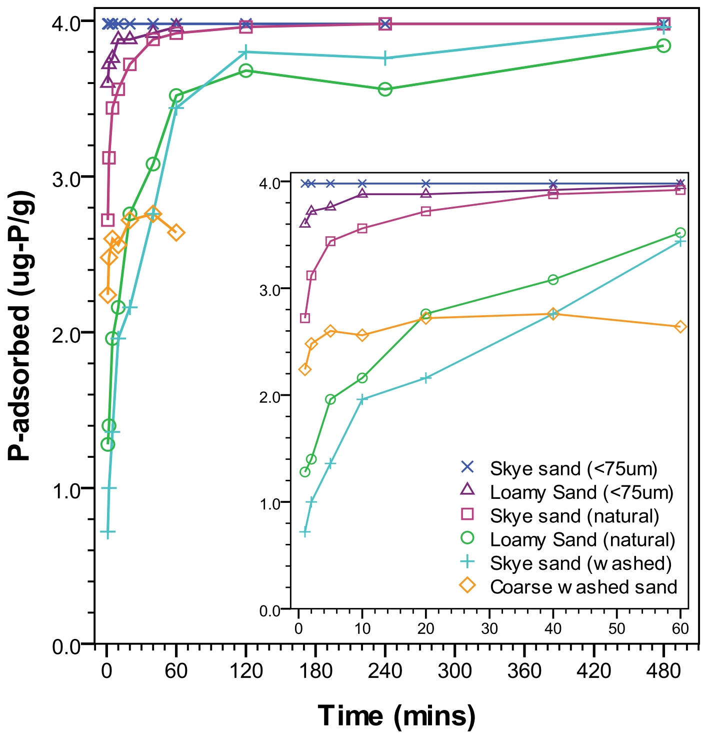

Figure 3.6. Mass of P sorbed (µg-P/g) over 8 hours of agitation in a 0.1mg-P/L solution. Note: coarse washed sand and <75µm loamy sand data only available for <60 minutes. Insert chart highlights time between 0-60 minutes.

Based on the results of the kinetic batch-tests, a 2 hour incubation period was selected for the next round of batch-sorption tests which measured equilibrium P_i concentrations (C_e) for the different filter media across a range of solid/solution ratios. Using a 2-hour incubation period may underestimate the actual P_i sorption capacity of the filter media, since slow-sorption hysteresis reactions such as occlusion by Al/Fe precipitates, precipitation of phosphorus as insoluble secondary compounds and diffusion of phosphorus into particles, will not be taken into account, nor will the renewal of sorption sites following these reactions (Barrow et al. 1975; Chardon et al. 1998; Koopmans et al. 2004; Van Riemsdijk et al. 1984).

The incubation P_i concentrations used in the batch-sorption tests were equivalent to typical P_i concentrations in stormwater (measured as FRP) (0.1mg/l). The mass of P_i removed during the batch tests is illustrated in Figure 3.7. These results are presented numerically in Table 3.3. The mass of P_i removed was calculated by the subtracting the equilibrium P_i concentration of each sample measured after 2 hours from the initial phosphorus concentration (0.1mg/L) and multiplying by the volume of solution. Since no P_i release from the filter media was detected in the exchangeable ions test, subtracting this was not necessary. These values represent the mass of phosphorus that can be removed from the solution by the filter media before no more P_i sorption can occur (i.e. if the P_i sorption capacity of the filter media is reached, or there is no more phosphorus left in the solution to sorb). Where P_i removed is equivalent to 3.98µg-P, this reflects 100% removal from solution. Not surprisingly, all filter media demonstrated increasing P_i removal with increasing filter media mass. In the context of biofilters, these results imply that Skye sand will remove more P_i than loamy sand when the same quantity of filter media is used. However, the P_i removal capacity of filter media will diminish as the volume of stormwater passed through the biofilter increases and the ratio of filter media mass to stormwater volume treated decreases.

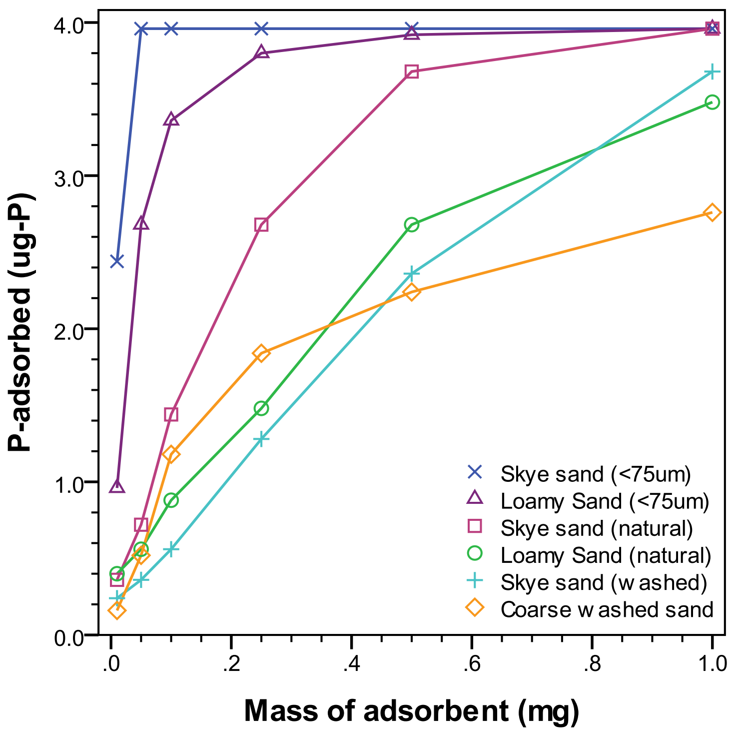

Figure 3.7. Mass of P_i removed (µm) by variable quantities (mg) of filter media following 2hrs of agitation in a 0.1mg-P/L solution (initial P_i in solution = 4.0µg).

Table 3.3. P_i removed in batch-tests using various quantities of filter media (initial P_i in solution = 4.0µg).

Filter Medium	P_i removed (µg-P)				
	0.05g	0.1g	0.25g	0.5g	1.0g
Skye sand <75um	3.96	3.98	3.98	3.98	3.98
Skye sand	0.72	1.44	2.68	3.68	3.96
Skye sand (washed)	0.36	0.56	1.28	2.36	3.68
Loamy sand <75um	2.68	3.36	3.80	3.92	3.96
Loamy sand	0.56	0.88	1.48	2.68	3.48
Coarse washed sand	0.52	1.18	1.84	2.24	2.76

These results imply that biofilters will not reach P_i saturation until the ratio of filter media mass to stormwater volume treated falls below 1.25(w/v) (Table 3.4). For a typical biofilter in Melbourne, sized to 2% of the contributing catchment area, this may represent a period of up to 20 years. However, the equilibrium P_i concentrations measured at the various filter media mass to stormwater volume treated ratios suggest that effluent P_i concentrations would exceed typical ecosystem protection objectives (i.e. effluent concentrations <0.02mg/L, ANZECC/ARMCANZ 2000) in loamy sand biofilters within 2 years, and Skye sand within 4 years. It is important to consider that these estimates are based on ideal contact between the filter media and stormwater, which is unlikely to occur in practice. As such, these lifespans could be overestimated. On the other hand, this scenario does not take into account the ability of biofilters to replenish P-sorption sites through interactions with plants and microbes (Henderson et al. 2007).

Table 3.4. Equilibrium P_i concentration reached between 40mL of P_i solution (incubation concentration, 0.1mg-P/L) and various quantities of filter media after 2 hours of agitation during batch-tests.

Media	Equilibrium P_i concentration (mg/L)				
	1.25 (w/v)	2.5 (w/v)	6.25 (w/v)	12.5 (w/v)	25 (w/v)
Skye sand <75um	0.001	0.0005	0.0005	0.0005	0.0005
Skye sand	0.08	0.06	0.03	0.008	0.001
Skye sand (washed)	0.09	0.09	0.07	0.04	0.008
Loamy sand <75um	0.03	0.02	0.005	0.002	0.001
Loamy sand	0.09	0.08	0.06	0.03	0.01
Coarse washed sand	0.09	0.07	0.05	0.04	0.03

The bivariate correlation analysis found a reasonably strong positive correlation between P_i removal and the surface area (R^2=0.67), Fe content (R^2=0.56) and Al content (R^2=0.70) of the filter media, which suggests that significantly (p<0.01) more P_i will be removed by filter media with these characteristics. The high reduction in P_i concentration achieved by the <75µm diameter fractions of Skye sand and loamy sand in the batch-tests is therefore not surprising. The <75µm Skye sand consistently removed more P_i than the <75µm loamy sand, particularly at low solid/solution ratios. Natural grade Skye sand also consistently removed more P_i than loamy sand. However, these differences were not statistically significant (p=0.05). Whether the higher concentration of Fe and Al, or greater volume of fine particles in the Skye sand, was responsible for this difference in P_i removal performance could not be explicitly determined, although both factors most likely contribute to P_i sorption. Washed Skye sand consistently removed more P_i than coarse washed sand.

This enhanced P_i sorption capacity was more likely a reflection of the higher concentration of Fe minerals in the washed Skye sand than surface area availability, since removal of the less than 100µm particle fraction made the grading of washed Skye sand resemble that of coarse washed sand.

The relationship between P_i removal per gram of adsorbent (q) and equilibrium-P_i concentration (C) was modelled using the Langmuir and Freundlich adsorption-isotherm equations. Adsorption of P_i by the various filter media showed better agreement with the Freundlich equation (R^2>0.8) than with the Langmuir isotherm across equilibrium concentrations ranging from 0 to 0.1mg-P/L (Figure 3.8). Sposito (1984) also found the Freundlich equation to be better predictor of P_i sorption than the Langmuir model at very low equilibrium concentrations. Similarly, when comparing P_i adsorption isotherms for a Western Australian soil, Barrow (1978) found that the Freundlich model had a much smaller residual sum of squares than the Langmuir, and therefore a better goodness-of-fit. The Freundlich isotherm plots in Figure 3.8 illustrate the modelled and observed batch-test data for each filter media. The plots emphasise that, as the amount of P_i removed by the filter media increases, so too does the equilibrium P_i concentration. This means that as P_i is sorbed to the filter media, and the P_i concentration of the filter media itself increases, the concentration in solution which must be exceeded before sorption will occur (i.e. the equilibrium concentration) increases. This suggests that as P_i sorption continues over time equilibrium P_i concentrations (C) will eventually meet or exceed incubation P_i concentrations (C_i), at which point no more P_i will be removed from the filter media and breakthrough will occur. Therefore, P_i removal by filter media is theoretically finite. However, depending on the composition of the filter media, sorption sites may be replenished through hysteresis (Koopmans et al. 2004; Van Riemsdijk et al. 1984).

The increase in P_i removal with equilibrium P_i concentrations is non-linear for most of the tested filter media, suggesting that the capacity of the filter media to remove phosphorus is not constant. For instance, the <75µm diameter fraction of Skye sand (SS<75µm) demonstrates very high P_i removal at low equilibrium P_i concentrations, suggesting that this medium has a strong affinity for P_i sorption. The loamy sand (<75µm) sample also removed high quantities of P_i at very low equilibrium concentrations, emphasising the influence of surface area on P_i sorption. The Skye sand and washed Skye sand Freundlich plots were indicative of a high-affinity type isotherm and very strong sorption interactions, such as the formation of inner-sphere complexes (Goldberg et al. 1985;

Van Riemsdijk et al. 1984). The shape of the loamy sand isotherm plot (ungraded) also suggests a high-affinity for P_i removal and indicates that chemisorption may be occurring. Conversely, the linear slope of the coarse washed sand isotherm resembles a constant-partition type isotherm, which is often observed when the concentration range in which sorption is being carried out is very narrow.

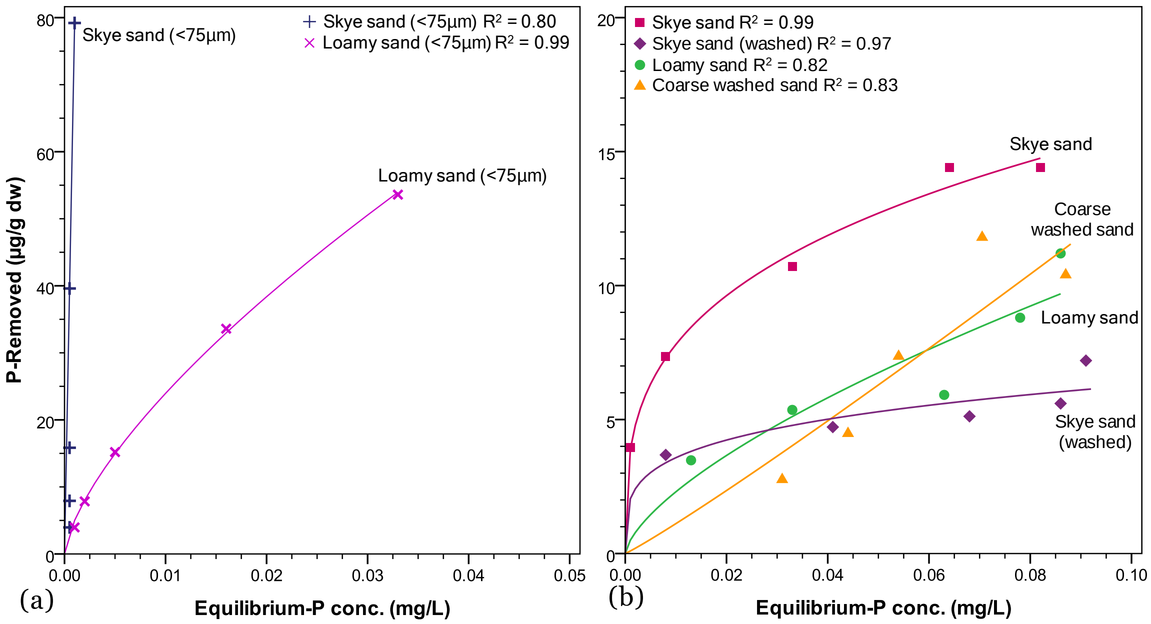

Figure 3.8. Freundlich adsorption-isotherms of P_i on filter media. Data points represent measured values. Solid lines represent model simulations according to equation 3.

The Langmuir equation in its linear form described the batch-test data between equilibrium P_i concentrations up to 0.1mg/L reasonably well with correlation coefficients (R^2) ranging from 0.59 for washed Skye sand to 0.99 for <75µm loamy sand (Figure 3.9). Due to the very high P_i removal achieved over a limited range of equilibrium-P_i concentrations, the <75µm Skye sand data could not be described by the linear Langmuir model. As such the isotherm is omitted from Figure 3.9. Estimates of the sorption maxima (Q) and the affinity of the filter media for P_i (b) determined by the Langmuir model are presented in Table 3.5. The Q values determined for the remaining media are somewhat lower than typically reported for sands and soils tested at high P_i incubation concentrations (e.g. 2.5-20mg/L) (Del Bubba et al. 2003; Egwu et al. 2010; López-Piñeiro et al. 1997). Restricting the incubation P_i concentration to 0.1mg/L may have limited the accuracy of Q, since P-sorption behaviour at high concentrations was not tested. However, in the context of biofilters, the affinity of the filter media for P_i (b) would be considered more important to maintaining treatment effectiveness and longevity than the sorption maxima, particularly since Q

values typically correlate with equilibrium-P_i concentrations outside the range that biofilters need to achieve to fulfil ecosystem protection objectives (i.e. >0.02mg/L).

The comparable *b* values for the washed and natural Skye sand suggest that after washing and removal of particles <100µm Skye sand still has strong P-binding strength. The *b* values for Skye sand (natural and washed) were considerably higher than those of loamy sand (<75um and natural) and coarse washed sand, suggesting that Skye sand has a stronger affinity for P_i. Conversely, the *Q* values for Skye sand (natural and washed) were considerably lower than those of loamy sand (<75um and natural) and coarse washed sand. However, Skye sand was able to reduce equilibrium-P_i to far lower concentrations than loamy sand and coarse washed sand (see Figure 3.9).

Table 3.5. Maximum adsorption values (Q), binding energy constants (b) and correlation coefficients (R2) estimated by the Langmuir-isotherms.

Filter Medium	*Q* (µg/g)	*b* (l/mg)	R^2
Skye sand	15	133	0.89
Skye sand (washed)	6.3	148	0.58
Loamy sand <75µm	101	33.3	0.99
Loamy sand	23.6	8.1	0.78
Coarse washed sand	435	0.31	0.81

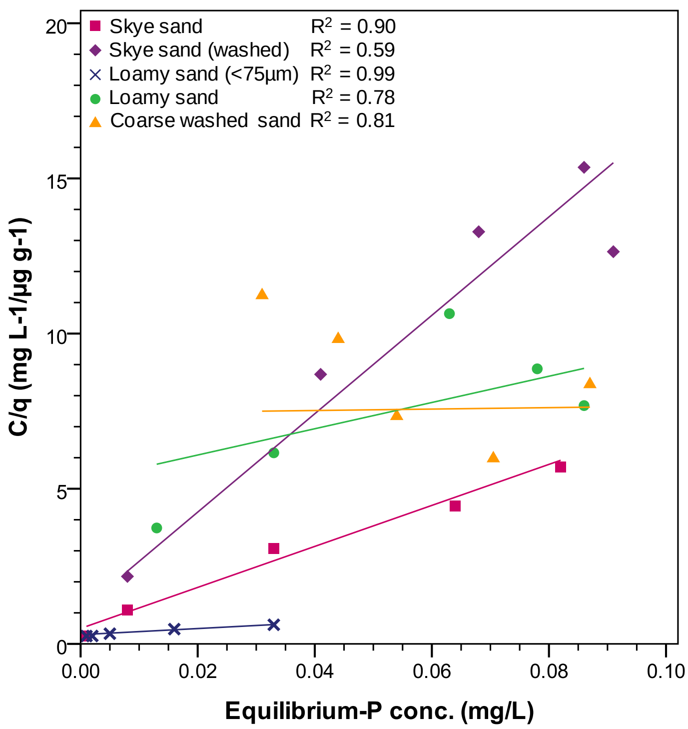

Figure 3.9. Linear Langmuir adsorption-isotherms of P_i on filter media. Data points represent measured values. Solid lines represent model simulations according to equation 2.

3.3.3 Through-flow columns

3.3.3.1 Water Quality

The P_i concentration of effluent samples collected from the columns (C_o) (measured as FRP) is presented in Figure 3.10 as a function of time simulated. Phosphate removal varied considerably between the two filter media configurations over the course of the experiment. During the first 22 months of rainfall simulated, the Skye sand augmented loamy sand filter media maintained effluent P_i concentrations below typical receiving water quality guidelines (0.02mg/L). Conversely, this concentration was exceeded by the loamy sand columns almost immediately after dosing commenced.

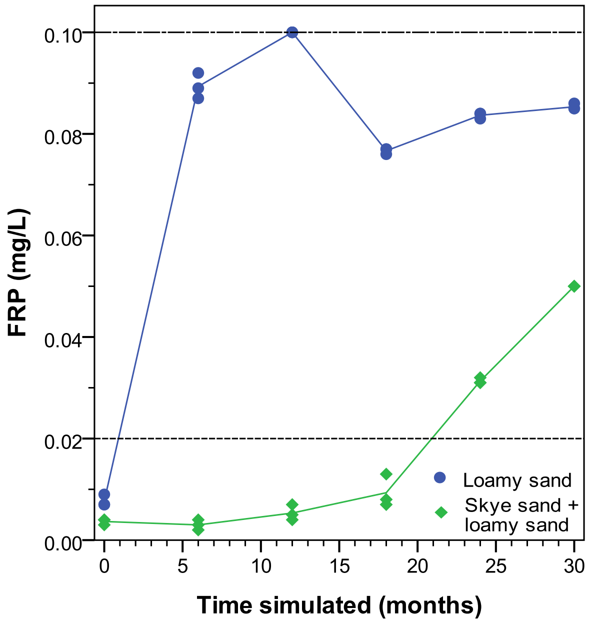

Figure 3.10. P_i concentrations in column outflow (measured as FRP). Data points represent each of the three replicates. Upper reference line denotes the inflow concentration, lower reference line represents the FRP guideline concentration for protection of slightly-moderately disturbed lowland rivers in south-east Australia (ANZECC & ARMCANZ, 2000).

The trend of gradually increasing P_i effluent concentrations from the Skye sand ameliorated columns is indicative of a typical adsorbate-adsorbent relationship. In contrast, P_i effluent concentrations from the loamy sand controls were inconsistent, showing fluctuations, albeit minor (0.09±0.01 mg/L), after 6 months of rainfall had passed. Because these fluctuations were consistent between the replicates, the number of dosing hours passed prior to collecting the samples were compared with effluent concentrations to determine if sampling times had influenced P_i removal, however no consistent pattern between these factors was discerned. This led to the conclusion that the properties of the loamy sand itself were responsible for this unique behaviour, which may have been a consequence of desorption of previously sorbed-P_i during overnight dry periods and re-sorption in subsequent re-wetting. Total phosphorus concentrations (not shown) were negligibly higher than P_i, denoting only minor wash-out of filter media bound phosphorus.

Monitoring of Fe in the columns' outflow indicated that Fe concentrations were highest at the onset of the experiment, most likely owing to mobilisation of loosely held filter media (Figure 3.11). For the duration of the study outflow Fe concentrations from both configurations were typically below detection limits (<0.02mg-Fe/L), resembling the inflow. Thus, under these conditions, leaching of Fe from Skye sand was not a concern.

Total organic carbon concentrations in the loamy sand control columns' outflow were also highest at the outset of the experiment, again, most likely owning to particulate wash-out (Figure 3.12). This was not observed in the Skye sand ameliorated columns. Indeed, outflow TOC concentrations from the Skye sand ameliorated columns were initially below the inflow, suggesting that some adsorption of humic substances occurred initially in these columns. Thereafter, outflow TOC concentrations from both configurations closely mirrored that of the inflow. Whether the presence of TOC in the effluent was due to ineffective adsorption of humic acid by the filter media or TOC leaching from the filter media itself is unclear. In the case of the former, this could be attributable to competitive adsorption between P_i and the humic substances. Otherwise, the binding strength between the functional groups in humic acid (i.e. carboxyl/hydroxyl groups) and the ions in the filter media (i.e. Mg^{2+}, Ca^{2+}, Fe^{2+} and Fe^{3+} oxides) may have been insufficient to form complexes between these compounds (Tipping 1994). The poor P_i and TOC removal demonstrated by the loamy sand control columns suggests that this could be the case. However, the mechanistic understanding of sorption interactions needed to confirm this hypothesis lies outside the scope of this study.

Leaching of TOC has been a problem with previously tested filter media for use in biofiltration systems (Hatt et al. 2008). These results therefore are promising given that TOC leaching from the filter media was negligible, if not absent, in both column configurations. It is worth noting that dissolved humic substances in urban stormwater typically absorb to suspended solids, which are removed in biofilters through filtration. The same argument could be made for P_i, which may explain, at least in part, the poor P_i removal demonstrated by the loamy sand control columns. Perhaps loamy sand biofilters rely more on trapped suspended solids to adsorb dissolved pollutants than the filter media. Comparing the P_i removal performance of the loamy sand control and Skye sand ameliorated columns in this study certainly shows a distinct benefit in terms of improved P_i sorption when Skye sand is added to the filter media.

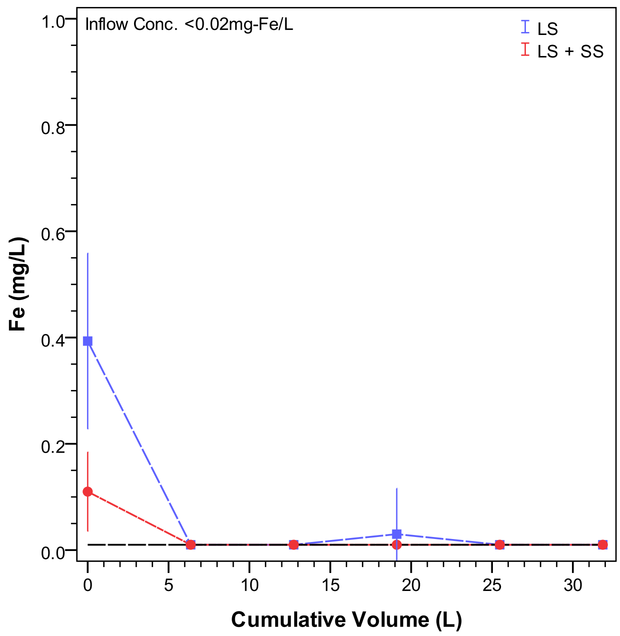

Figure 3.11. Fe (mg/L) in outflow from the loamy sand (LS) and blended loamy sand and Skye sand (LS + SS) columns**.** Dashed black line represents inflow concentration. Data points represent samples collected at volume intervals equivalent to 6 months of rainfall, 2.5 years in total. Error bars represent the 95% confidence interval.

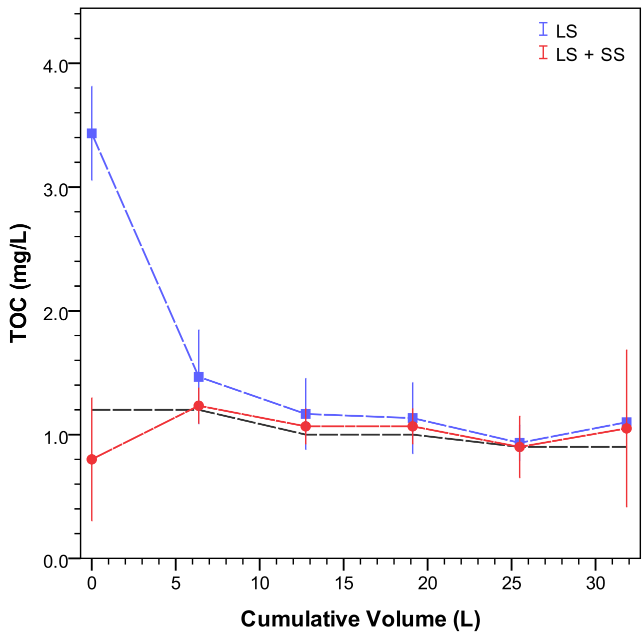

Figure 3.12. TOC (mg/L) in outflow from the loamy sand (LS) and blended loamy sand and Skye sand (LS + SS) columns. Dashed black line represents inflow concentration (N.B. Inflow concentration does not match the target of 3.0mg/L due to dilution errors). Data points represent samples collected at volume intervals equivalent to 6 months of rainfall, 2.5 years in total. Error bars represent the 95% confidence interval.

3.3.3.2 Phosphorus accumulation in the filter media

Figure 3.13 depicts the concentration profile of P_i in the filter media following the experiment (measured as FRP). The initial concentration of P_i in both filter media was <0.2µg/g, thus all P_i measured was attributable to P_i sorption during the column experiment. The profiles indicate that the Skye sand-augmented loamy sand filter media contained approximately 12µg/g of P_i, whilst the loamy sand filter media alone contained approximately 4.0µg/g. Concentrations of P_i decrease gradually down the Skye sand-ameliorated column profile, indicating that this filter media has not become fully P_i saturated. This is not surprising since these columns did not exceed their P_i sorption capacity. On the other hand, the loamy sand control columns, which did reach their P_i sorption capacity, show fairly consistent P_i concentrations along the filter media profile.

The mass of P_i removed by the columns was also estimated using the water quality results (see Equation 2). Overall, the blended Skye sand and loamy sand columns retained 2.5mg of P_i, equivalent to 80% P_i removal. The P_i removal capacity (i.e. the mass of adsorbate retained per unit mass of adsorbent at equilibrium, q) of the blended filter media was thus 23µg/g. Conversely, the loamy sand control columns retained only 0.4mg-P, or 13% of P_i, giving a q value of 3.5µg/g. These results suggest that blending Skye sand with loamy sand in these quantities increased the P_i removal capacity of the filter media six-fold. However, this q value may underestimate the total P_i removal capacity of the filter media since breakthrough was not reached in the Skye sand augmented columns.

The mass balance yielded approximately the same result as the filter media analysis when estimating the P_i content of the loamy sand columns. However, the P_i content of the Skye sand augmented filter media estimated by the mass balance was almost twice that determined by the filter media analysis. This suggests that estimating P_i removed using water quality monitoring data collected at intervals during the experiment may have overestimated the amount of P_i sorbed, for instance if P_i removal diminished between sampling events, or if loosely sorbed P_i was released from the columns subsequent to rewetting.

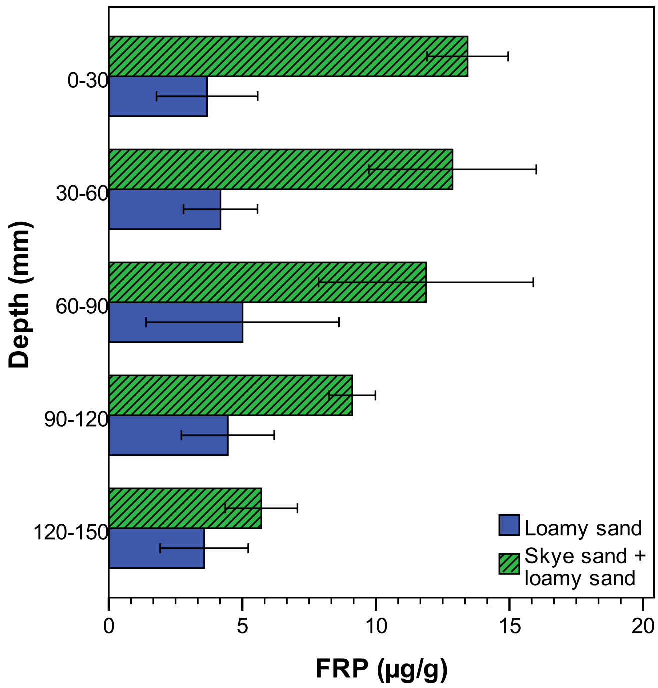

Figure 3.13. P_i accumulation down the filter media profile (measured as FRP). Data represents the mean of three replicates across the depth range indicated, error bars indicate the 95% confidence interval.

3.3.4 Use of bench-scale tests to measure the P_i removal capacity of filter media

The batch- and column-tests used in this study provided a simple method of evaluating and comparing the P_i sorption characteristics of filter media for use in stormwater biofilters. The results of these experiments recognised distinct differences in the P_i sorption properties of the different filter media and gave useful insight into understanding the role of filter media in removing and retaining P_i in biofilters. Further, the data obtained from these studies can be integrated into predictive models (e.g. the bed-depth-service-time (BDST) model (Bohart et al. 1920)) to estimate outflow P_i concentrations from biofilters over time (Feng et al. 2012). However, the direct applicability of these studies to realistic biofilter operating conditions is limited. As such, the filter media P_i removal life-span estimates extrapolated from these results should be approached with consideration of the experimental context. For instance, the batch-test estimates are based on an ideal mixing scenario, whereas in a field-scale biofilter contact between individual particles and stormwater is limited to a few seconds. Through-flow column-tests arguably provide a more realistic representation of soil-water contact in biofilters. However, whether these results can be accurately translated to a field-scale scenario is also debatable. Furthermore, these tests were conducted without sediment or vegetation, which drive major mechanisms of P_i removal in biofilters (Fletcher et al. 2006; Henderson et al. 2007). Ultimately, field-scale experiments should be conducted to verify the results of these controlled, but inherently limited, laboratory tests.

3.3.5 Outcomes for the use of Skye sand in biofilters

Investigating the P_i sorption behaviour of filter media using batch-tests determined that Skye sand has a greater capacity for P_i sorption than loamy sand, particularly at low equilibrium concentrations. Skye sand was also found to have a higher P_i binding energy than loamy sand, which reduces the risk of P_i desorption/dissolution occurring when equilibrium P_i concentrations exceed inflow P_i or physico-chemical conditions in biofilters change (i.e. redox reactions occur). A high P_i affinity filter media also gives P_i an advantage when competing with organic matter or other natural polymeric compounds in stormwater for sorption sites (Gu et al. 1994; Sposito 1984). Further, a higher binding energy increases the filter media's capacity for less reversible P_i removal to occur, for instance through precipitation as insoluble secondary compounds or slow diffusion into solids (Barrow et al. 1975).

However, using filter media with a high P_i binding strength many also present challenges. For instance, the strong ability of Skye sand to sorb P_i may hinder P_i acquisition by plants and microbes, which is essential to replenishing sorption sites in the media and prolonging the P_i removal lifespan of the system. Consequently, when selecting plants for use in biofilters containing Skye sand it should be considered whether the species have traits or symbioses known to increase the efficiency of P_i uptake (Bucher 2007; Gahoonia et al. 1998; Lambers et al. 2006; Read et al. 2010; Tibbett 2000; Van Tichelen et al. 2000) or biochemical strategies to transform phosphorus into a bioavailable form (Geelhoed et al. 1999; Petersen et al. 1991; Staunton et al. 1996).

In terms of P_i removal performance, the column study found that after dosing with the equivalent of 2.5 years of stormwater inflow, columns containing blended loamy sand and Skye sand filter media removed 80% of influent P_i compared with only 13% removed by the loamy sand only columns. From this test it was inferred that blending Skye sand with loamy sand at a ratio of ~2:1 increases the functional P_i removal lifespan of the filter media (i.e. the period during which effluent P_i concentrations remained below typical Australian guidelines for aquatic ecosystem protection, 0.02mg/L) by a factor of 6. These results imply that a 1:1 blend of Skye sand and loamy sand filter media would increase the functional P_i removal lifespan by a factor of 4, and a 1:4 blend by a factor of 2. However, monitoring of field-scale systems has shown that biofilters can maintain effective P_i removal for several years after construction when suitable filter media (i.e. low phosphorus content) and vegetation are incorporated (Davis 2007; Hatt et al. 2009; Komlos et al. 2012). This suggests that the P_i removal lifespan of biofilters is not dictated by the P_i sorption capacity of filter media alone. Indeed, as suggested by Henderson (2008), rather than providing a long-term retention pool for P_i the role of filter media primarily is to provide a short-term pool for P_i retention before assimilation by plants and microbes occurs. Consequently, biological uptake would be considered the critical process for maintaining long-term P_i removal in biofilters. Nevertheless, the P_i sorption capacity of the filter media still plays a critical role in enabling biofilters to capture and retain P_i until biological uptake can occur.

In this regard the use of filter media with a high affinity for P_i sorption presents pros and cons. For example, during periods of plant senescence or when microbial processing slows down, the role of filter media may become more critical. Moreover, during periods of frequent rainfall, use of filter media with a high P_i sorption capacity could be essential to retaining P_i long enough for biological uptake to occur. However, as abovementioned, the use of filter media with a strong P_i binding energy may also limit P_i bioavailability. Therefore, in order to determine whether Skye sand can enhance the effectiveness or increase the life-span of P_i removal in biofilters, its application needs to be studied in combination with vegetation and established microbial communities.

3.4 Conclusions

Phosphate sorption properties of filter media were investigated to evaluate the potential for using Skye sand to ameliorate the P_i sorption capacity of biofilters. Batch-sorption and column experiments determined that Skye sand has a higher P_i sorption capacity and stronger affinity for P_i than do loamy sand and coarse washed sand. The results show that blending loamy sand with Skye sand can prolong the period during which effluent P_i concentrations satisfy typical ecosystem protection objectives.

The broader implications of this study relate to whether ameliorating the P_i sorption capacity of filter media using Skye sand is necessarily the right strategy to enhance P_i removal in biofilters. The results of the batch- and column-tests suggest that facilitating biological assimilation of sorbed phosphate is critical to sustaining the long-term sorption capacity of filter media, which will otherwise be quickly exhausted (perhaps in less than 2 years based on Melbourne average annual rainfall). As such, when seeking to enhance P_i removal in biofilters the focus should be on increasing biological uptake rather than enhancing P_i retention in the filter media. Although, as biofilters mature and rates of biological uptake diminish, the capacity for filter media to provide effective long-term phosphorus sorption will become more critical. In this regard, Skye sand filter media has demonstrated a very good capacity to enhance P_i removal and the potential to sustain long-term P_i sequestration in biofilters. Further research is needed to understand the broader pollutant removal and hydraulic performance of Skye sand in biofilters operating under field-representative conditions and in combination with vegetation.

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Chapter 4: The Influence of Biofilter Design on Phosphorus Removal

Implications for Co-optimising N and P Removal

Foreword

This chapter presents the results of a stormwater biofilter column study investigating the influence of biofilter design (filter media type, presence of vegetation and inclusion of a saturated zone and carbon source) and seasonal hydrologic variability on N and P removal in biofilters. The influence of extended dry periods and high inflow volumes on intra-event N and P removal is also investigated.

The chapter is presented in the format of two journal papers:

Glaister, B. J., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (2014). Co-optimisation of Phosphorus and Nitrogen Removal in Stormwater Biofilters: the Role of Filter Media, Vegetation and Saturated Zone. Water Science & Technology 69(9): 1961-1969.

Glaister, B. J., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (unpublished). Intra-event Nutrient Removal Dynamics in Stormwater Biofilters.

The first is currently available online and is presented in the format submitted to the journal. Numbering of sections, figures, tables and pages has been altered for consistency within this thesis. This paper is based upon a published peer-reviewed conference paper:

Glaister, B. J., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (2013). Co-optimisation of Nitrogen and Phosphorus Removal in Stormwater Biofilters: the Role of Filter Media, Vegetation and Saturated Zone. 8th International Conference on Planning and Technologies for Sustainable Urban Water Management Novatech. Lyon, France.

The second paper (unpublished) is also based upon a published peer-reviewed conference paper:

Glaister, B. J., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (2016). Intra-event nutrient removal dynamics in stormwater biofilters: the influence of system design. 9th International Conference Novatech, Lyon, France, June 28 – July 1.

The abovementioned published journal and conference papers as well as supplementary information for this chapter can be found in the Chapter 4 Appendix. References for the two papers are combined at the end of the chapter to avoid duplication.

Objectives and hypotheses

This chapter presents experimental research associated with a stormwater biofilter column study. This work extends the investigation of Skye sand presented in Chapter 3 by examining the performance of this filter media in combination with vegetation under realistic biofilter operating conditions. Moreover, this research aimed to determine whether biofilter design can be co-optimised for N and P removal using Skye sand and other design characteristics known to improve nitrogen removal (saturated zone and carbon source). This chapter aims to answer the following questions:

- how does Skye sand perform under operating conditions representative of field conditions?
- can a biofilter achieve co-optimised nutrient removal?
- does including a saturated zone augmented with a carbon source lead to leaching of P from (i) reduction of iron-phosphate compounds or (ii) biodegradation of the carbon source?
- can nutrient outflow concentrations satisfy local water quality guidelines for ecosystem protection?
- how is nutrient removal affected by a variable hydrologic regime?
- do nutrient concentrations in biofilter outflow vary during events?
- how do biofilter design characteristics affect intra-event variations in nutrient removal?

The main hypotheses tested are as follows:

- leaching of P from organic matter in the saturated zone can be prevented through selection of low P content carbon sources
- reduction of Fe^{3+} in the saturated zone can lead to dissolution of iron oxide bound phosphates and P leaching
- inclusion of a saturated zone can:
    - enhance nutrient removal, mainly N, by increasing retention time and maintaining optimal function of plants and microbes
    - protect biofilters during and maintain nutrient removal following dry periods
    - reduce fluctuations in outflow nutrient concentrations during events

Co-optimisation of phosphorus and nitrogen removal in stormwater biofilters: the role of filter media, vegetation and saturated zone

Bonnie J. Glaister[1], Tim D. Fletcher[2], Perran L. M. Cook[3] and Belinda E. Hatt[1]

[1] CRC for Water Sensitive Cities, Water for Liveability Centre, Department of Civil Engineering, Monash University, Victoria, 3800, Australia (E-mail: bonnie.glaister@monash.edu)

[2] Waterway Ecosystem Research Group, Department of Resource Management and Geography, Melbourne School of Land and Environment, the University of Melbourne, Victoria, 3121, Australia

[3] CRC for Water Sensitive Cities, Water Studies Centre, School of Chemistry, Monash University, Victoria, 3800, Australia

Keywords

Biofilter, nitrogen, phosphorus, saturated zone, Skye sand, stormwater

Abstract

Biofilters have been shown to effectively treat stormwater and achieve nutrient load reduction targets. However, effluent concentrations of nitrogen and phosphorus typically exceed environmental targets for receiving water protection. This study investigates the role of filter media, vegetation and a saturated zone in achieving co-optimised nitrogen and phosphorus removal in biofilters. Twenty biofilter columns were monitored over a 12-month period of dosing with semisynthetic stormwater. The frequency of dosing was altered seasonally to examine the impact of hydrologic variability. Very good nutrient removal (90% total phosphorus, 89% total nitrogen) could be achieved by incorporating vegetation, saturated zone and Skye sand, a naturally occurring iron-rich filter medium. This design maintained nutrient removal at or below water quality guideline concentrations throughout the experiment, demonstrating resilience to wetting–drying fluctuations. The results also highlighted the benefit of including a saturated zone to maintain treatment performance over extended dry periods. These findings represent progress towards designing biofilters which co-optimise nitrogen and phosphorus removal and comply with water quality guidelines.

4.1 Introduction

Urban stormwater runoff has a significant impact on the health and ecological function of receiving waters (Walsh et al. 2004). Discharge of nutrient-rich stormwater into waterways can be particularly detrimental, leading to increased biological productivity and eutrophication (Duncan 1999; Kadlec and Knight 1996). Stormwater biofilters (also known as biofiltration systems, bioretention systems or raingardens) have the potential to reduce this impact. Extensive laboratory and field testing has demonstrated the effectiveness of biofilters to remove nitrogen and phosphorus from urban stormwater, confirming that these systems reliably meet load reduction targets for total suspended solids (TSS) and nutrients (TSS 80%, total phosphorus (TP) 45%, and total nitrogen (TN) 45% in Victoria, Australia). However, N removal rates remain variable and reported N and P concentrations are near or above typical Australian and New Zealand receiving water guidelines (ANZECC/ARMCANZ 2000; Davis et al. 2009; Hatt et al. 2009; Hunt et al. 2006). To provide effective protection for receiving waters, biofilters must be co-optimised for N and P removal, and achieve effluent concentrations below environmental protection guidelines.

N and P removal is governed by a range of biogeochemical processes. N removal relies on either the transformation of N species into a gaseous form (N_2) through the processes of ammonification, nitrification and denitrification or biological assimilation by plants and microbes (Vymazal 2007). Particulate-associated P is removed predominantly by physical straining and sedimentation. Removal of dissolved P is facilitated by sorption, precipitation and biological uptake (Hatt et al. 2007b; Kadlec and Knight 1996). While it has been suggested that plant uptake represents only a fraction of overall nutrient removal (Dietz et al. 2006) the role of plants in supporting nutrient removal processes has been well established in the literature (Browning et al. 2003; Read et al. 2008; Vymazal 2007) and demonstrated by several studies (e.g. Bratieres et al. 2008; Henderson et al. 2007a; Lucas et al. 2008). The importance of plant species selection as well as the influence of inter-species competition and planting regime on nutrient removal performance have also been tested (Ellerton et al. 2012; Read et al. 2010). Australian biofiltration design guidelines (see FAWB 2009) recommend the inclusion of a saturated zone (SZ) to promote anaerobic conditions between wetting events and thus enhance N removal through denitrification. The inclusion of a saturated zone has also been shown to support plant health and protect biofilters against drying during dry weather periods (Blecken et al. 2009). The variable wetting and drying cycles which biofilters experience dramatically alter oxygen concentrations and the distribution of denitrifying bacteria in the saturated zone (Chen et al. 2013; Korom 1992). Seasonality and antecedent dry weather periods therefore have a significant influence on the effectiveness of the saturated zone, which has achieved mixed success in both field and laboratory experiments (Dietz et al. 2006; Hsieh et al. 2007b; Hunt et al. 2006; Lucas et al. 2008; Zinger 2012). Furthermore, if not configured correctly the saturated zone may become an internal source of P, for instance if P retained in redox sensitive pools (e.g. Fe-bound P) becomes remobilised under reducing conditions (Boström et al. 1988), or if the organic carbon added to facilitate denitrification has a high P content. These are important aspects to consider when incorporating a saturated zone in terms of co-optimising N and P removal.

Biofilters have a finite P retention capacity (Del Bubba et al. 2003; Hsieh et al. 2007a; Wild 1950). Factors which influence this include, native P concentration, depth, chemical composition, particle size and surface area of the filter media, and the presence of other P removal pathways in the system. Presently, our knowledge regarding the role of filter media in facilitating long-term P retention remains limited. Henderson et al. (2007a; b) argue that filter media is unlikely to retain nutrients in the long-term, however, it may provide an important function by extending retention time so plant uptake and microbial assimilation can occur. Others have suggested that filter media could enable complex P sorption and precipitation processes through interactions with P attracting ions, which may strongly, or even permanently, bind P to the filter media (Arias et al. 2001; Del Bubba et al. 2003; Lucas et al. 2008). A recent study by Glaister et al. (2011) found that under simple laboratory testing a naturally occurring iron- (Fe) and aluminium- (Al) oxide rich sand, known as Skye sand, demonstrated superior phosphate removal performance compared with loamy sand, which is the filter medium currently recommended by Australian biofiltration system guidelines (FAWB 2009). Configuring biofilters with Skye sand may enhance P removal and facilitate long-term P-retention.

The present study investigates the role of filter media, vegetation and saturated zone in co-optimising N and P removal by comparing the nutrient removal performance of biofilters configured with Skye sand and loamy sand in conjunction with and without vegetation and saturated zone. Climatic variability imposed during the experiment also investigates the influence of wet and dry periods on filter media durability and treatment resilience.

4.2 Method

4.2.1 Experimental design

Column Construction & filter media selection

Twenty biofilter columns (Figure 4.1a) were constructed using PVC pipe (150mm diameter) and acrylic to create a 200mm ponding zone. The columns were designed in accordance with Australian biofiltration system guidelines (see FAWB 2009). Columns without a saturated zone drained freely from the base while a riser pipe was attached to the outlet of those with a saturated zone to maintain a 300mm pool of water in the lower half of the column (Figure 4.1b). Elemental characteristics of the Skye sand and loamy sand filter media are described in Table 4.1. An organic carbon source mixture of pine woodchips (bark removed) (26.5g) and pine flour ('sawdust') (9.3g) was blended into the saturated zone filter media to facilitate the denitrification process (total material added was equivalent to 5% of the volume of the SZ). These materials were selected on the basis of their biodegradability and low P content (10.2 mg P/kg). The biofilters were configured into four main layers shown in Figure 4.1b: (1) filter media (300mm) loamy sand or Skye sand planted with *Carex appressa*; (2) sand transition layer (200mm) coarse washed sand; (3) pea gravel drainage layer (70mm); (4) gravel drainage layer (30mm).

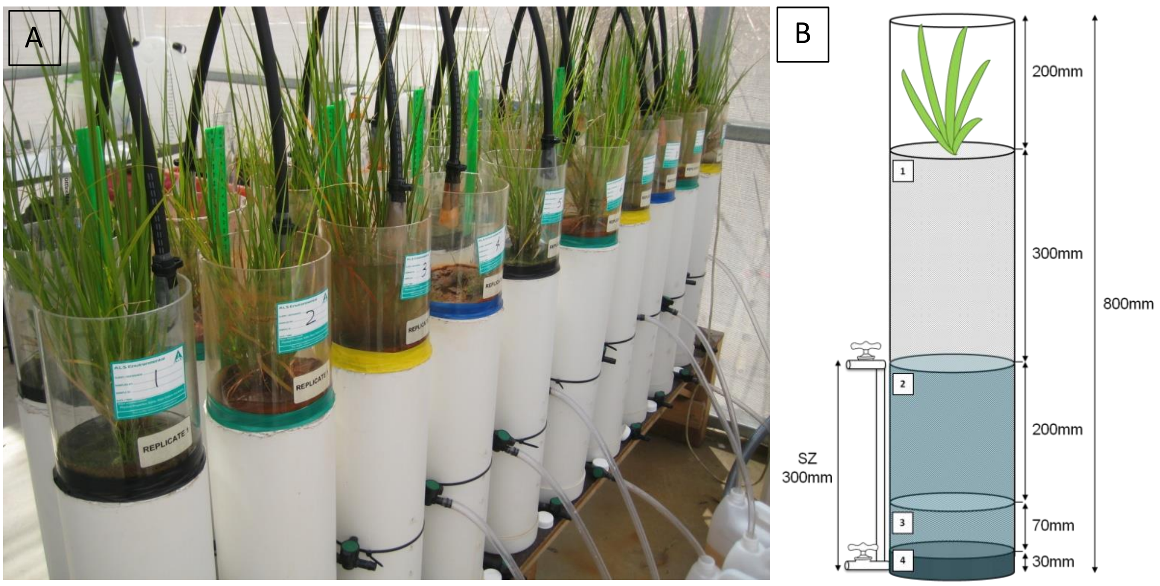

Figure 4.1 a. Experimental set-up of biofilter columns in greenhouse **b.** Schematic diagram of the biofilter columns (with saturated zone riser outlet attached)

Table 4.1. Elemental characteristics of loamy sand and Skye sand filter media (parentheses represent range)

Media	Fe[a]	Al[a]	Fe_2O_3[b]	Al_2O_3[b]	SiO_2[b]
Loamy sand	1,000 (±200)	900 (±100)	0.21	0.58	99
Skye sand	21,000 (±2000)	1,000 (±100)	1.8	2.2	94

[a]Analysed using inductively coupled plasma mass spectroscopy (ICP-MS; n = 2) (mg/kg).
[b]Analysed using X-ray fluorescence (XRF; %w/w).

Column configuration & establishment

Four design configurations were tested (with five replicates of each). The configurations are described in Table 4.2. Filter media layers 2, 3 and 4 remained constant between configurations. These configurations enabled three key relationships between design characteristics to be analysed: (i) loamy sand vs. Skye sand vegetated with SZ; (ii) Skye sand non-vegetated with SZ vs. Skye sand vegetated with SZ; and (iii) Skye sand vegetated with SZ vs. Skye sand vegetated without SZ.

Table 4.2. Biofilter column design configurations

Configuration	Filter Medium	Vegetation	Saturated Zone
Loamy sand, vegetated, saturated zone (LS-V-S)	Loamy sand	*C.appressa*	SZ
Skye sand, non-vegetated, saturated zone (SS-NV-S)	Skye sand	Non-vegetated	SZ
Skye sand, vegetated, saturated zone (SS-V-S)	Skye sand	*C. appressa*	SZ
Skye sand, vegetated, no saturated zone (SS-V-NS)	Skye sand	*C. appressa*	No SZ

The columns were filled manually then compacted using a weighted hammer (as described by ASTM F1815-11 2011). The compaction required was determined by the layer thickness and media porosity. Once filled, vegetation was transplanted into the top 100mm of the columns. The Australian native species *C. appressa* was selected because of its drought tolerance and resilience to climate fluctuations. Previous biofilter column studies have found that this species maintains very good nutrient removal under high loading conditions and inflow concentrations (Bratieres et al. 2008; Read et al. 2008). Prior to transplanting the plants were matured in a glasshouse (at 25°C) for 12 weeks. Following construction, the columns were placed in purpose-built ventilated greenhouse and dosed twice-weekly for 5 weeks with semi-synthetic stormwater to establish the plants, inoculate the soil microbial community and flush free particles out of the filter media.

4.2.2 Experimental procedure

Semi-synthetic stormwater

Due to limitations associated with the use of real stormwater, a semi-synthetic stormwater mixture was used instead. This approach minimised inflow concentration variability whilst maintaining realistic composition. Several studies have adopted this method and demonstrated consistency in maintaining target concentrations throughout the experimental period (e.g. Hatt et al. 2007b). Sediment was collected from a nearby stormwater retarding basin and strained through a 1,000µm sieve. The concentration of solids in the sieved slurry was measured prior to mixing with a known amount of dechlorinated tap water to ensure the target TSS concentration was achieved (150mg/L). Target concentrations for TSS and nutrients were matched with typical values for worldwide and Melbourne urban stormwater quality reported by Duncan (2006) and Taylor et al. (2005) respectively. The mixture was topped up using chemicals where necessary to make up the deficit in nutrient concentrations (Table 4.3).

Table 4.3 Typical Melbourne stormwater nutrient concentrations (based on concentrations reported by Duncan (2006) and Taylor et al. (2005).

Pollutant	Concentration (mg/L)	Chemical additives
Total Suspended Solids (TSS)	150	Sediments
Total Nitrogen (TN)	2.13	From N additives
Ammonia (NH_3)	0.29	Ammonium chloride (NH_4CL)
Oxidized Nitrogen (NO_x)	0.74	Potassium nitrate (KNO_3)
Organic N (ON)	1.1	Sediments and DON
Dissolved ON	0.6	Nicotinic acid ($C_6H_5O_2N$)
Total Phosphorus (TP)	0.35	Sediments and FRP
PO_4- (Phosphate ortho=FRP)	0.12	Potassium phosphate (KH_2PO_4)

Stormwater dosing, sampling & analysis

The stormwater dosing regimen reflected Melbourne average annual rainfall volumes, for a biofilter sized to 2.5% of its contributing catchment area, based on Australian design guidelines (see Hatt et al. 2007b). The columns received 3.7L of stormwater during each dosing event. The dosing campaign simulated wet and dry climate conditions by altering the frequency of events (see Figure 4.2). Each climate reflected typical Melbourne rainfall patterns (average annual effective rainfall, 540mm) (Bureau of Meteorology 2013). During the wet periods (April-November) the columns were dosed twice-weekly. During the dry period (December - March) the column dosing gradually transitioned from 6 to 18 antecedent dry days to reduce the risk of plant fatality. Sampling took place for 10 select dosing events over the 12-month period from August 2011 to July 2012. Column effluent was collected until flow ceased (approximately 3.0 of the 3.7L). This bulk sample was mixed thoroughly then sub-sampled for analysis. Samples were analysed for TSS, TN, TP and their dissolved species. Samples analysed for dissolved nutrients were filtered through a 0.45µm filter (Bonnet Scientific). All water chemical analyses were undertaken by NATA (National Association for Testing Authorities) certified laboratories using standard analysis methods (APHA/AWWA/WPCF 2001). At several points during the campaign discrete water samples were collected from ports installed along the column to measure dissolved oxygen (DO) concentrations in the saturated zone before and after dosing events using a fiber-optic oxygen meter (PyroScience FireStingO_2).

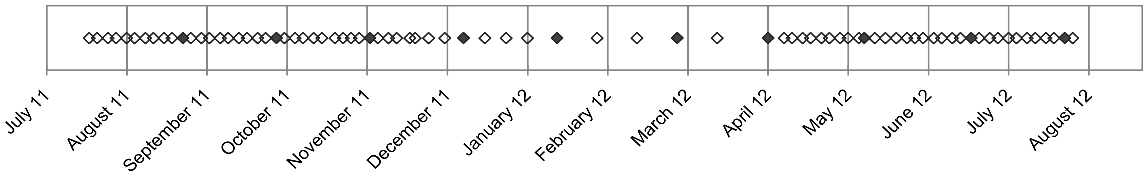

Figure 4.2. Stormwater dosing and sampling regime (filled markers denote sampled events).

Data analysis

All statistical analyses were performed using SPSS (version 20. IBM, USA). Analysis of variance (ANOVA) was used to compare performance between biofilter configurations and climate periods, with post-hoc tests used to compare individual pairs (Tukey's HSD where inequality of variance occurred and Tamhane's where not). Data reported below detection limits (e.g. <0.001) were analysed at half the limit of reporting value (e.g. 0.0005). Data from the first sample event (September) were omitted from the analysis because at this stage the columns were still establishing. Additionally, sample data from the SS-V-NS columns were omitted for the eighth event (May), as infiltration had ceased due to sediment clogging of the surface layer. This sediment layer was disturbed manually by gently scraping the surface, allowing regular infiltration to resume.

4.3 Results and Discussion

4.3.1 Phosphorus removal performance of alternative biofilter designs

The influence of filter media

Analysis of TP outflow concentrations from the loamy sand (LS-V-S) and Skye sand (SS-V-S) columns suggests that filter medium type did not significantly influence TP removal (Figure 4.3). This finding is at least partially attributed to the fact that very effective TSS removal (92-98%) was achieved by both filter media types and approximately ~70% of TP is associated with particulates (Duncan 2006) (Table 4.4). However, all design configurations also consistently achieved very good removal of PO_4^{3-} (>97%, Table 4.4) and there were no significant differences between the two filter media types. Perhaps it is not altogether unsurprising that no differences in PO_4^{3-} removal were observed given that the testing period (1 year) was relatively short and neither loamy sand nor Skye were likely to approach PO_4^{3-} saturation during this time. The role of filter media may become more important as plants reach maturity and P uptake and release (due to plant senescence) approach equilibrium. Given that Skye sand has higher concentrations of Fe and Al oxides, to which PO_4^{3-} is readily adsorbed, the sorption capacity and life-span of this media is expected to extend beyond that of loamy sand (Glaister et al. 2011).

Interactions with vegetation and saturated zone

Vegetation had a significant effect on PO_4^{3-} removal ($p<0.001$) but not TP. This is perhaps not surprising, given that PO_4^{3-} is chemically and biologically driven, while TP removal is primarily related to removal of TSS. TP removal was improved by the addition of vegetation (Figure 4.3). Vegetation provides a removal pathway for dissolved nutrients through plant uptake, and supports biological activity in the rhizosphere, which also contributes to P removal through microbial assimilation. Furthermore, vegetation improves soil structure, which provides resilience to cracking and the formation of preferential flow pathways during dry periods. The saturated zone was also found to have a significant influence on P removal (TP and PO_4^{3-}). Inclusion of the saturated zone reduced the infiltration rate by decreasing the hydraulic head, effectively creating a buffer to high-velocity flow, thereby minimising mobilisation of P-laden particles into the effluent. Retention of stormwater in the saturated zone also increases detention time between dosing events, allowing P to undergo further biological uptake and chemical complexation.

The sustained PO_4^{3-} removal throughout the campaign suggests that biodegradation of the carbon source did not contribute to P leaching and that reduction of Fe-bound P in the filter media did not occur.

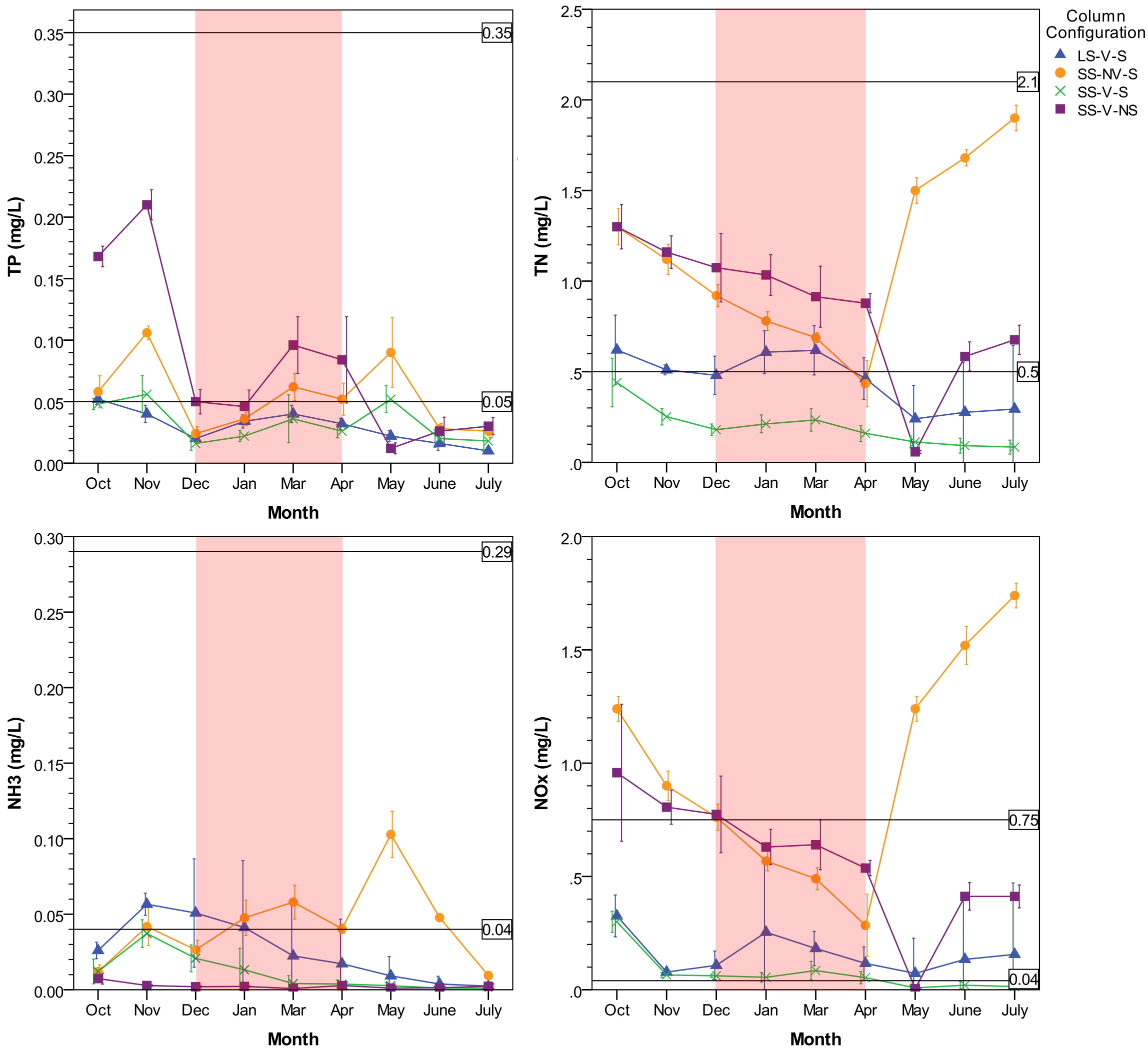

Figure 4.3. Biofilter column outflow concentrations (mg/L) from October 2011 to July 2012 (TP, top left; TN, top right; NH3, bottom left; NOx, bottom right). Data points represent the mean (n=5) and error bars represent ±1 standard deviation from the mean. Upper horizontal reference line denotes inflow concentration; lower horizontal reference line represents the water quality guideline concentration for slightly disturbed lowland rivers in South-Eastern Australia (ANZECC/ARMCANZ 2000). Shaded area represents the dry dosing period.

Table 4.4. Average inflow and outflow nutrient concentrations for wet and dry dosing periods (mg/L). Inflow concentration range and percentage removal are given in parentheses following the inflow and outflow concentrations respectively.

	TSS	TP	PO_4^{-3}	TN	NO_x
Inflow conc.	125 (±45)	0.38 (±0.08)	0.18 (0.1)	1.83 (0.35)	0.93 (0.18)
		LS-V-S	**SS-NV-S**	**SS-V-S**	**SS-V-NS**
	Wet[a]	4.70 (97)	10.69 (92)	11.96 (92)	12.13 (91)
TSS	**Dry**	4.64 (97)	8.64 (95)	14.07 (92)	10.71 (94)
	Wet[b]	2.26 (98)	2.49 (98)	3.87 (97)	2.98 (97)
	Wet[a]	0.046 (88)	0.082 (79)	0.052 (87)	0.19 (52)
TP	**Dry**	0.032 (92)	0.044 (89)	0.025 (93)	0.069 (82)
	Wet[b]	0.016 (95)	0.048 (86)	0.030 (91)	0.028 (92)
	Wet[a]	0.003 (99)	0.002 (99)	0.002 (99)	0.004 (98)
PO_4^{3-}	**Dry**	0.002 (99)	0.003 (98)	0.003 (99)	0.003 (98)
	Wet[b]	0.002 (98)	0.002 (97)	0.001 (98)	0.003 (98)
	Wet[a]	0.56 (70)	1.2 (35)	0.34 (82)	1.2 (33)
TN	**Dry**	0.54 (69)	0.71 (60)	0.20 (89)	0.97 (44)
	Wet[b]	0.27 (85)	1.7 (8)	0.096 (95)	0.63 (66)
	Wet[a]	0.041 (89)	0.027 (93)	0.026 (93)	0.005 (99)
NH_3	**Dry**	0.037 (88)	0.043 (84)	0.012 (96)	0.002 (99)
	Wet[b]	0.005 (99)	0.053 (85)	0.002 (99)	0.001 (100)
	Wet[a]	0.20 (80)	1.1 (-10)	0.18 (81)	0.88 (9)
NO_X	**Dry**	0.17 (81)	0.53 (41)	0.064 (93)	0.65 (27)
	Wet[b]	0.13 (86)	1.5 (-59)	0.013 (99)	0.41 (59)

[a]Wet period August–November
[b]Wet period April–July

4.3.2 Nitrogen removal performance of alternative biofilter designs

The influence of filter media

TN removal trends were similar for LS-V-S and SS-V-S throughout the campaign, although concentrations were consistently lower from the SS-V-S configuration (see Figure 4.3). ANOVA confirmed this, indicating a significant difference in TN and NH_3 removal between LS-V-S and SS-V-S ($p<0.001$). This may be attributed to greater adsorption of ionised ammonia (NH_4^+) in the Skye sand filter medium, which has a higher clay content than loamy sand. Filter medium type did not have a significant influence on NO_x removal, as was discussed in relation to PO_4^{3-}, and this is not surprising, given that NO_x removal is chemically and biologically driven. The very low TN and NO_x concentrations recorded in May (following clogging of the columns) highlights the sensitivity of these systems to changes in hydraulic conductivity and emphasises the influence of detention time on treatment performance. While the clogging may appear to have been beneficial for N treatment it is important to remember that under these conditions the biofilters were not operating within the infiltration rate guidelines of 200-400mm/hr.

Interactions with vegetation and saturated zone

Vegetation and the inclusion of a saturated zone had a significant influence on NO_x treatment (and subsequently TN). This was exemplified by the results for the non-vegetated (SS-NV-S) and non-saturated (SS-V-NS) configurations, which both showed poor NO_x removal throughout the experimental period (see Figure 4.3). Inclusion of vegetation supports biological removal pathways for NO_x captured from incoming stormwater and produced between events through nitrification. Mean DO concentrations in the saturated zone before (2.1 mg/L) and after (3.7 mg/L) dosing events indicated that conditions were not depleted to the point where denitrification would occur (<0.5mg/L). However, it is nevertheless possible that anaerobic microsites exist within the saturated zone where denitrifying bacteria are active (Parkin 1987). The improved NO_x removal demonstrated in the saturated zone inclusive columns may also be explained by the extended detention time imposed between events, providing further opportunity for biological uptake to occur. NH_3 removal was not affected by the presence or absence of the saturated zone, presumably because it was retained or nitrified in the upper aerobic layers. However, given the important role which the saturated zone plays in NO_x removal, its inclusion is recommended to ensure effective overall N removal.

4.3.3 Resilience to variable inflow hydrology

Outflow concentrations from the biofilters during the three climate periods, wet[a] (October-November), dry (December-March), and wet[b] (April-July) are summarised in Table 4.4. Treatment performance for all nutrients remained relatively consistent between the periods in configurations inclusive of vegetation and saturated zone (i.e. LS-V-S and SS-V-S). TP concentrations from the SS-V-S columns increased marginally when wet dosing resumed. This was attributed to particulate P mobilisation upon re-wetting. TP concentrations returned to pre-rewetting concentrations in the next sample (June). Therefore, both filter media tested were found to be resilient over extended dry periods when coupled with vegetation and a saturated zone. The saturated zone supported nutrient removal processes during the extended dry period by providing access to a permanent pool of water to sustain plant health, increasing detention time for biological removal processes to occur, and supporting hydro-chemical conditions to facilitate denitrification.

The absence of vegetation had a persistent effect on NH_3 removal performance, which gradually declined over the dry and into the second wet period. The vegetated configurations show that NH_3 removal can otherwise be maintained throughout wet and dry periods, with or without the inclusion of a saturated zone. Vegetation provides a pathway for NH_3 removal under dry conditions, when biological processes slow down limiting nitrification. The impact of wetting and drying in the non-vegetated configurations (SS-NV-S) was most detrimental to NO_x removal (and consequently TN). NO_x removal was maintained over the extended dry period owing to increased retention time, which facilitated advanced biological uptake of NO_x, and perhaps also the formation of anaerobic microsites within the saturated zone to promote denitrification (Parkin 1987). Extended detention. When regular dosing resumed, the non-vegetated systems responded immediately and began to leach NO_x which continued for the remainder of the experiment. This suggests that NO_x removal can be maintained over dry periods in non-vegetated, saturated zone inclusive columns. But, when dosing frequency increases, oxygen conditions change and detention time in the saturated zone is reduced, compromising NO_x treatment. Conversely, very good NO_x removal was maintained in the LS-V-S and SS-V-S configurations (>80% removal). This highlights the role of biological uptake in N removal and the importance of coupling vegetation with the inclusion of a saturated zone.

4.3.4 Performance relative to ecosystem protection guidelines

Table 4.5 summarises biofilter performance relative to typical Australian and New Zealand receiving water nutrient guideline concentrations (ANZECC/ARMCANZ 2000). TP concentrations less than or equal to the guideline targets were successfully achieved by the SS-V-S and LS-V-S columns throughout the experiment. At the time of the last sampling event all configurations were meeting the TP water quality guideline concentrations. All configurations maintained PO_4^{3-} concentrations below the guideline throughout the experiment. TN concentrations were maintained below guidelines throughout the experiment by the SS-V-S columns. Minimal variation between SS-V-S replicates and consistent results over the sampling events represents a success as studies often cite variability in this regard. LS-V-S outflows also remained close to the TN target concentration, increasing only marginally during the transition into the dry climate. Conversely, TN concentrations from the non-vegetated (SS-NV-S) and non-saturated (SS-V-NS) configurations remained above the guideline for the duration of the experiment. Similar trends were apparent in terms of NO_x removal, although only the SS-V-S configuration achieved the target values. The non-vegetated columns (SS-NV-S) did not achieve the NH_3 targets, although the non-saturated, vegetated configuration (SS-V-NS) achieved this target consistently. The SS-V-S and LS-V-S began to meet the NH_3 target concentration halfway through the experiment, most likely coinciding with the growth of plant roots into the saturated zone where trapped NH_3 could be accessed.

Table 4.5. Summary of success in achieving Australian and New Zealand Environment Conservation Council water quality guideline concentrations (based on trigger guideline values for lowland rivers) (ANZECC/ARMCANZ 2000).

Column	TP	PO_4^{3-}	TN	NO_x	NH_3
LS-V-S	✓	✓	✓	×	✓
SS-NV-S	✓	✓	×	×	×
SS-V-S	✓	✓	✓	✓	✓
SS-V-NS	✓	✓	×	×	✓
Guideline concentration (mg/L)	0.05	0.02	0.5	0.04	0.02

4.4 Conclusions

This study investigated nutrient removal performance of biofilter columns under the influence of design modifications (filter media type, vegetation and saturated zone) and variable climate conditions. The results demonstrated that a vegetated biofilter configured with Skye sand and saturated zone can maintain very good N and P removal, and achieve receiving water protection targets in wet and dry climates. The importance of vegetation and saturated zone to maintain co-optimised N and P removal under variable climate conditions was also highlighted. However, this experiment was undertaken over a relatively short time period, during which the plants experienced substantial growth. The nutrient removal performance exhibited by these biofilter columns should therefore be verified by research quantifying N and P removal performance as system establishment stabilises and as filter media approach P saturation. In practice, these results may have significant relevance when designing biofilters in areas which experience prolonged dry periods, or where the protection of receiving waters is a priority.

4.5 Acknowledgements

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Intra-event Nutrient Removal Dynamics in Stormwater Biofilters

Bonnie J. Glaister[a], Tim D. Fletcher[b], Perran L. M. Cook[c] and Belinda E. Hatt[a]

[a] Department of Civil Engineering, Monash University, Victoria, 3800, Australia

[b] Waterway Ecosystem Research Group, School of Ecosystem & Forest Sciences, Faculty of Science, the University of Melbourne, Burnley, Victoria, 3121, Australia

[c] Water Studies Centre, School of Chemistry, Monash University, Victoria, 3800, Australia

Abstract

Treatment performance of stormwater biofilters is typically reported as an event mean concentration. Consequently, little is currently understood about how pollutant removal fluctuates during events or how biofilter design features affect intra-event treatment. To investigate how design characteristics (filter media, vegetation and a saturated zone) and operating conditions influence intra-event nutrient removal performance, 20 laboratory-scale stormwater biofilter columns were monitored during two simulated rainfall events. Sequential sampling of biofilter outflow during the events found that vegetation and inclusion of a saturated zone have a significant influence on intra-event nutrient removal, in particular nitrogen. By imposing detention between events, the saturated zone provided further opportunity for biological uptake to occur, enhancing nutrient treatment and minimising variability in outflow concentrations during the following event. Including a saturated zone also minimised mobilisation of particulate-bound nitrogen and phosphorus. Nutrient species responded differently to changes in inflow volume and antecedent dry weather, making optimisation of nutrient removal a challenge. Biofilters containing a naturally occurring iron-coated sand, 'Skye sand', demonstrated less intra-event variability in nitrogen removal following extended dry periods than those containing loamy sand. These findings suggest that biofilters that incorporate appropriate filter media, vegetation and a saturated zone can satisfy nutrient treatment objectives with relatively good consistency during rainfall events, which is critical for biofilters that are intended to protect nutrient sensitive ecosystems.

4.6 Introduction

Urban stormwater runoff has been shown to have a detrimental impact on the water quality and hydrology of receiving waterways (Walsh et al. 2005). Nutrient-rich stormwater poses a particularly severe threat to aquatic ecosystems, causing excessive plant growth, depleted oxygen concentrations and eutrophication (Smith et al. 1999). Biofiltration systems (also known as bioretention systems, biofilters, and rain gardens) are recognised as an effective technology for the interception and treatment of stormwater (Davis et al. 2009; Hatt et al. 2009). Previous laboratory and field-scale research has demonstrated that biofilters are capable of achieving effective and reliable phosphorus (P) removal (80-90%) (Davis et al. 2001). However, reported nitrogen (N) removal continues to be variable (Bratieres et al. 2008; Davis et al. 2006), particularly following dry weather periods (Hatt et al. 2007a; Zinger et al. 2007a). Inter-event fluctuations in N removal and instances of N leaching have often been attributed to NO_x production within biofilters due to nitrification of retained ammonium (Cho et al. 2009; Hsieh et al. 2007b). Maintaining robust nutrient treatment following dry periods is a critical objective for biofilters, particularly in semi-arid climates like Australia. Inclusion of suitable vegetation and a saturated zone has been shown to enhance N removal, diminish the effects of drying, and reduce inter-event N removal variability (Glaister et al. 2014; Kim et al. 2003; Payne et al. 2014b; Zinger et al. 2007b), but this is sometimes achieved to the detriment of P removal (Zinger et al. 2013). Further, reported outflow concentrations of total nitrogen (TN), total phosphorus (TP) and their dissolved species from biofilters typically exceed Australian water quality guideline trigger levels for aquatic ecosystem protection (ANZECC/ARMCANZ 2000).

Whether nutrient concentrations in biofilter outflow remain above guideline levels during part of or throughout events is unclear, since concentrations are typically reported in terms of an event mean concentration (EMC) (Davis 2007). While this method provides a good overall estimation of mass load reduction, it does not give insight into the mechanisms that govern nutrient processing or how outflow concentrations fluctuate during events. Intra-event fluctuations in nutrient concentrations have the potential to significantly impact small streams or disturbed ecosystems that are sensitive to concentration changes. As such, understanding the extent to which nutrient concentrations fluctuate during events and how operational conditions influence treatment is critical to ensuring biofilters are designed to meet waterway protection objectives.

Consecutive event monitoring has been used to examine the extent to which previous events and intervening periods affect nutrient removal processes (e.g. Brown et al. 2013), however, studies monitoring intra-event fluctuations in nutrient removal are limited (Davis 2007; Hatt et al. 2009). How the inclusion of a saturated zone affects intra-event nutrient removal performance is a particularly important knowledge gap yet to be investigated.

Using sequential sampling, this study assesses the intra-event variability of nutrient removal from 20 laboratory-scale biofilter columns. The results demonstrate that nutrient concentrations in biofilter outflow vary during events and that the extent of this variation is affected by dry weather periods and the presence or absence of design elements, particularly vegetation and a saturated zone. These findings suggest that biofilters can achieve co-optimised intra-event nitrogen and phosphorus removal and satisfy ecosystem protection guidelines under a range of conditions.

4.7 Method

4.7.1 Experimental Design

Biofilter configurations

Four biofilter configurations were designed to compare nutrient removal performance between systems with different filter media, with and without vegetation (*C. appressa*), and with and without a saturated zone (see Table 4.6). Two filter media were tested: loamy sand, which is currently recommended for use in biofilters (Payne 2015), and 'Skye sand', a naturally occurring iron-coated sand from Skye, Victoria (Australia) (see Table 4.7 for physical and chemical properties). Previous testing has indicated that Skye sand has a greater capacity to adsorb dissolved P than loamy sand (Glaister et al. 2011) and can achieve enhanced N removal in conjunction with vegetation and a saturated zone (Glaister et al. 2014).

Table 4.6. Biofilter column design configurations

Configuration	Filter Medium	Vegetation	Saturated Zone
Loamy sand, vegetated, saturated zone (LS-V-S)	Loamy sand	*C.appressa*	SZ
Skye sand, non-vegetated, saturated zone (SS-NV-S)	Skye sand	Non-vegetated	SZ
Skye sand, vegetated, saturated zone (SS-V-S)	Skye sand	*C. appressa*	SZ
Skye sand, vegetated, no saturated zone (SS-V-NS)	Skye sand	*C. appressa*	No SZ

Table 4.7. Elemental and physical properties of loamy sand and Skye sand (parentheses = range). Surface area measured using the Brunauer-Emmett-Teller (BET) method (Brunauer et al. 1938). The coefficient of uniformity (d_{60}/d_{10}) is the ratio between the particle diameter at 60% passing (d_{60}) and 10% passing (d_{10}).

Media	Fe[a]	Al[a]	Fe_2O_3[b]	Al_2O_3[b]	SiO_2[b]	LOI[c]	d_{10}[d]	d_{60}[d]	d_{60}/d_{10}	Surface area[e]
Loamy sand	1,000 (±200)	900 (±100)	0.21	0.58	99	0.2	0.6	290	480	4.8
Skye sand	21,000 (±2,000)	1,000 (±100)	1.8	2.2	94	<0.1	100	390	3.9	1.0

[a] Analysed using inductively coupled plasma mass spectroscopy (ICP-MS; *n=2*) (mg/kg), [b] Analysed using X-ray fluorescence (XRF; %w/w), [c] Loss on ignition (LOI; %), [d] Analysed using a particle size analyser (Malvern Mastersizer 2000; µm), [e] Analysed using a particle size analyser (Malvern Mastersizer 2000; m^2/g).

Column construction

Twenty biofilter columns, five replicates of each configuration, were constructed using PVC pipe (150mm diameter) joined to a transparent acrylic pipe to provide a 200mm ponding zone. The filter media (300mm deep) was underlain by a coarse washed sand transition zone (200mm), pea gravel (70mm) and a gravel drainage layer (30mm). A cross section of the columns is shown in Figure 4.4a. Columns without a saturated zone drained freely from the base while a riser pipe was attached to the outlet of those with a saturated zone to maintain a 300mm internal ponding zone in the lower half of the column (Figure 4.4b). The coarse washed sand in the saturated zone inclusive columns was blended with a mixture of pine woodchips (bark removed) (26.5 g) and sawdust (9.3 g) to provide a carbon source for denitrifying bacteria. The total organic material added was equivalent to 5% of the volume of the saturated zone. The vegetated columns were planted with *C. appressa*; a relatively drought tolerant Australian sedge species found to provide excellent nutrient removal performance in biofilters (Bratieres et al. 2008; Payne et al. 2014b).

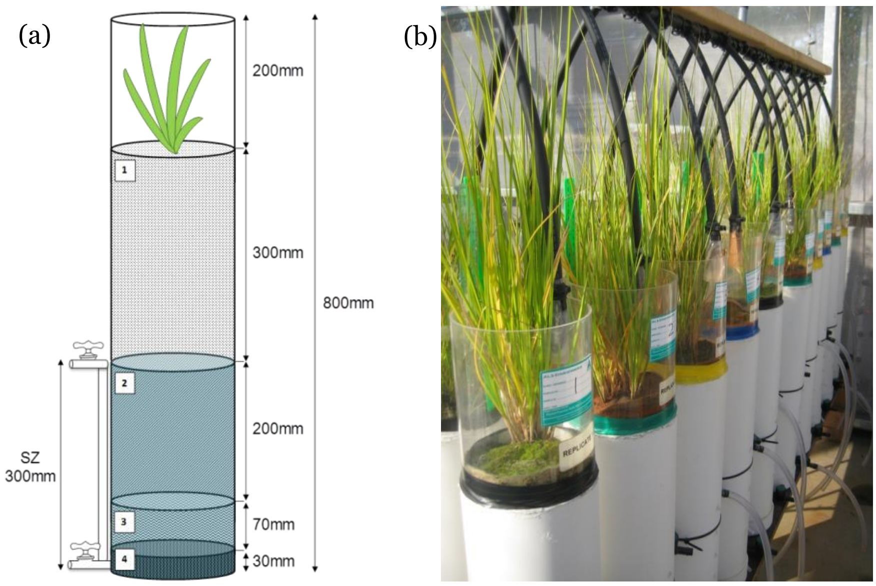

Figure 4.4 a. Cross section of the biofilter columns (with saturated zone riser outlet attached) and **b.** experimental set-up of biofilter columns in the greenhouse.

4.7.2 Experimental Procedure

Stormwater preparation and dosing

Because of the uncertainty and inconsistency associated with the use of natural stormwater, this study utilised a semi-synthetic stormwater prepared using methods described by previous studies (e.g. Bratieres et al. 2008; Hatt et al. 2007b). This approach uses natural sediment (collected from a stormwater retention pond) and laboratory grade chemicals to produce a semi-synthetic stormwater of a quality consistent with typical stormwater pollutant concentrations (Duncan 2006; Taylor et al. 2005). Stormwater dosing occurred over a 12 month period with volumes designed to reflect rainfall received by a biofilter sized to 2.5% of its catchment area in Melbourne, Australia, where the annual effective rainfall is approximately 540mm (Bureau of Meteorology 2013). Beginning in August 2011, columns were dosed twice weekly were 3.7L, equivalent to a 5mm rainfall event. During warmer months (December-March) longer periods between dosings were instigated (variable 4-18 days). Twice weekly stormwater dosing recommended in April 2012 until cessation of the campaign in August 2012. The stormwater infiltration rate through the columns was recorded periodically during the dosing campaign using a falling head method, where the ponding depth was recorded at one minute intervals to determine an average infiltration rate.

Sequential sampling procedure

During the 12 month dosing period two sequential sampling experiments were conducted to measure the intra-event variability of nutrient concentrations in the biofilters' outflow. The first experiment took place in April 2012, eight months after column establishment and following 18 dry days. All columns were dosed with the standard dosing volume (3.7L). Three consecutive effluent samples of approximately 1L each were collected. The rationale for this sampling frequency was to capture all "old water" retained in the saturated zone from the previous event (pore volume; ~1.5L) in the first sample, a mixture of old and new in the second and "new water" in the third. To compare intra-event variability under different climate conditions a second experiment was conducted in August 2012 after 12 months of dosing and following two dry days. This experiment utilised only 12 biofilter columns due to resource constraints (three replicates of each design configuration) and simulated a high-volume event (7.4L) equivalent to 10mm of rainfall. Using a higher-volume of stormwater elongated the event 'pollutograph' enabling trends to be examined over larger rainfall events. During the high volume event 12-13 consecutive 500mL samples were collected from the columns, of which every 'odd' numbered sample was analysed. Approximately 6.0-6.5L of treated stormwater was recovered from each biofilter column. This sampling method enabled an event 'pollutograph' to be constructed, providing greater insight into intra-event nutrient removal variability. The details of the experiments are summarised in Table 4.8. Inflow concentrations were analysed at the time of sampling for quality assurance (Table 4.9). The volume of stormwater and time it took to recover the stormwater varied slightly between columns owing to differences in infiltration rate and losses associated with evaporation and evapotranspiration between events.

Table 4.8. Experimental overview of the sampling events.

Experiment	Stormwater volume (L)	Rainfall equiv. (mm)	Antecedent dry days	Months after construction	No. of samples	Sample volume (L)
April	3.7	5	18	8	3	1
August	7.4	10	2	12	12-13	0.5

Table 4.9. Inflow N and P concentrations measured during the two stormwater dosing events (mg/L).

Experiment	TP	FRP	TN	NH_3	NO_x	DON
April	0.36	0.20	2.00	0.34	0.82	0.54
August	0.41	0.23	2.20	0.34	0.91	0.55

Water quality analysis

The biofilter effluent samples were analysed for TP (detection limit of 0.01mg/L), TN (0.02 mg/L), total dissolved nitrogen (TDN) (0.02mg/L), ammonia (NH_3) (0.01mg/L) (which in stormwater is present as ammonium, NH_4^+), nitrate and nitrite (NO_x) (0.01mg/L) and filterable reactive phosphorus (FRP) (0.01mg/L) using flow injection analysis (FIA) (Lachat, QuikChem® 8000). Where effluent concentrations were below detection limits a value equal to half the limit was assigned (<2% of data). Concentrations of dissolved and particulate organic nitrogen (DON, PON) and particulate phosphorus (PP) were calculated from these results. Samples for dissolved nutrient analysis were filtered immediately following collection through a 0.45µm filter (Bonnet Scientific). Water analyses were undertaken in a NATA (National Association for Testing Authorities) certified laboratory using standard methods and quality control procedures (APHA/AWWA/WPCF 2001). To assess whether conditions in the saturated zone were likely to promote denitrification, discrete water samples were extracted from the columns through sampling ports at a depth of 500mm and analysed for dissolved oxygen (DO) before and after stormwater dosings using a fibre-optic oxygen meter (PyroScience FireStingO_2).

Data analysis

Differences in treatment performance between the biofilter configurations with different filter media, with and without vegetation, and with and without a saturated zone were statistically evaluated using a multiple comparison parametric test with post-hoc analyses (Tukey and Tamhane), where significance was defined as $p \leq 0.05$. A 2-Independent sample non-parametric test (Mann Whitney), was also performed for validation of the parametric test results. Based on the Bonferroni post-hoc method these values should be multiplied by 3 when testing for significance over multiple comparisons, however, the reliability of such adjustment methods has been called into question (Perneger 1998; 1999). In light of such criticism unadjusted '*p*' values are presented rather than correcting for multiple comparisons. Nevertheless, sufficient information is provided to allow readers to perform their own adjustments if required (see Table 4.10).

4.8 Results and Discussion

4.8.1 Total phosphorus intra-event removal performance

Total phosphorus concentrations from the biofilters with a saturated zone were initially low in the April event (<0.02mg/L). TP concentrations increased thereafter as stormwater retained in the saturated zone began to mix with freshly applied stormwater. Outflow concentrations from the non-saturated biofilters were significantly higher (~0.13mg/L) in the first sample collected, although decreased substantially thereafter, resulting in concentrations comparable to the saturated zone inclusive biofilters (~0.04-0.06mg/L). The role vegetation plays in TP removal was most evident in the last sample collected during the April event, wherein TP concentrations from the non-vegetated biofilters were at least two times higher than the vegetated systems (0.1mg/L and <0.05mg/L respectively). These results suggest that TP concentrations can be high following extended dry periods, due to the wash-out of P-bound particles that have loosened between events (i.e. filter media, and detritus associated with microbial lysis and plant die-off), however, this can be mitigated with the inclusion of vegetation and a saturated zone.

The saturated zone mitigates particle mobilisation following dry periods in two ways (i) by protecting biofilters against the effects of drying; and (ii) by acting as a buffer to high-velocity flows. Inclusion of a saturated zone reduced the effective rate of infiltration through the vegetated Skye sand biofilter columns from ~280mm/hr to ~80mm/hr in SS-V-NS and SS-V-S respectively and to

~160mm/hr in the non-vegetated Skye sand columns. Vegetation also acts as a buffer to flow and protects biofilters during dry periods by maintaining soil stability. As such, both vegetation and a saturated zone would be recommended to achieve optimal TP removal performance where biofilters are likely to experience extended dry weather periods.

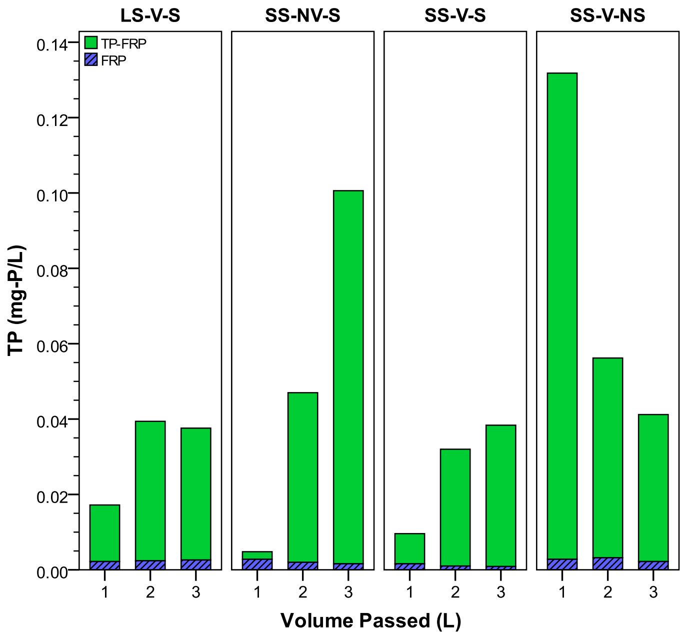

Figure 4.5. TP concentrations (mg/L) in consecutive 1L effluent samples during the April event represented in terms of constituent species. Particulate phosphorus (PP) was measured as TP-FRP. Bars represent the mean of five replicates. Panels left to right represent the biofilter configurations (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone). See Table 4.9 for inflow concentrations.

Fewer differences and no clear trends in TP removal were observed during the August event, suggesting that vegetation and a saturated zone become less important for TP when biofilters receive regular inflows (i.e. every 2-3 days) (Figure 4.6). The pollutograph showed TP concentrations from the Skye sand biofilters all increased then decreased, indicative of particulate washout with the movement of fresh stormwater into the effluent. This was confirmed by visual examination of the outflow samples (Figure 4.7). The wash-out of fine Skye sand particles, which have a very high sorption capacity, is unlikely to be an issue in receiving waters. Nevertheless, this wash-out could be avoided, and the P-removal integrity of the filter media maintained, by blending Skye sand with another medium (i.e. loamy sand) to rectify its gap-grading and minimise losses of fines. TP removal variability within and between the Skye sand configurations decreased with volume passed indicating that outflow concentrations tended toward a 'steady state' once comprised mostly of fresh stormwater (i.e. >2L). Comparing the April and August events showed that initial

TP concentrations from the non-saturated biofilters were 2-3 times higher after the 18 day dry period, which supports the conclusion that particle mobilisation was the determining factor in TP removal. Overall, the vegetated, saturated zone inclusive biofilters (LS-V-S- and SS-V-S) exhibited the best TP removal (Figure 4.5, Figure 4.6), which was most consistent the in the loamy sand biofilters (Table 4.11).

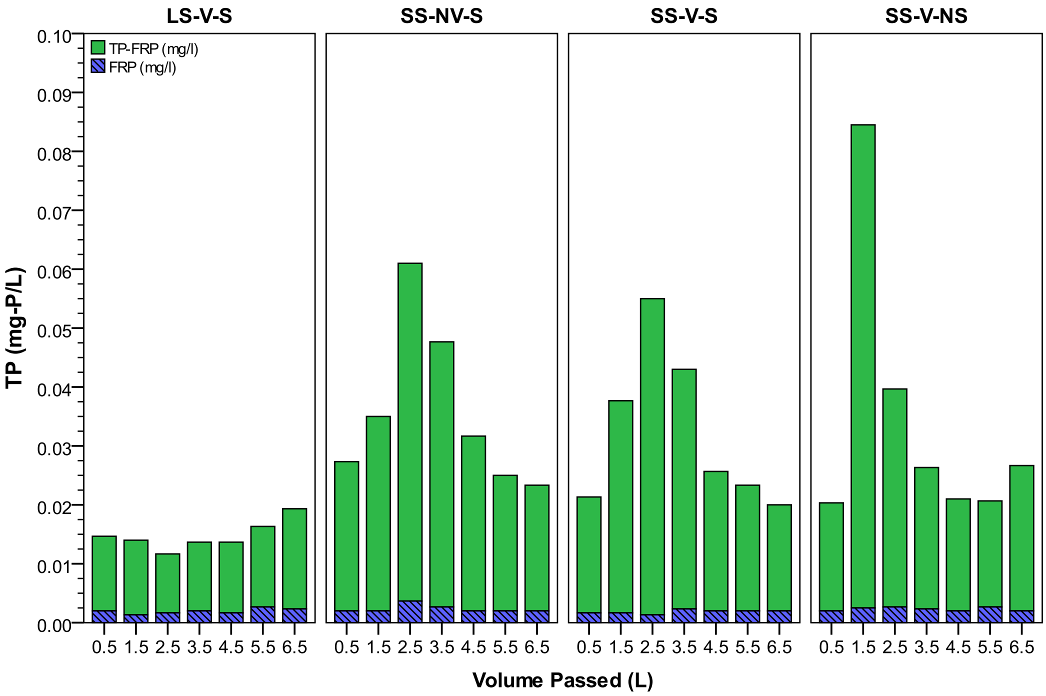

Figure 4.6. TP (mg/L) concentrations in outflow samples consecutively collected from biofilter columns during August event represented in terms of constituent P species. Bars represent the mean value of the replicates (*n=3*). Panels left to right represent the biofilter configurations (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone).

Excellent FRP removal (>98%) was exhibited by all biofilter configurations throughout both events, thus FRP accounted for only a minor fraction of TP (Figure 4.5). This finding emphasises the capacity of these recently constructed systems to readily remove phosphate. However, this capacity will diminish as the systems age and plants reach maturity, at which point the influence of filter media type and other design characteristics on FRP removal will likely become more apparent. There was no evidence of FRP leaching from the columns due to either biodegradation of the carbon source or reduction of iron-phosphate compounds in the saturated zone. This carbon source mix (pine woodchips and sawdust) could therefore be considered a suitable alternative to other carbon sources (e.g. pea straw) which have been associated with nutrient leaching (Zinger et al. 2013).

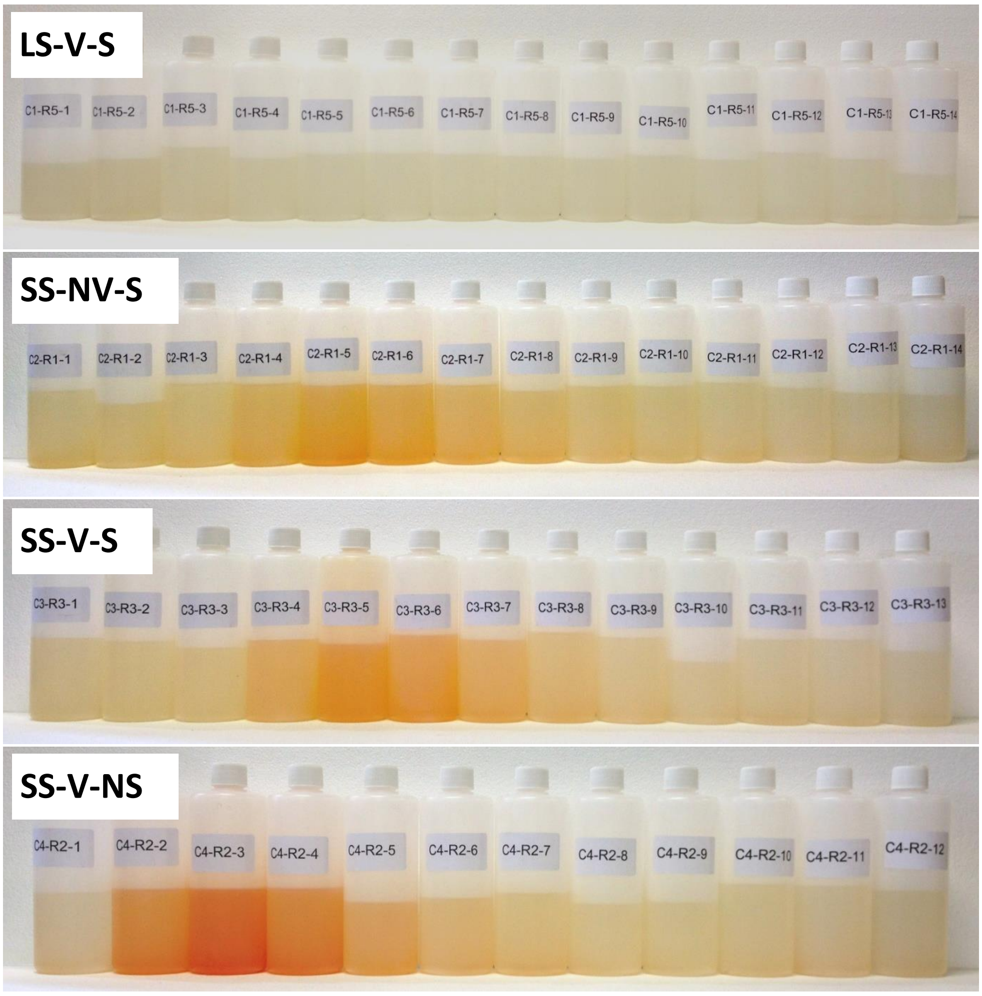

Figure 4.7. Biofilter column effluent samples consecutively collected during the high-volume stormwater dosing experiment: Row (i) LS-V-S; (ii) SS-NV-S; (iii) SS-V-S; (iv) SS-V-NS.

Table 4.10. Significance of key design elements during the two events determined by comparison of outflow nutrient concentrations from different biofilter columns. Significance determined using the Mann-Whitney U test for 2-independent non-parametric samples. Significant values (i.e. $p<0.05$) are presented in bold.

Design element tested (biofilters compared)	Event	TP	FRP[a]	TN	NH_3	NO_x	DON	PON
Filter media (LS-V-S v. SS-V-S)	April	0.377	**<0.001**	**0.001**	**0.016**[b]	0.780	**<0.001**	**<0.001**
	August	**<0.001**	0.737	0.403	0.957	0.207	**0.037**	0.109
Vegetation (SS-V-S v. SS-NV-S)	April	0.290	**0.001**	0.057	**<0.001**	0.112	0.425	0.561
	August	0.225	**0.013**	**<0.001**	**<0.001**	**<0.001**	0.272	0.182
Saturated Zone (SS-V-S v. SS-V-NS)	April	**0.001**	**<0.001**	**<0.001**	0.683	**<0.001**	**<0.001**	0.158
	August	0.574	**0.012**	**<0.001**	**0.006**	**<0.001**	**0.023**	0.251

[a] Statistical significance in April event may be driven by zero difference between replicates
[b] Statistical significance driven by outlier (see Table 4.11 for coefficient of variance)

4.8.2 Total nitrogen intra-event removal performance

TN concentrations after 18 days of dry weather were initially comparable between the biofilter designs (<0.5mg/L), although the saturated zone inclusive systems, particularly those containing Skye sand, performed slightly better. In subsequent samples, TN concentrations from the non-saturated columns were 2-3 times higher (~1.2mg/L) suggesting that after 18 days without water plants had become stressed and thus less able to intercept N (mostly NO_x) upon rewetting. More difference in TN concentrations between the saturated zone inclusive configurations was evident once freshly applied stormwater entered the outflow (i.e. >2L), suggesting interplay between TN removal, vegetation and filter media type.

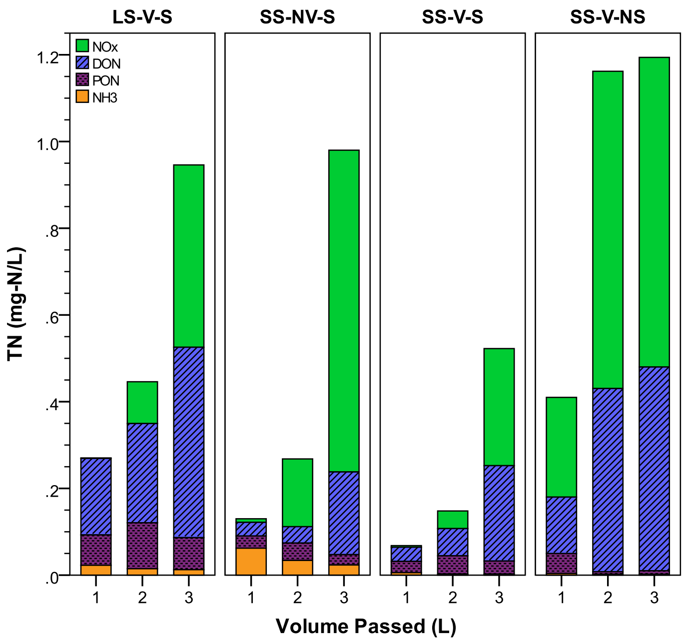

Figure 4.8. TN concentrations (mg/L) in consecutive 1L effluent samples during the April event represented in terms of constituent species. Bars represent the mean of five replicates. Panels left to right represent the biofilter configurations (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone). See Table 4.9 for inflow concentrations.

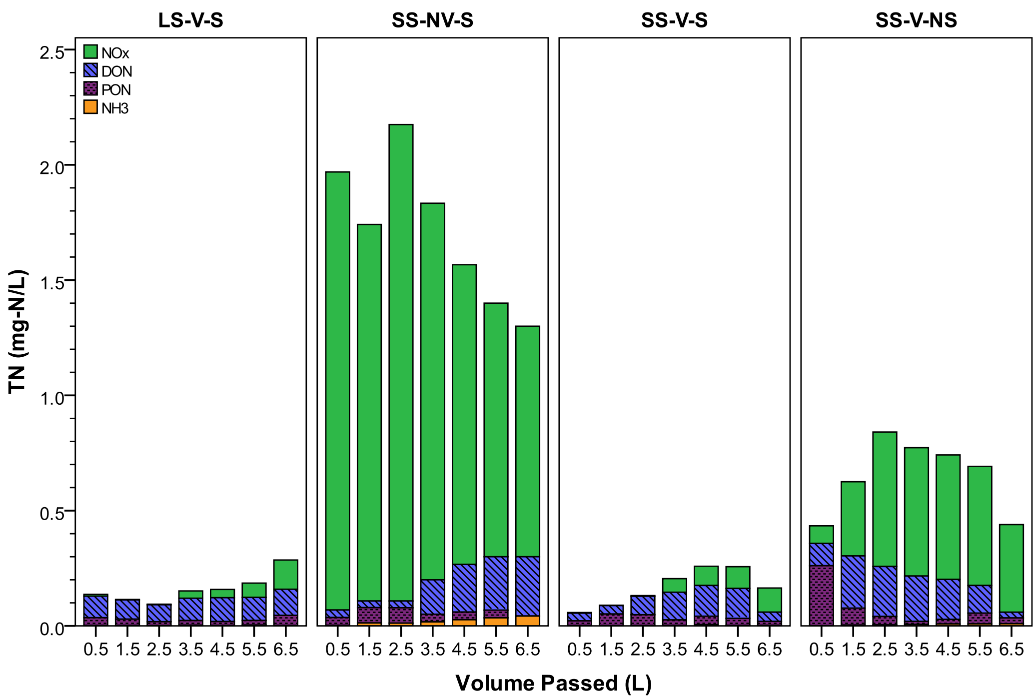

Figure 4.9. TN (mg/L) concentrations in outflow samples consecutively collected from biofilter columns during the high-volume dosing event represented in terms of constituent N species. Bars represent the mean value of the replicates (*n=3*). Panels left to right represent the biofilter configurations (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone).

Initial TN concentrations from the vegetated, saturated zone inclusive biofilters (SS-V-S & LS-V-S) were roughly the same after two dry days as after the 18 day dry period (Figure 4.8, Figure 4.9). However, unlike the April event, TN removal remained very good in these configurations beyond 2.5L of stormwater, maintaining concentrations below 0.5mg/L (~90% removal). This suggests that the LS-V-S and SS-V-S biofilters had a better capacity for N removal during the regular dosing period than after the 18 day dry spell, perhaps due to the absence of plant stress. Conversely, TN concentrations from the non-vegetated biofilters were approximately 10 times higher in the first sample collected after two dry days (~2.0mg/L) than after 18 dry days. Although TN removal in non-vegetated biofilters improved progressively during the event (~1.3mg/L), NO_x concentrations exceeded inflow throughout. Overall, the intra-event variability in TN removal observed during the events was driven mostly by NO_x and DON (Figure 4.8, Figure 4.9, Table 4.11).

All configurations exhibited a similar trend of increasing DON concentrations during the April event, however, concentrations from the loamy sand (LS-V-S) and non-saturated biofilters were higher. This could be attributed to desorption of loosely-sorbed DON from the filter media, or biodegradation of organic material built-up within the biofilter over the 18 day dry period, which would have been exacerbated by the effects of drying in the absence of a saturated zone. Breakdown of organic material could also account for the higher PON concentrations from the loamy sand biofilters. Because Skye sand has a high concentration of iron oxyhydroxides, to which DON readily adsorbs (Table 4.7) (Korshin et al. 1997), this media would be expected to perform better than loamy sand in terms of DON removal. Filter media also had a significant effect on DON in the August event (Table 4.10). However, this was driven by a lack of consistency between the Skye sand replicates rather than a difference in DON overall removal (see Figure A4.6 in the Chapter 4 Appendix).

DON concentrations in the first 2.5L of outflow from the non-vegetated columns were very low, suggesting that, even in the absence of vegetation DON can be almost completely removed through biological processing between events when a saturated zone is included. NO_x concentrations following the 18 day dry period suggest the same is possible for NO_x provided there is sufficient time between events to undergo biochemical processing (i.e. ammonification, nitrification, and denitrification). However, as fresh stormwater passes through the non-vegetated biofilters DON and NO_x concentrations increase due to the absence of a plant-uptake pathway and rhizosphere microbes that turn-over DON.

Whether the initially low NO_x concentrations from the non-vegetated, saturated-zone inclusive biofilters (SS-NV-S) in the 'old vs. new' event was attributed to microbial assimilation or complete denitrification during the 18 day dry period was not specifically investigated. However, mean dissolved oxygen concentrations measured in the saturated zone before (1.8 mg/L) and after the April event (2.2 mg/L) suggest that DO concentrations were not depleted to the point where denitrification would occur (<0.5mg/L). Moreover, after recommencement of regular dosing (every 2-3 days) leaching of internally produced NO_x quickly became an issue in the non-vegetated biofilters, indicating insufficient time between events for denitrification to occur (Glaister et al. 2014). As such plant-uptake would be considered the primary pathway for NO_x removal. This conclusion is supported by the findings of Payne et al. (2014a).

Vegetation was also critical for NH_3 removal (Table 4.10). However, in the absence of vegetation, NH_3 was still mostly removed (via transformation into NO_x or assimilation by microbes) if retained in a saturated zone between events provided the intervening period is not long enough for ammonification of organic nitrogen and or dissimilatory nitrate reduction to ammonium (DNRA) to occur, which was perhaps the driver for the poor NH_3 removal after the 18 day dry period. Nevertheless, these effects were easily negated by including vegetation.

Overall, N removal was most effective in the vegetated, saturated zone inclusive biofilters (LS-V-S- and SS-V-S). The loamy sand biofilters (LS-V-S) demonstrated more consistent intra-event TN removal under dry conditions (April event), while the vegetated, saturated zone inclusive Skye sand biofilters showed more consistent intra-event removal during the wet (August event) (Table 4.11). These results illustrate that including a saturated zone benefits N removal by (i) extending retention time between events, further entablesabling biological uptake and biochemical transformations to occur; (ii) reducing the effective rate of infiltration thus increasing opportunity for biological removal during events; and (iii) protecting biofilters against the effects of drying and supporting plant health during dry periods (Payne et al. 2014a).

Table 4.11. Intra-event variability between the samples for each pollutant (measured as coefficient of variance).

Configuration	Event	TP	FRP	TN	NH_3	NO_x	DON	PON
LS-V-S	April	0.330	0.578	0.211	1.680	1.203	0.480	0.278
	August	0.236	0.523	0.343	0.585	1.765	0.180	0.596
SS-NV-S	April	0.827	0.927	0.300	0.434	1.264	0.894	0.734
	August	0.387	0.162	0.313	0.658	0.253	0.873	1.306
SS-V-S	April	0.531	0.900	0.385	1.248	1.309	0.868	0.303
	August	0.472	0.788	0.265	0.896	1.077	0.821	0.477
SS-V-NS	April	0.717	0.415	0.217	1.200	0.444	0.464	1.911
	August	0.723	0.552	0.248	0.839	0.569	0.709	0.730

4.8.3 Implications for meeting water quality guidelines

Table 4.12 summarises the extent to which water quality targets for ecosystem protection were met during the events; measured as the percentage of samples collected which satisfied the ANZECC/ARMCANZ (2000) water quality guidelines for slightly disturbed lowland rivers in South-Eastern Australia. Total phosphorus concentrations from the vegetated, saturated zone inclusive biofilters rained close to or below water quality guideline concentrations (≤0.05mg/L) in both events. This is a positive finding given that TP removal following dry periods has been problematic (Hatt et al. 2007a). FRP targets (<0.02mg/L) were consistently met throughout each event.

Total nitrogen water quality targets (≤0.5mg/L) were generally satisfied under regular dosing conditions when the biofilters included both vegetation and a saturated zone. Achieving TN targets under dry conditions was more challenging, however, the Skye sand biofilters with vegetation and a saturated zone met the target concentrations for ~90% of the event. The vegetated configurations consistently satisfied the NH_3 water quality targets (≤0.02mg NH_4^+/L) in both events, except in the case of LS-V-S which met the targets 80% of the time during the April event, most likely owing to observed poor plant health in one replicate. Even with the inclusion of vegetation and a saturated zone satisfying NO_x water quality guidelines (≤0.04mg/L) remains a challenge. Nevertheless, achieving these concentrations >50% of the time demonstrates progress, especially given that issues with NO_x leaching are often cited in biofilter studies (Bratieres et al. 2008; Dietz et al. 2006; Zinger 2012).

Table 4.12. Percentage of event satisfying water quality targets (measured as % of samples collected).

Configuration	Event	TP	FRP	TN	NH_3	NO_x
LS-V-S	April	100%	100%	53%	80%[a]	53%
	August	100%	100%	100%	100%	74%
SS-NV-S	April	53%	100%	67%	7%	33%
	August	93%	100%	0%	57%	0%
SS-V-S	April	93%	100%	86%	100%	64%
	August	83%	100%	100%	100%	54%
SS-V-NS	April	40%	100%	20%	100%	0%
	August	89%	100%	89%	100%	11%
Guideline value (mg/L)		0.05	0.02	0.5	0.02	0.04

[a] Outlier driving result (see Table 4.11). If omitted result would be 100%.

4.9 Conclusions

This study investigated the influence of design characteristics and variable antecedent dry weather periods on intra-event nutrient removal in biofilters. The results indicate that the influence of design is dynamic, and in some cases, more critical under wet or dry conditions. For instance, vegetation becomes more critical for nitrate/nitrite removal during periods of regular stormwater dosing when retention time in the saturated zone is limited. Quantifying intra-event variability emphasised the treatment benefits of vegetation and retaining water within a saturated zone between events, both of which enhanced biological processing and reduced mobilisation of particulate-bound or loosely-sorbed N and P into the effluent upon rewetting. Particle mobilisation was an issue for Skye sand filter media, which is gap-graded. However, blending Skye sand with well graded sand (i.e. loamy sand) would diminish this effect.

Biofilters with Skye sand, vegetation and a saturated zone achieved the most effective and least variable nutrient removal overall and mostly satisfied N and P concentration targets for ecosystem protection. Therefore, in the interest of optimising biofilter design for N and P removal and achieving water quality targets, biofilters that discharge to surface waters (i.e. possess an underdrain) should incorporate Skye sand (perhaps as an ameliorant), vegetation and a saturated zone. The disparity in treatment undergone by stormwater retained in the saturated zone and fresh stormwater can be reduced by incorporating a biofilter large enough to capture a standard rainfall event. This is particularly important for biofilters that drain into small, nutrient sensitive or disturbed ecosystems. However, intra-event variability and meeting water quality guidelines could be more easily addressed by using infiltration-based systems that extend detention times by infiltrating water into underlying soils wherever possible, such that the biofiltration process continues.

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Chapter 5: The Influence of Biofilter Design on Plant Growth and Morphology

Implications for Nutrient Removal via Plant Uptake

Foreword

In this chapter the influence of biofilter design on plant growth and morphology is analysed and correlated with biofilter treatment performance for phosphorus and nitrogen. Chapter 5 draws upon the soil chemistry knowledge gained from Chapter 3 and the biofilter performance quantification and design comparison outcomes of Chapter 4. In doing so, this chapter brings together and applies an understanding of nutrient removal in biofilters to investigate links between novel design elements, plant growth characteristics and nutrient removal performance.

This chapter comprises a journal paper:

Glaister, B. J., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (2017). Interactions between design, plant growth and the treatment performance of stormwater biofilters. Ecological Engineering. 105:21-31.

The paper is currently available online and is presented in the format submitted to the journal. Numbering of sections, figures, tables and pages has been altered for consistency within this thesis. This paper and supplementary information for this chapter can be found in the Chapter 5 Appendix.

Objectives and hypotheses

The experiment presented in this chapter aims to further relate biofilter design to nutrient removal performance. Through the analysis of plant growth characteristics the effect of design variations on plant growth and morphology is investigated with the objective of:

- investigating the influence of Skye sand, loamy sand and the presence of a saturated zone on plant growth and morphology in biofilters
- correlating plant growth characteristics and morphological traits with nutrient removal performance under wet and dry conditions
- understanding how, by influencing plant growth and morphology, filter media and a saturated zone affect phosphorus and nitrogen removal processes in biofilters

The main hypotheses tested are as follows:

- Skye sand biofilters have a strong P-sorption capacity and are likely to cause nutrient limitation in plants
- to satisfy nutritional requirements under nutrient limited conditions plants adapt their morphology (i.e. root length, surface area and fineness) to exploit a larger area of soil
- root length, surface area and fineness correlate strongly with nutrient removal in biofilters particularly dissolved N and P species
- the nutrient limited conditions imposed by Skye sand may be advantageous for nutrient removal via plant uptake
- including a saturated zone increases nutrient acquisition and plant growth thus improves nutrient removal

Interactions between Design, Plant Growth and the Treatment Performance of Stormwater Biofilters

Bonnie J. Glaister[a], Tim D. Fletcher[b], Perran L. M. Cook[c] and Belinda E. Hatt[a]

[a] Department of Civil Engineering, Monash University, Victoria, 3800, Australia

[b] Waterway Ecosystem Research Group, School of Ecosystem & Forest Sciences, Faculty of Science, the University of Melbourne, Burnley, Victoria, 3121, Australia

[c] Water Studies Centre, School of Chemistry, Monash University, Victoria, 3800, Australia

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Abstract

Plants play a critical role in the nutrient removal performance of stormwater biofilters. However, the influence of biofilter design on plant growth and subsequent implications for treatment performance are not well understood. A 12 month, laboratory-scale biofilter column experiment was conducted to investigate the response of *Carex appressa* to variations in biofilter design and implications for nutrient removal performance. Plant growth in Skye sand, a natural iron-coated sand with a strong capacity to immobilize phosphorus, was evaluated against a typical loamy sand filter media in biofilters with and without a saturated zone. Plant biomass correlated strongly with nutrient removal and was significantly greater in biofilters with a saturated zone, suggesting that inclusion of a saturated zone facilitates nutrient uptake. In the presence of a saturated zone, plants grown in Skye sand had a significantly higher specific root length, surface area and volume than plants grown in loamy sand, illustrating *C. appressa's* ability to adapt root morphology to maintain growth under nutrient limited conditions. These root traits also correlated strongly with nutrient removal, suggesting that use of Skye sand in biofilters rather than loamy sand would be advantageous for nutrient removal. However, root adaptations, in particular increased etiolation, can make plants vulnerable to stressful environments (e.g. prolonged drying). Therefore, it is critical that a saturated zone be included in stormwater biofilters to increase growth and protect against drying.

5.1 Introduction

Stormwater biofilters provide passive treatment of urban runoff by harnessing the natural bioremediation properties of plant-soil systems (Fletcher et al. 2006; PGC 2002). Extensive research in laboratory- and field-scale settings has demonstrated that plants play a critical role in facilitating stormwater treatment, particularly nutrient removal (Bratieres et al. 2008; Davis et al. 2006; Lucas et al. 2008; Payne et al. 2014a; Read et al. 2008). Nevertheless, achieving co-optimised nitrogen and phosphorus (P) removal (particularly phosphate) remains a challenge for biofilters, as does meeting nutrient removal objectives for ecosystem protection (Davis et al. 2006; Glaister et al. 2014). Whilst nitrogen removal relies predominately on biological processes, which has been shown to improve with the inclusion of an internal water storage or 'saturated zone' (Zinger et al. 2013), the predominant mechanism by which phosphate is removed in plant-soil systems is through sorption to filter media (Erickson et al. 2007; Reddy et al. 1999).

The endeavour to improve the effectiveness of P removal in biofilters, among other stormwater and wastewater treatment systems, has led to many alternate filter media types being investigated (Bachand 2003; Ballantine et al. 2010; Vohla et al. 2011). The affinity of iron-rich soils and sediments for P sorption (Goldberg et al. 1985) has motivated numerous researchers to test how augmenting the filter media of stormwater and wastewater treatment systems with iron-rich materials affects the P removal performance and retention capacity (Arias et al. 2006; Ayoub et al. 2001; Boujelben et al. 2008; Dobbie et al. 2009; Erickson et al. 2012). Recent research has shown that using 'Skye sand', a natural iron-coated filter media with a strong affinity for phosphorus (see *Chapter 3*), in conjunction with a saturated zone, can improve N and P removal and enable biofilters to achieve ecosystem protection objectives (Glaister et al. 2014). However, while success in ameliorating N and P removal has been demonstrated, the influence of Skye sand on plant growth in biofilters has not been specifically tested. As such, further research is needed to develop an understanding of how Skye sand filter media influences plant growth and nutrient treatment in biofilters.

Iron-rich soils are typically associated with limited nutrient availability (Handreck 1997; Lambers et al. 2008; White et al. 2008; Wild 1950). The ability of plants to respond to such conditions is fundamentally important to environmental adaptation. Root development responses to nutrient limited conditions can have a profound effect on root system architecture and nutrient acquisition

(Lambers et al. 2008; López-Bucio et al. 2003; Schmidt et al. 2001). Such responses include: elongation of primary roots; formation of lateral roots, to increase the exploratory capacity of the root system; and the formation of root hairs, which increase the total surface area of primary and lateral roots and allow roots to exploit a considerably larger cylinder of soil (López-Bucio et al. 2003).

Previous studies investigating plant traits that enhance nutrient removal in biofilters have found that plant biomass and root traits, such as root length, surface area and fineness, are strongly correlated with nutrient removal, particularly dissolved N and P species (Payne et al. 2014b; Read et al. 2010; Read et al. 2008). As such, nutrient limited conditions may present advantageous conditions for the development of plant traits which correlate with enhanced nutrient removal. This may explain in part why the use of Skye sand filter media has been shown to be beneficial for nutrient removal.

Building upon existing studies of the influence of plant traits on nutrient removal (Payne et al. 2014b; Read et al. 2010), the present study aims to investigate how using Skye sand as a filter medium affects the growth and morphology of plants in biofilters and the implications for nutrient removal performance. Investigating plant responses to Skye sand in conjunction with a saturated zone is a key focus of this study and an essential part of the research needed to develop a better understanding of how co-optimisation of N and P removal in biofilters can be achieved.

5.2 Materials and Methods

5.2.1 Experimental design

N.B. This experiment was the final stage of the biofilter column study, the experimental design for which is described in detail in Chapter 4. A brief summary of the experiment is outlined herein, however, please refer to Chapter 4 for detailed design information.

Three biofilter column configurations were designed to compare nutrient removal performance and plant growth characteristics of loamy sand and Skye sand biofilters with a saturated zone and Skye sand biofilters with and without a saturated zone (Table 5.1). A saturated zone inclusive biofilter with loamy sand filter media was not included because nutrient removal performance and plant growth characteristics of this configuration have been thoroughly investigated by a number of preceding studies, using the same experimental apparatus and testing facility (Bratieres et al. 2008;

Payne et al. 2014b). Five replicate columns were constructed for each configuration. The columns were made of PVC (600 mm x150 mm diameter) with a 200 mm acrylic collar attached to create a ponding zone. The configurations without a saturated zone drained freely from the base, while a riser pipe was attached to the outlet of the saturated zone inclusive systems to maintain a300 mm pool of water in the lower half of the column. The biofilters contained four layers of media (from top to bottom): (1) loamy sand or Skye sand filter media (300 mm); (2) coarse, washed sand transition layer (200 mm); (3) pea gravel drainage layer (70 mm); (4) gravel drainage layer (30 mm). A cross section of the columns is shown in Figure 5.1a.

Table 5.1. Biofilter column configurations.

Configuration ID	Filter Medium	Saturated Zone (Y/N)
Loamy sand (S)	Loamy Sand	Y
Skye sand (S)	Skye Sand	Y
Skye sand (NS)	Skye Sand	N

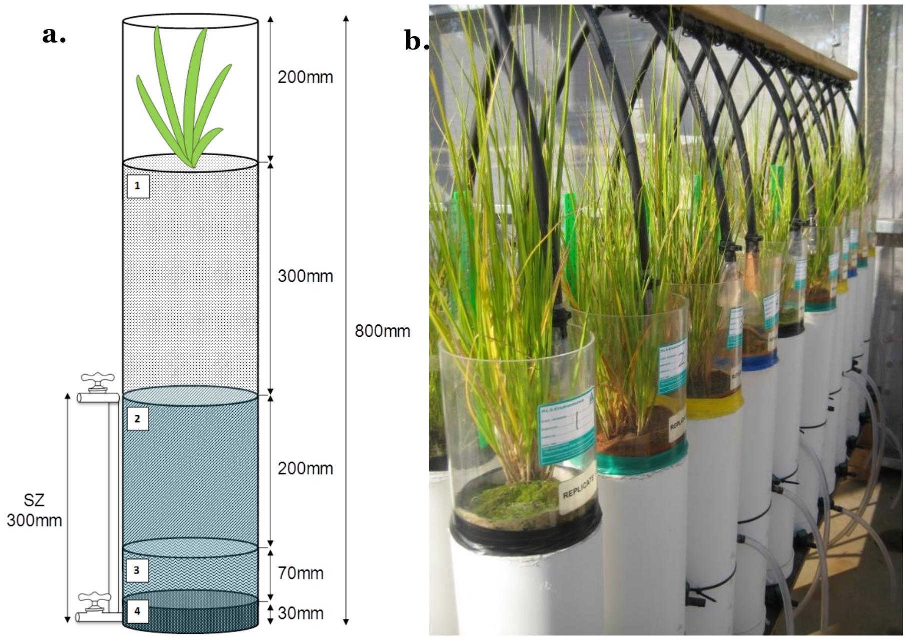

Figure 5.1 a. Schematic diagram of the biofilter columns (with SZ riser outlet attached) and **b.** set-up of biofilter columns in the open-air shade house.

The biofilter columns were each planted with a single *C. appressa* plant. *C. appressa* is an Australian tall sedge that is relatively drought tolerant and has been found to provide effective nutrient removal in biofilters (Bratieres et al. 2009; Read et al. 2008). Prior to transplanting into the columns, the plants were established for 12 weeks in small pots containing either loamy sand or Skye sand, depending on their destination biofilters. The pots were housed in a greenhouse maintained at 25°C and watered twice weekly with tap water. The biofilter columns were constructed in July and placed in an open-air shade house (Figure 5.1b). After an initial flush with tap water to settle the filter media, stormwater dosing commenced in early August.

Because of the uncertainty and inconsistency associated with the use of real stormwater, a semi-synthetic stormwater was prepared using methods described by previous biofilter column studies (e.g. Bratieres et al. 2008; Hatt et al. 2007). This approach utilises natural sediment collected from a stormwater retention pond and laboratory-grade chemicals to produce a semi-synthetic stormwater of a quality consistent with typical stormwater pollutant concentrations (Duncan 2006; Taylor et al. 2005). The mixture was topped up using chemicals where necessary to make up the deficit in nutrient concentrations (Table 5.2).

Table 5.2 Typical Melbourne stormwater nutrient concentrations (based on concentrations reported by Duncan (2006) and Taylor et al. (2005).

Pollutant	Concentration (mg/L)	Chemical additives
Total Suspended Solids (TSS)	150	Sediments
Total Nitrogen (TN)	2.13	From N additives
Ammonia (NH_3)	0.29	Ammonium chloride (NH_4CL)
Oxidized Nitrogen (NO_x)	0.74	Potassium nitrate (KNO_3)
Organic N (ON)	1.1	Sediments and DON
Dissolved ON	0.6	Nicotinic acid ($C_6H_5O_2N$)
Total Phosphorus (TP)	0.35	Sediments and FRP
PO_4- (Phosphate ortho=FRP)	0.12	Potassium phosphate (KH_2PO_4)

The frequency and volume of dosings were designed to simulate typical Melbourne rainfall patterns. During 'wet' periods (August-November and April-July) the columns were dosed twice weekly with stormwater. Throughout the intervening 'dry' months (December-March) the dosing schedule varied, with up to 18 antecedent dry days occurring between events. Dosing volumes remained constant at 3.7L per event, which is equivalent to the rainfall received by a biofilter sized to 2.5% of its catchment area in Melbourne (540mm effective annual rainfall, Bureau of Meteorology 2013). Water quality was monitored by collecting bulk effluent samples from each column every five weeks for twelve months and analysing for total phosphorus (TP), total nitrogen (TN), ammonium (NH_4^+), nitrate/nitrite (NO_x), dissolved organic nitrogen (DON), particulate organic nitrogen (PON) and filterable reactive phosphorus (FRP) using standard methods and quality controls (APHA/AWWA/WPCF 2001).

5.2.2 Column deconstruction and plant harvesting

In order to quantify the effect of biofilter design on plant growth and morphology, the plants were harvested from the vegetated columns (15 plants; 5 replicates per configuration) at the end of the experimental period. A longitudinal quarter segment of each column casing (the PVC pipe) was removed to allow visual examination of the filter media layers and plant roots (Figure 5.2). Filter media samples were collected before the plants were removed from the columns by carefully washing away the filter media. After washing, the clean plants were stored for a few days (maximum of 14) in 10L buckets filled with tap water until growth and morphological analysis commenced.

Figure 5.2. Partial removal of the biofilter column casing allowed visual inspection of the filter media and root architecture.

5.2.3 Plant growth and morphological analysis

Plant morphology was characterised using several techniques (Table 5.3). The longest root and shoot length of each plant was measured, along with the bulk root length (the length to which approximately 95% of roots grew to) and bulk shoot length (length of ~95% of shoots). Each plant was then separated into roots, shoots (i.e. leaves), and stems. Roots were cut into 2–4 cm segments and placed in 10L buckets filled with water. This allowed the roots to separate and mix well. Approximately 10g wet weight of roots were sub-sampled from each plant and spread out over a transparent acrylic tray containing a few millimetres of water to help maintain separation between the roots. The sub-sample size was based on the results of a bootstrapping and sensitivity analysis performed by Payne (2013), who conducted a similar study. The samples were scanned (EPSON Flatbed scanner Expression 10000XL 1.8 V3.49) at a resolution of 800 dpi and analysed using the

WinRHIZO software package (v. 2009©, Regent Instruments Canada Inc.). After scanning, the roots were oven-dried at 60°C to constant weight. Shoots were analysed using a similar approach to the root analysis. First, the healthy shoots from each plant (i.e. shoots not dead or showing signs of die-off) were counted. From these, a sub-sample of 20 shoots was randomly collected and cut into three segments of approximately equal length. The shoots were pressed onto an adhesive sheet to ensure that the whole area of the shoot was visible to the scanner. The shoots were scanned and analysed and then oven-dried at 60°C to constant weight. The unscanned roots, shoots and stems of each individual plant were also dried to determine total plant biomass, above-ground biomass and root mass.

5.2.4 Data analysis

The plant morphological data did not all fit the assumptions of normality and homogeneous variability required for parametric tests, even when log-transformed. As such, statistical significance was measured using non-parametric tests. A 2-Independent sample Mann Whitney test (significance accepted at $p<0.05$) was performed to test for significance between the design configurations (i.e. loamy sand (S) vs. Skye sand (S) and Skye sand (S) vs. Skye sand (NS)). Based on the Bonferroni post-hoc method these values should be multiplied by 2 when testing for significance, however, the reliability of such adjustment methods has been challenged (Perneger 1998; 1999). In light of this, unadjusted '*p*' values are presented to minimise the chance of overlooking a true relationship.

To investigate relationships between plant characteristics and nutrient removal in biofilters, effluent nutrient concentrations from the last water quality monitoring event conducted (i.e. that closest in time to the plant harvest) were correlated with the plant growth and morphology data. This event was conducted in July 2012 during the 'wet' dosing period. Relationships between water quality and plant growth characteristics were investigated across all biofilter configurations simultaneously using a bivariate correlation analysis and quantified by the Pearson correlation coefficient and two-tailed significance tests. To determine if plant characteristics become more or less important during dry spells the water quality results for April (which followed an 18 day dry period) were also correlated with the plant growth characteristics using a bivariate analysis. Although this water quality data was collected four months prior to harvesting it was assumed that plant growth characteristics between these periods would be relative.

Table 5.3. Plant growth and morphological characteristics measurement methodology. dw = dry weight

Characteristic	Method of measurement/calculation	Units
longest root	Manual measurement	mm
longest shoot	Manual measurement	mm
bulk root length (95%)	The length to which 95% of the roots grow to is visually estimated then manually measured	mm
bulk shoot length (95%)	The length to which 95% of the roots grow to is visually estimated then manually measured	mm
number of shoots	Counted manually after disassembling the plants	-
root sub-sample mass (dw)	Scanned roots were dried to a constant weight in a 60°C oven	g
shoot sub-sample mass (dw)	Scanned shoots were dried to a constant weight in a 60°C oven	g
total root mass (dw)	Unscanned roots were dried to a constant weight in a 60°C oven. Unscanned root mass and root sub-sample mass were added determine the total root mass.	g
total shoot and stem mass (dw)	Unscanned shoots and stems were dried to a constant weight in a 60°C oven. Unscanned shoot mass and shoot sub-sample mass were added determine the total shoot and stem mass.	g
total plant mass (dw)	Sum of total root mass and total shoot and stem mass	g
average root diameter	Calculated by WinRHIZO	mm
root length	Calculated by WinRHIZO. Represents total length of all roots	cm
root surface area	Calculated by WinRHIZO. Represents total root surface area	cm^2
root volume	Calculated by WinRHIZO. Represents total volume of roots	cm^3
shoot length	Calculated by WinRHIZO. Represents total length of all shoots	cm
shoot surface area	Calculated by WinRHIZO. Represents total shoot surface area	cm^2
root length per gram	root length/root sub-sample mass (dw)	cm/g dw
root surface area per gram	root surface area/root sub-sample mass (dw)	cm^2/g dw
root volume per gram	root volume/root sub-sample mass (dw)	cm^3/g dw
shoot length per gram	shoot length/shoot sub-sample mass (dw)	cm/g dw
shoot surface area per gram	shoot surface area/shoot sub-sample mass (dw)	cm^2/g dw
total root length	root length per gram*total root mass	cm
total root surface area	root surface area per gram*total root mass	cm^2
total root volume	root volume per gram*total root mass	cm^3
total shoot length	shoot length per gram*total shoot and stem mass	cm
total shoot surface area	shoot surface area per gram*total shoot and stem mass	cm^2
root length, surface area and volume distributed across root diameter classes	Calculated by WinRHIZO. Root diameter class boundaries: 0<n<0.04, 0.04<n<0.08, 0.08<n<0.16, 0.16<n<0.2, 0.2<n<0.25, 0.25<n<0.3, 0.3<n<0.35, 0.35<n<0.4, 0.04<n<0.45, 0.45<n<0.5, 0.5<n<0.6, 0.6<n<0.8, 0.8<n<1.0, 1.0<n<2.0, n>2.0	mm

5.3 Results and Discussion

5.3.1 In-situ observations

Visual observation of the plants when the PVC column segments were removed indicated that the roots of *C. appressa* grown in the biofilters containing a saturated zone grew deeper than those with no saturated zone. In the saturated zone-inclusive biofilters, roots typically grew to the base of the columns where they formed a dense mat tightly woven into the shade cloth swatches located between the gravel drainage layer and the outflow pipe (Figure 5.3). The formation of a dense mat of root hairs such this has been recognised as a strategy to improve P acquisition in nutrient-poor soils (Shane et al. 2005). In contrast only a small amount of fine roots (<2mm) were observed in the base of the non-saturated columns. Payne et al. (2014b) also observed shallow root growth in non-saturated biofilter columns planted with *C. appressa*. In heterogeneous soils, roots tend to proliferate in zones with a high availability of nutrients rather than depleted zones, thus maximising the efficiency of each unit of root production (Lambers et al. 2008). Therefore, given that the saturated zone stores nutrient-rich stormwater between events it is not surprising that plants in the saturated zone-inclusive biofilters established deeper root systems.

Figure 5.3. Dense root growth at the column base was more extensive in the saturated zone-inclusive biofilters.

5.3.2 Plant growth and morphological analysis

5.3.2.1 Manual measurements

Neither filter media type nor the presence of a saturated zone had a significant effect on the longest root (Figure 5.4a) or bulk root length (Figure 5.4b) ($p>0.05$), however, these measurements were notably more variable in the loamy sand configuration. Longest shoot length was significantly affected by filter media type ($p<0.01$) although not by the presence of a saturated zone (Figure 5.4c).

5.3.2.2 Biomass analysis

Biofilter media is deliberately nutrient poor so that plants rely on stormwater to meet their nutritional requirements, therefore, nutrient availability to plants is at least partially dependent on the ability of filter media to capture and retain nutrients. Plant biomass allocation was not significantly affected by filter media ($p>0.05$) (Figure 5.5), indicating that plants can successfully acquire nutrients from Skye sand, which therefore can reliably support plant growth. However, further testing of Skye sand with plant species other than *C. appressa* is warranted.

Inclusion of a saturated zone resulted in plants with a significantly higher total and above-ground biomass ($p<0.01$) and total number of shoots ($p<0.05$) (Figure 5.5b, d). This implies that prolonged detention promotes increased nutrient acquisition, which is consistent with the findings of other studies (Lambers et al. 2008; Taylor et al. 2005). However, the presence of a saturated zone did not significantly affect total root mass ($p>0.05$) (Figure 5.5a), suggesting perhaps that water stress and poor nutrient diffusion during dry months prompted plants in non-saturated zone inclusive systems to prioritise root growth. Under P-limited conditions plants often increase their root mass, by inhibiting shoot growth in favour of root growth, to increase the absorptive surface area of the root system and improve phosphate acquisition efficiency (López-Bucio et al. 2003; Lynch 1995; Lynch et al. 2008).

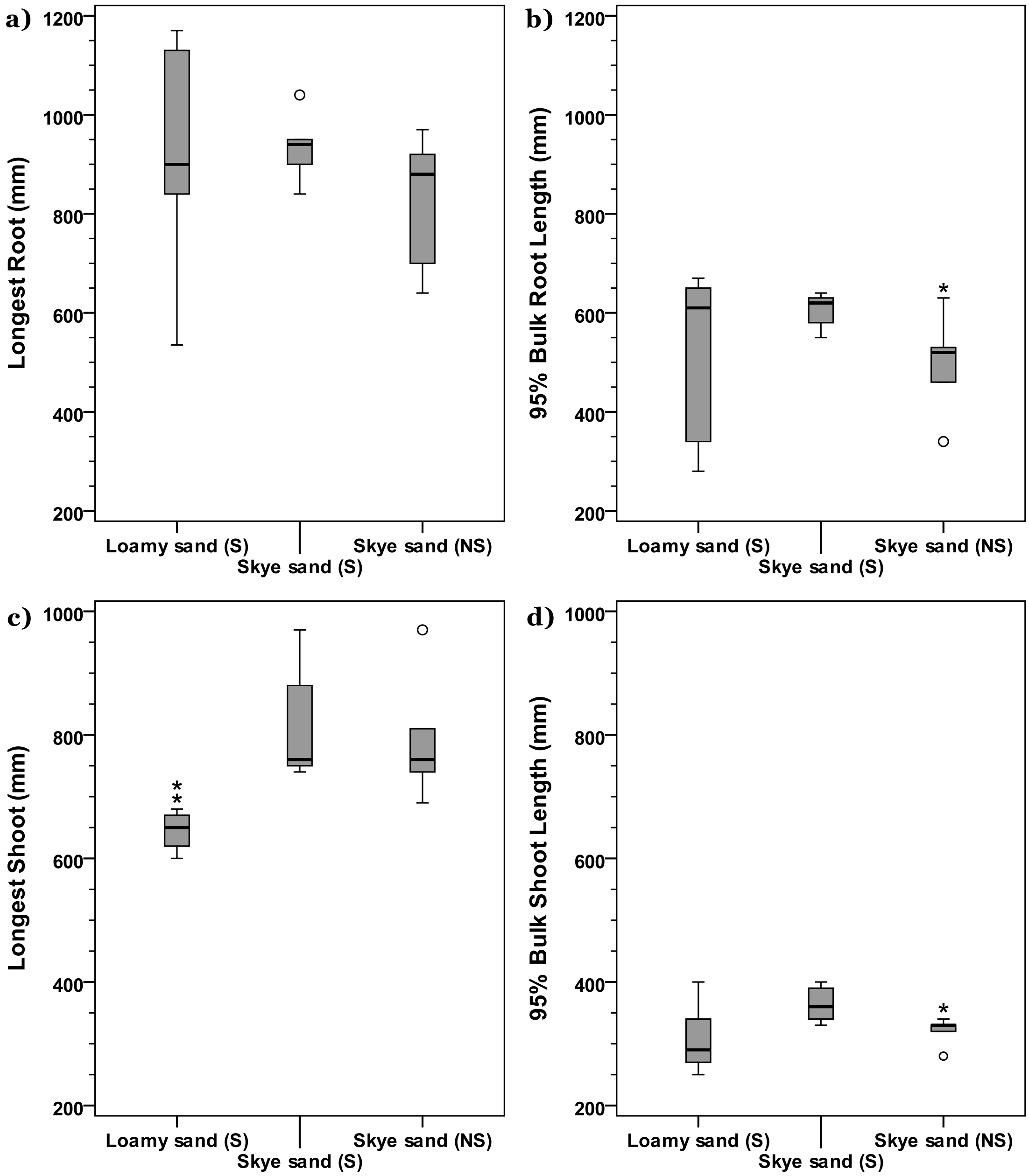

Figure 5.4. Effects of filter media and saturated zone on root and shoot characteristics (manually measured) (n = 5). S, saturated zone; NS, no saturated zone. '**' and '*' represent a statistically significant difference (*p<0.01* and *p<0.05* respectively) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

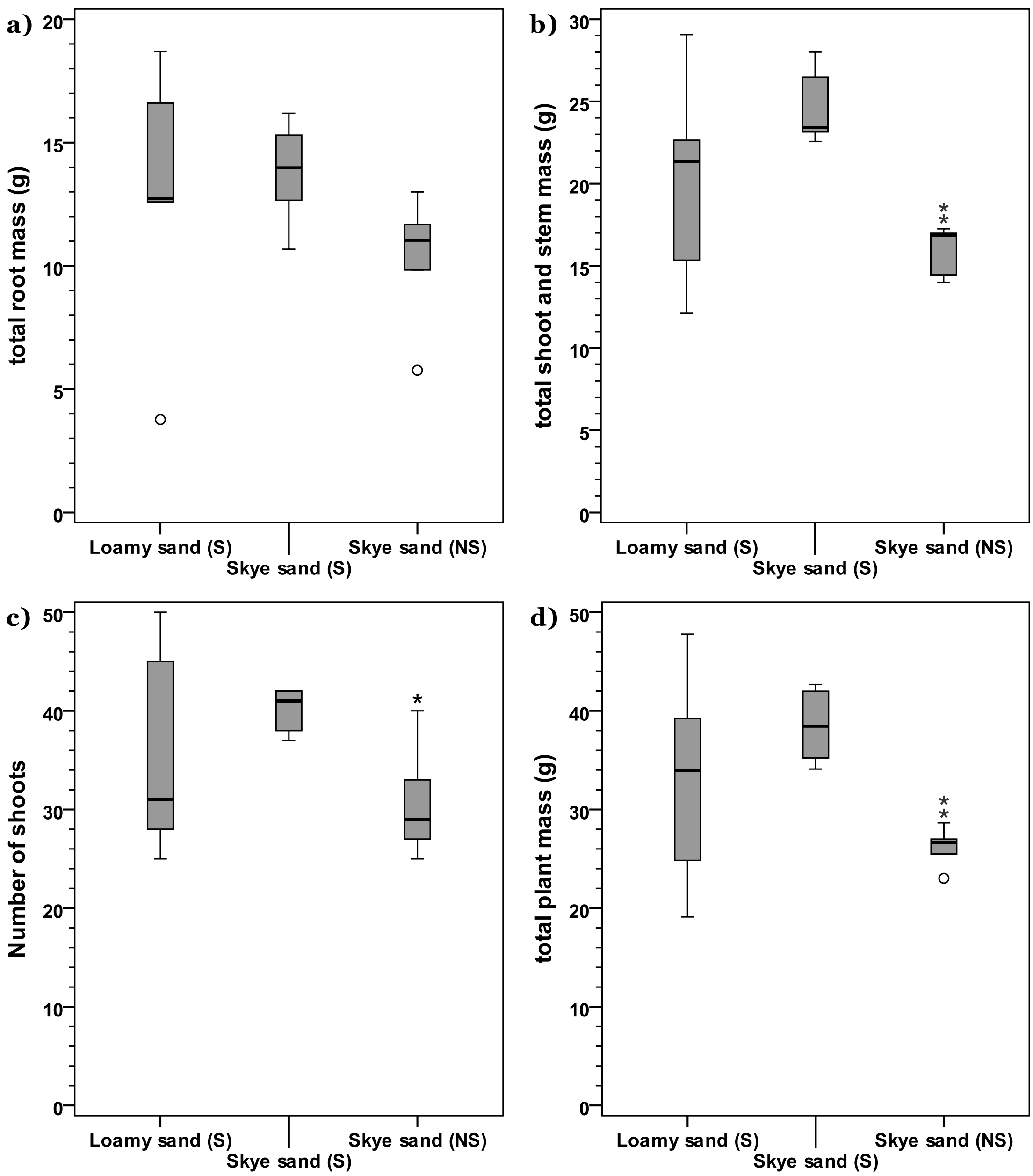

Figure 5.5. Effects of filter media and saturated zone on plant biomass allocation (n = 5). S, saturated zone; NS, no saturated zone. '**' and '*' represent a statistically significant effect (*p<0.01* and *p<0.05* respectively) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

5.3.2.3 Root morphology

Inclusion of a saturated zone had a significant effect on root traits when scaled for the whole plant (*p<0.05*) (Figure 5.6b, d, f) however, specific root length (i.e. root length per unit root dry mass), specific root surface area and specific root volume were not significantly influenced by inclusion of a saturated zone (*p>0.05*) (Figure 5.6a, c, e). In contrast, filter media type significantly affected root length (*p<0.05*), surface area (*p<0.01*) and volume (*p<0.05*) per unit weight but not when scaled for the whole plant, except in the case of total root length (Figure 5.6b). The average specific root length, which is typically used to describe root etiolation ('fineness'), was far greater in the saturated and non-saturated Skye sand configurations (21,200 cm/g and 22,700 cm/g respectively) than the loamy sand (14,000 cm/g). These results imply that *C. appressa* adapts its root architecture in response to growing in Skye sand filter media, most notably by increasing the available absorptive root surface area. This is not surprising, given that Skye sand has a strong affinity for phosphorus sorption and in P-limited environments plants typically favour the development of fine roots, which require less energy to construct and forage through soils (Lambers et al. 2008). However, root etiolation increases exploration at the expense of mechanical strength and also creates vulnerabilities such as high turnover rates, desiccation intolerance, and susceptibility to herbivores (Eissenstat et al. 2000).

5.3.2.4 Root diameter class characteristics

Neither filter media nor inclusion of a saturated zone had a significant effect on average root diameter ($p>0.05$), which across the three configurations ranged from 0.13 to 0.19mm. The root diameter class analysis revealed that, in all biofilter configurations, approximately 80% of total root length and 40% of total root surface area was associated with very fine roots <0.16mm diameter. Accordingly, the root structure of the plants analysed would be considered very fine, with a high proportion of root hairs. In a low-P environment, root hairs may be responsible for as much as 90% of phosphate uptake (Gahoonia et al. 1998). This is largely related to the high absorptive surface area of root hairs which can account for up to 70% of total root surface area (López-Bucio et al. 2003). The diameter of roots typically involved in ion uptake ranges from 0.15 to 1 mm (Lambers et al. 2008). The percentage of total root surface area associated with roots in this diameter range was between 52 and 60% across all biofilter configurations. This may explain in part why *C. appressa* has consistently been found to provide excellent nutrient removal performance in biofilters (Bratieres et al. 2008; Payne et al. 2014b; Read et al. 2008).

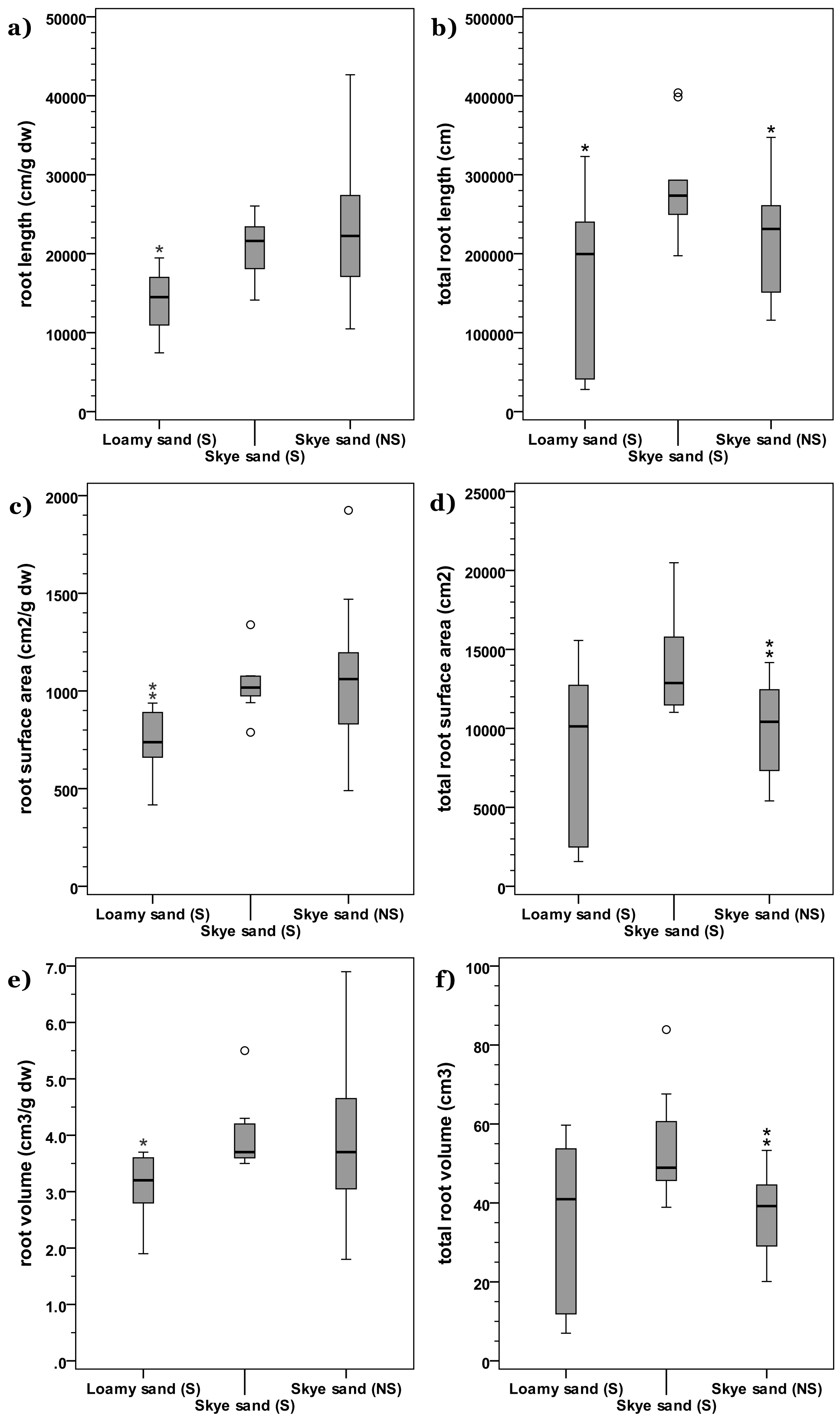

Figure 5.6. Effect of filter media and saturated zone on root characteristics per unit root dry mass (a, c, e) and for the entire plant (b, d, f) (measured using WinRHIZO). S, saturated zone; NS, no saturated zone. '**' and '*' represent a statistically significant difference ($p<0.01$ and $p<0.05$ respectively) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

5.3.2.5 Shoot morphology

Shoot length represents the sum of the length of all shoots scanned. Neither filter media nor the presence of a saturated zone had a significant influence on specific shoot length (i.e. shoot length per unit shoot dry mass) or total shoot length ($p>0.05$) (Figure 5.7a, b). Inclusion of a saturated zone significantly increased total shoot surface area in the Skye sand configuration (Figure 5.7d) but not specific surface area (Figure 5.7c), suggesting that this relationship is being driven by the significant difference in above-ground biomass between the Skye sand configurations (Figure 5.5b).

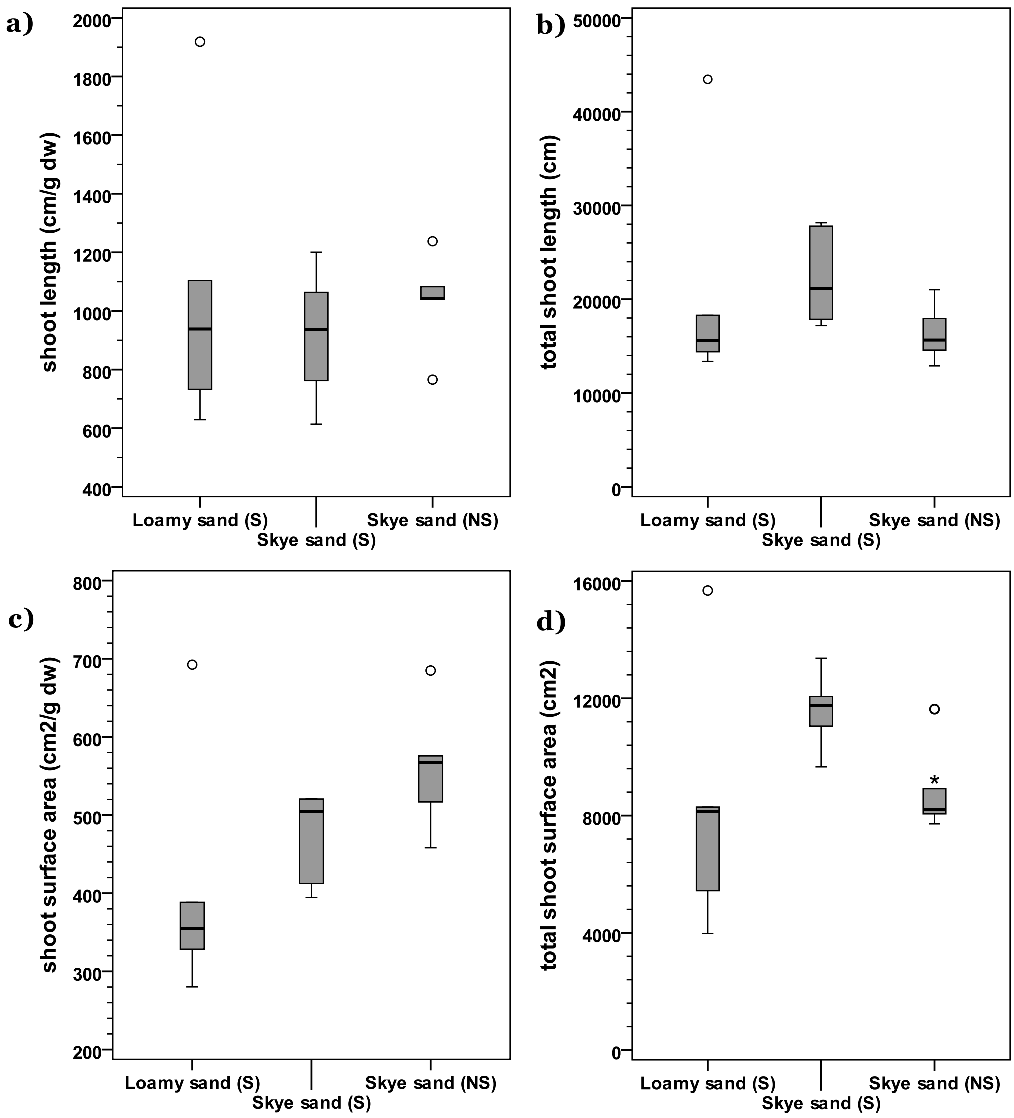

Figure 5.7. Effect of filter media and saturated zone on shoot characteristics per gram of roots (i.e. specific shoot characteristics) (left) and for the entire plant (right) (analysed using WinRHIZO). S, saturated zone; NS, no saturated zone. '*' represents a statistically significant difference ($p<0.05$) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

5.3.3 Correlation between nutrient removal and plant characteristics

Significant correlations between plant biomass characteristics (total plant mass, total shoot and stem mass and total root mass) and nutrient removal (i.e. total nitrogen (TN), nitrate + nitrite (NOx), dissolved organic nitrogen (DON), particulate organic nitrogen (PON) and filterable reactive phosphate (FRP)) were observed under both wet and dry conditions (Table 5.4). When scaled for the entire plant, root traits (total root length, total root surface area and total root volume) also correlated significantly with nutrient removal under wet and dry conditions; this was driven largely by correlations with total root mass. This is demonstrated by the significant correlations between ammonium (NH_4^+) and NO_x concentrations and total root characteristics during the dry and wet periods, respectively (Table 5.4).

Total phosphorus (TP) concentrations correlated significantly with total shoot and stem mass during the dry period (Table 5.4). Suggesting that, following dry spells, soil desiccation and formation of preferential flow paths may compromise filter media function, increasing the reliance on adhesion to above ground biomass to filter or adhere P-bound sediment. Specific shoot surface area also correlated with PON concentrations during the dry period, further emphasising the role of above-ground biomass in particulate adhesion.

Under dry conditions, no significant correlations were identified between NO_x concentrations and total root characteristics (Table 5.4), suggesting that during dry periods, when oxygen concentrations become depleted, the division of NO_x removal between plant-uptake and denitrification may shift towards the latter. However, this is unlikely to be the case in the non-saturated ‘freely draining’ systems in which dry conditions are likely to increase nitrification while limiting conditions for denitrification (Parkin 1987). Total nitrogen maintained a strong correlation with total root volume under dry conditions driven by correlations between total root volume and NH_4^+ and DON removal (Table 5.4).

During the wet period, no significant correlations were identified between specific root characteristics (specific root length, specific root surface area, specific root volume) and nutrient removal (Table 5.4), implying that under wet conditions plant biomass is a more significant driver of nutrient removal than specific root traits. Under dry conditions, all root characteristics, both dependent and independent of total root mass, correlated significantly with NH_4^+ removal. This is perhaps because NH_4^+ removal is governed mainly by rapid adsorption to the filter media and nitrification by soil microbes, which are highly active under wet conditions (Lambers et al. 2008; Mortland et al. 1965). Accordingly, plant-uptake becomes more critical for NH_4^+ removal during dry periods, when microbial processing slows down and filter media desiccation reduces the effectiveness of adsorption.

Table 5.4. Significant (*p<0.05*) ('*') and highly significant (*p<0.01*) ('**') correlations between plant growth characteristics and nutrient treatment during 'dry' and 'wet' periods. Pearson's correlation coefficient values (r) are shown in parentheses.

Characteristic	**Water Quality Monitoring Period**	
	Dry	**Wet**
total root mass (g)	NH_4^+ (-0.60)*	TN (-0.75)** NO_x (-0.78)** DON (-0.53)* FRP (-0.57)*
total shoot & stem mass (g)	TP (-0.54)* TN (-0.72)** NO_x (-0.67)** DON (-0.63)* FRP (-0.57)*	TN (-0.73)** NO_x (-0.70)** DON (-0.72)** PON (-0.56)* FRP (-0.68)**
total plant mass (g)	TN (-0.68)** NO_x (-0.66)** DON (-0.56)* FRP (-0.56)*	TN (-0.82)** NO_x (-0.81)** DON (-0.71)** PON (-0.59)* FRP (-0.70)**
total root length (cm)	NH_4^+ (-0.63)* FRP (-0.62)*	TN (-0.63)* NO_x (-0.65)*
total root surface area (cm^2)	NH_4^+ (-0.60)* DON (-0.55)* FRP (-0.66)*	TN (-0.69)** NO_x (-0.70)** DON (-0.55)* FRP (-0.58)*
total root volume (cm^3)	NH_4^+ (-0.56)* TN (-0.58)* DON (-0.59)* FRP (-0.67)*	TN (-0.72)** NO_x (-0.73)** DON (-0.60)* FRP (-0.62)*
average root diameter (mm)		TP (-0.83)** PON (-0.54)*
specific root length (cm/g)	NH_4^+ (-0.60)* PON (-0.54)*	
specific root surface area (cm^2/g)	NH_4^+ (-0.60)*	
specific root volume (cm^3/g)	NH_4^+ (-0.56)* FRP (-0.63)*	
specific shoot surface area (cm^2/g)	PON (-0.54)*	

Filterable reactive phosphorus and PON were significantly negatively correlated with specific root traits under dry conditions (Table 5.4). However, biofilter effluent concentrations of FRP and PON were consistently low regardless of design (standard deviation <0.001) (Table 5.5). Therefore, although statistically significant, these correlations are of little practical importance. This could also be said for the negative correlations between TP and PON concentrations and average root diameter observed under wet conditions, which are also somewhat counter-intuitive because mechanical straining of particulates is typically enhanced by a fine root structure.

The correlations identified between nutrient concentrations and plant characteristics highlight the importance of high plant biomass, in particular root mass, and fine root architecture in facilitating nutrient removal under both wet and dry conditions. These findings corroborate the results of previous studies investigating plant traits that enhance pollutant removal in biofilters. For instance, in a study across 20 plant species, Payne et al. (2014b) found that plants with a high root surface area and root mass performed best in terms of N removal. Read et al. (2010), in a study of 20 plant species, also identified significant correlations between N and P concentrations and total plant mass, total root mass, total root length and the percentage of fine roots (<0.25 mm diameter). Read et al. (2010) found that these characteristics had a strong negative correlation with TP concentrations. This correlation was not observed in the present study since only one species was tested and TP was consistently removed in all biofilter configurations.

5.3.4 Interactions between design, plant growth and nutrient removal

Analysis of root morphology determined that plants grown in Skye sand filter media had a significantly higher total root length, specific root length, specific root surface area and specific root volume than those grown in loamy sand. Synthesising these findings with the correlations observed between nutrient removal and plant traits infers that using Skye sand filter media would be advantageous for nutrient removal, most notably NH_4^+ during dry periods and NO_x during wet. Inclusion of a saturated zone significantly increased plant biomass and total root traits. Given that these characteristics correlated significantly with enhanced removal of N and P species during both wet and dry periods, including a saturated zone would be considered advantageous for nutrient removal in stormwater biofilters under all operating conditions. Including a saturated zone also provides additional benefits for biofilters such as protection of roots against the vulnerabilities of increased etiolation and prolonged dry periods.

Table 5.5. Mean outflow pollutant concentrations (mg/L, n = 5) and removal rates, measured in April (dry period) and July (wet period). Standard deviations are shown in parentheses.

Configuration		Loamy Sand (S)		Skye Sand (S)		Skye Sand (NS)	
Monitoring Period		Dry	Wet	Dry	Wet	Dry	Wet
TP	Conc. (mg/L)	0.03 (0.004)	0.01 (0.0)	0.03 (0.005)	0.02 (0.008)	0.08 (0.03)	0.03 (0.007)
	Removal (%)	92 (1.1)	98 (0.0)	93 (1.4)	95.6 (1.8)	77 (8.7)	93 (1.5)
TN	Conc. (mg/L)	0.46 (0.1)	0.29 (0.35)	0.16 (0.04)	0.08 (0.04)	0.88 (0.05)	0.68 (0.08)
	Removal (%)	77 (5.1)	88 (13)	92 (2.0)	96.5 (1.4)	56 (2.4)	72 (3.0)
NH_4^+	Conc. (mg/L)	0.017 (0.026)	0.002 (0.001)	0.004 (0.002)	0.001 (0.000)	0.003 (0.002)	0.002 (0.002)
	Removal (%)	95 (7.8)	99 (0.1)	99 (0.7)	99.7 (0.1)	99 (0.6)	99 (0.4)
NO_X	Conc. (mg/L)	0.12 (0.06)	0.16 (0.32)	0.05 (0.02)	0.01 (0.02)	0.54 (0.03)	0.41 (0.05)
	Removal (%)	86 (7.9)	83 (31)	94 (2.9)	98.4 (1.6)	35 (3.7)	55 (4.9)
DON	Conc. (mg/L)	0.24 (0.03)	0.10 (0.03)	0.07 (0.01)	0.04 (0.004)	0.32 (0.01)	0.22 (0.02)
	Removal (%)	56 (6.1)	80 (5.5)	87 (2.3)	92 (0.8)	41 (2.3)	59 (3.1)
PON	Conc. (mg/L)	0.005 (0.0)	0.03 (0.005)	0.005 (0.0)	0.03 (0.02)	0.005 (0.0)	0.05 (0.02)
	Removal (%)	71 (3.4)	94 (0.8)	89 (1.3)	95 (3.6)	94 (2.5)	92 (2.9)
FRP	Conc. (mg/L)	0.002 (0.0)	0.001 (0.0)	0.001 (0.0)	0.001 (0.0)	0.003 (0.0)	0.002 (0.0)
	Removal (%)	99 (0.2)	96 (0.2)	99 (0.2)	99 (0.0)	99 (0.2)	99 (0.2)

5.4 Conclusions

Plants play an essential role in the removal of nutrients from stormwater in biofilters. However, the extent to which plants can assimilate N and P is largely dependent on root structure, stormwater detention time and the ability of plants to acquire nutrients from filter media. The capacity of filter media to provide primary nutrient retention is also a factor. Skye sand filter media had a significant effect on the root morphology of *C. appressa*, increasing total root length, specific root length and root fineness compared with the loamy sand configuration and this increased root etiolation resulted in better nutrient removal. The increased opportunity for nutrient uptake facilitated by prolonged detention was demonstrated by the significantly higher biomass and extensive root system growth in the saturated zone inclusive biofilters. Inclusion of a saturated zone would be recommended in conjunction with Skye sand filter media to protect plants against the vulnerabilities of increased etiolation and prolonged dry periods. Future research should be undertaken to validate the use of Skye sand biofilter media by testing its nutrient removal performance in combination with a broader variety of plant species.

5.5 Acknowledgements

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Chapter 6: The Influence of Biofilter Design on Phosphorus Accumulation and Partitioning in Filter Media

Implications for P removal and retention

Foreword

The present chapter investigates phosphorus accumulation and partitioning within biofilters. Filter media collected from laboratory- and field-scale biofilters was subjected to a sequential extraction scheme designed to measure the concentration of phosphorus in four storage pools (bioavailable, adsorbed, mineral bound and organic). By investigating P accumulation and partitioning in filter media this study aims to provide new insight into the short- and long-term capacity of biofilters to retain phosphorus. These outcomes will assist practitioners when designing biofilters and developing maintenance strategies to achieve optimal phosphorus removal and retention.

This chapter is presented in the format of a journal paper and includes material from a previously published peer-reviewed conference paper:

Glaister, B. J., T. D. Fletcher, P. L. M. Cook and B. E. Hatt (unpublished). The Influence of Biofilter Design on Phosphorus Accumulation and Partitioning in Filter Media.

Glaister, B. J., P. L. M. Cook, T. D. Fletcher and B. E. Hatt (2013). Long-term phosphorus accumulation in stormwater biofiltration systems at the field scale. 8th International Conference on Water Sensitive Urban Design. Gold Coast, Australia.

This conference paper and supplementary information for this chapter can be found in the Chapter 6 Appendix.

Objectives and hypotheses

The effectiveness of phosphorus removal and retention in biofilters is largely dependent on the storage pool in which phosphorus is held, however, phosphorus storage is not static. Transition between biogeochemical P-storage pools is continuous and essential to maintaining the long-term P-removal capacity of biofilters. Understanding P-partitioning between storage pools in biofilters is an important area of research, particularly in terms of determining the suitability of Skye sand as a filter media. Quantification of P-partitioning is also needed to improve knowledge of P-cycling in biofilters and provide data upon which estimates of P-removal longevity can be made. The present study aims to fulfil these objectives by quantifying P-accumulation in biofilters and assessing the relative contribution of various storage pools to overall P-retention.

The main hypotheses tested are:

- Fe plays a key role in the short and long term retention of P in biofilters.
- Phosphorus partitioning is dynamic and changes as biofilters mature.
- Phosphorus retained in reversible forms may become labile under reducing conditions, which can occur in poorly draining systems or where a saturated zone is included.
- P-saturation can be perpetually avoided with careful maintenance (i.e. plant harvesting & replanting).

The Influence of Biofilter Design on Phosphorus Accumulation and Partitioning in Filter Media

Bonnie J. Glaister[a], Tim D. Fletcher[b], Perran L. M. Cook[c] and Belinda E. Hatt[a]

[a] Department of Civil Engineering, Monash University, Victoria, 3800, Australia

[b] Waterway Ecosystem Research Group, School of Ecosystem & Forest Sciences, Faculty of Science, the University of Melbourne, Burnley, Victoria, 3121, Australia

[c] Water Studies Centre, School of Chemistry, Monash University, Victoria, 3800, Australia

Abstract

Previous research has demonstrated that biofilters are an effective technology for the removal of phosphorus (P) from stormwater. However, stormwater biofiltration is a relatively new technology and most field-scale systems are still fairly young, therefore little is understood about how P is retained in biofilters and their long-term capacity to act as a sink for P. The present study aims to address this knowledge gap by examining filter media from 20 laboratory-scale biofilter columns following 12 months of stormwater dosing and six field-scale biofilters ranging in maturity from 5 to 11 years. A four-step sequential extraction scheme was utilised to quantify P accumulation and partitioning across the following P storage pools: bioavailable-P, adsorbed-P, mineral-P and organic-P. Results show that P accumulation in biofilters varies spatially (areally and with depth). Phosphorus concentrations were highest near stormwater inlets and typically decreased with depth, predominantly between 0 and 10cm. Both the laboratory- and field-scale biofilters showed that mineral- and organic-P accounts for most surface layer P, corresponding with the build-up of trapped sediment. Phosphorus partitioning in biofilter columns showed that in immature systems adsorption to metal-ions primarily facilitates orthophosphate ($PO_4^{3}{-}P$) removal. Partitioning results from the field scale biofilters suggests that adsorbed $PO_4^{3}{-}P$ transforms into more fixed forms (i.e. mineral and organic) over time. These findings suggest that biofilters are well designed for long-term P retention. However, P adsorbed to reducible metal-ions may be susceptible to desorption under anaerobic conditions. These findings reaffirm the importance of maintaining good hydraulic function in biofilters to prevent clogging. Moreover, this study shows that biofilters are well suited for long-term P retention and provides practitioners with new insights into how biofilters can be designed and maintained to improve short- and long-term P removal performance.

6.1 Introduction

Biofiltration systems are a popular and effective passive treatment technology for stormwater in urban areas (Davis et al. 2009; Duncan 2006). Widespread implementation of biofilters has occurred across Australia and worldwide over the last decade and is expected to continue as adoption of water sensitive urban design practices becomes increasingly conventional. Biofilters treat stormwater by filtering through a vegetated porous media, typically loamy sand. As the stormwater percolates through the media, pollutants are removed through myriad physical, chemical and biological processes (Henderson et al. 2007a). Removal of phosphorus (P), a major stormwater pollutant of concern, is governed by multiple processes. Total phosphorus (TP), which is largely particulate-associated, is removed predominately by physical straining and sedimentation. Removal of inorganic phosphorus (i.e. orthophosphate), which constitutes approximately 30% of TP in stormwater (Duncan 2006), is facilitated primarily by geochemical processes (adsorption and/or precipitation) (Kadlec and Knight 1996; Reddy et al. 1999). As stormwater infiltrates through the filter media rapid and highly reversible P-adsorption occurs through electrostatic ion-exchange with outer sphere hydroxyl complexes. Over time slower more irreversible specific adsorption reactions through mono- and bidentate chemical bonding with inner-sphere complexes and precipitation of cation-P complexes can occur (Barber 2002; Lucas et al. 2008). Biological assimilation and plant-soil interactions also play an important role in P-removal. Plants increase the availability of sorption sites in the filter media through root growth and oxidation of ferrous iron and direct uptake of $PO_4^3{-}P$ from sorption sites in the filter media by plants and rhizosphere microorganisms (Bolan 1991; Lucas et al. 2008; Read et al. 2010). Transition between these biogeochemical P-storage pools is continuous and essential to maintaining the long-term P-removal capacity of biofilters. Transfer of adsorbed-P into 'fixed' geochemical or organic forms replenishes rapid sorption sites for further uptake and reduces the risk of P mobilisation from reversible bonds that are sensitive to hydro-chemical environment variations (i.e. reducing conditions) (Boström et al. 1988; Jansson 1987). Results from field- and laboratory-scale biofilter experiments demonstrate very good removal of P from stormwater - when configured correctly (e.g. Davis 2007; Hatt et al. 2009; Henderson et al. 2007a; Lucas et al. 2008). Yet these studies typically use a "black box" approach to estimate P-removal and therefore do not quantify or investigate P accumulation or retention properties. Since biofiltration is a relatively new technology and most field-scale systems are still fairly young, the availability of empirical data about P retention in biofilters is limited, thus little is understood about the long-term ability of biofilters to act as a sink for P. Studies of the long-term P retention capacity of bioretention media have been mostly limited to compressed-time laboratory based sorption experiments (e.g. column studies) which are not wholly representative of field-scale environments (e.g. Erickson et al. 2007; Hsieh et al. 2007). In a more recent study, Komlos and Traver (2012) investigated P-retention a field scale biofiltration system after nine years of operation. They concluded that while the top 10cm of the infiltration bed was saturated with $PO_4^{3}-P$ saturation at deeper depths would not occur for >20 years. This research provided new insight into the long-term P removal capacity of biofilters. However, this study did not quantify the contribution of different P-pools to P retention. More detailed quantification of P-partitioning in biofilters is needed to improve knowledge of P-cycling and improve the accuracy of P-removal longevity estimates. Furthermore, quantification of P retained in reversible forms (e.g. bound to Fe(III)) is essential since this P may become labile under reducing conditions, which can occur in poorly draining systems or where a saturated zone is included. The present study aims to address these knowledge gaps by quantifying P accumulation in biofilters and assessing the relative contribution of various storage pools to overall P-retention.

6.2 Method

6.2.1 Laboratory-scale biofilters: filter media sampling and preparation

Filter media samples were collected from 20 biofilter columns after 12 months of stormwater dosing (methodology described in detail in Chapter 4). The 20 columns comprised four biofilter designs (n=5) to allow the P-retention properties of biofilters with different filter media, with and without vegetation, and with and without inclusion of a saturated zone (a permanent water storage designed to improve nitrogen removal) to be compared (Table 6.1).

Table 6.1. Biofilter column design configurations

Configuration ID	Filter Medium	Vegetation	Saturated Zone
LS-V-S	Loamy Sand (LS)	*Carex appressa* (V)	Yes (S)
SS-NV-S	Skye Sand (SS)	Non-vegetated (NV)	Yes (S)
SS-V-S	Skye Sand (SS)	*Carex appressa* (V)	Yes (S)
SS-V-NS	Skye Sand (SS)	*Carex appressa* (V)	No (NS)

Two filter media were compared: loamy sand, which is currently recommended for use in biofilters (FAWB 2009), and 'Skye sand', a naturally occurring iron-coated sand from Skye, Victoria (Australia) (physical and chemical properties of the filter media are described in detail in Chapter 3). Previous testing has shown that Skye sand has a greater capacity for P sorption than loamy sand (Glaister et al. 2011), and that in conjunction with vegetation and a saturated zone Skye sand can enhance nitrogen removal performance (Glaister et al. 2014). Figure 6.1(a) illustrates the column cross section and layout. In each configuration the filter media layer (1; 300mm deep) is underlain by coarse washed sand (2; 200mm), pea gravel (3; 70mm) and a gravel (~5mm) drainage layer (4; 30mm). Effluent drained freely from outlets at the base of the non-saturated columns while a riser pipe was attached to the outlet of those with a saturated zone to maintain a 300mm internal ponding zone in the lower part of the columns. This allowed water retained within the system between events to be released prior to freshly treated stormwater in subsequent dosings. A mixture of pine woodchips (bark removed) (26.5 g) and sawdust (9.3 g) was added to the coarse washed sand in the saturated zone inclusive columns to provide a carbon source for denitrifying bacteria. The total organic material added was equivalent to 5% of the volume of the saturated zone.

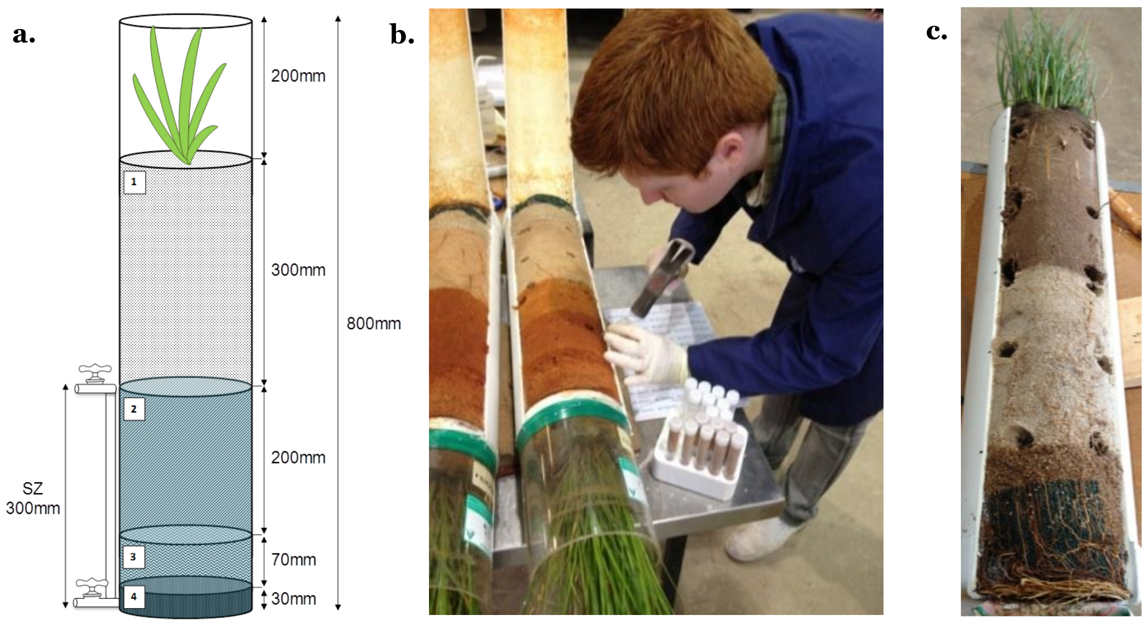

Figure 6.1. (a) Biofilter column schematic (b) biofilter column during filter media extraction and (c) after filter media extraction

Duplicate horizontal soil cores (10mm diameter) were removed from the biofilter columns at depths of 0, 25, 50, 75, 200, 300, 400 and 500mm (see Figure 6.1.(b,c)) (refer to Chapter 6 Appendix section A6.3 for cross-sectional photos of the post-experimental biofilter columns). The duplicate cores from each individual depth were homogenised, except 400mm and 500mm cores which were blended together (to give an approximation of concentrations in the upper layers of the saturated zone), giving a total of 7 filter media samples per column representing depths of 0, 25, 50, 75, 200, 300 and ~450mm. Two 0.5g sub-samples were collected from each depth increment filter media sample. The first was dried for 24 hours at 105°C to determine the dry weight of the media. The other was analysed using the four step sequential P-extraction scheme described in section 6.2.4.

6.2.2 Field-scale biofilters: site descriptions

Three existing field-scale biofilters in Melbourne (Cremorne St., Clifton Hill and Banyan Reserve) and Brisbane (Wakerley, Hoyland St. and Saturn Crescent) were selected for analysis. These biofilters varied in age, size, filter media configuration, vegetation and catchment characteristics (Table 6.2). While specific physical and chemical composition data was not available for the filter media used at these sites, the filter media was assumed to be compliant with the Australian biofilter guidelines, which recommend sand or loamy sand filter media (FAWB 2009). All biofilters were located in residential catchments, except for Cremorne St., which is located in an industrial/commercial area. Site photos and filter media core sampling locations are presented in Figure 6.2 and Figure 6.3 (see Chapter 6 Appendix section A6.2 for detailed site descriptions).

Table 6.2. Summary characteristics of the biofilters tested (Ratio refers to biofilter surface area as a proportion of the total catchment area).

Biofilter	Location	Year Constructed	Area (m^2)	Ratio (%)	Filter media depth (mm)	Sediment Pre-treatment
Hoyland St.	Brisbane	2001	720	4%	700	nil
Cremorne St.	Melbourne	2003/4	11	3.4%	400	nil
Saturn Cres.	Brisbane	2006	20	2%	400	nil
Wakerley	Brisbane	2006/7	2865	0.3%	800-1000	pond
Clifton Hill	Melbourne	2007	200	0.3%	500	sediment trap
Banyan	Melbourne	2008	3750	1.6%	400	pond/marshes

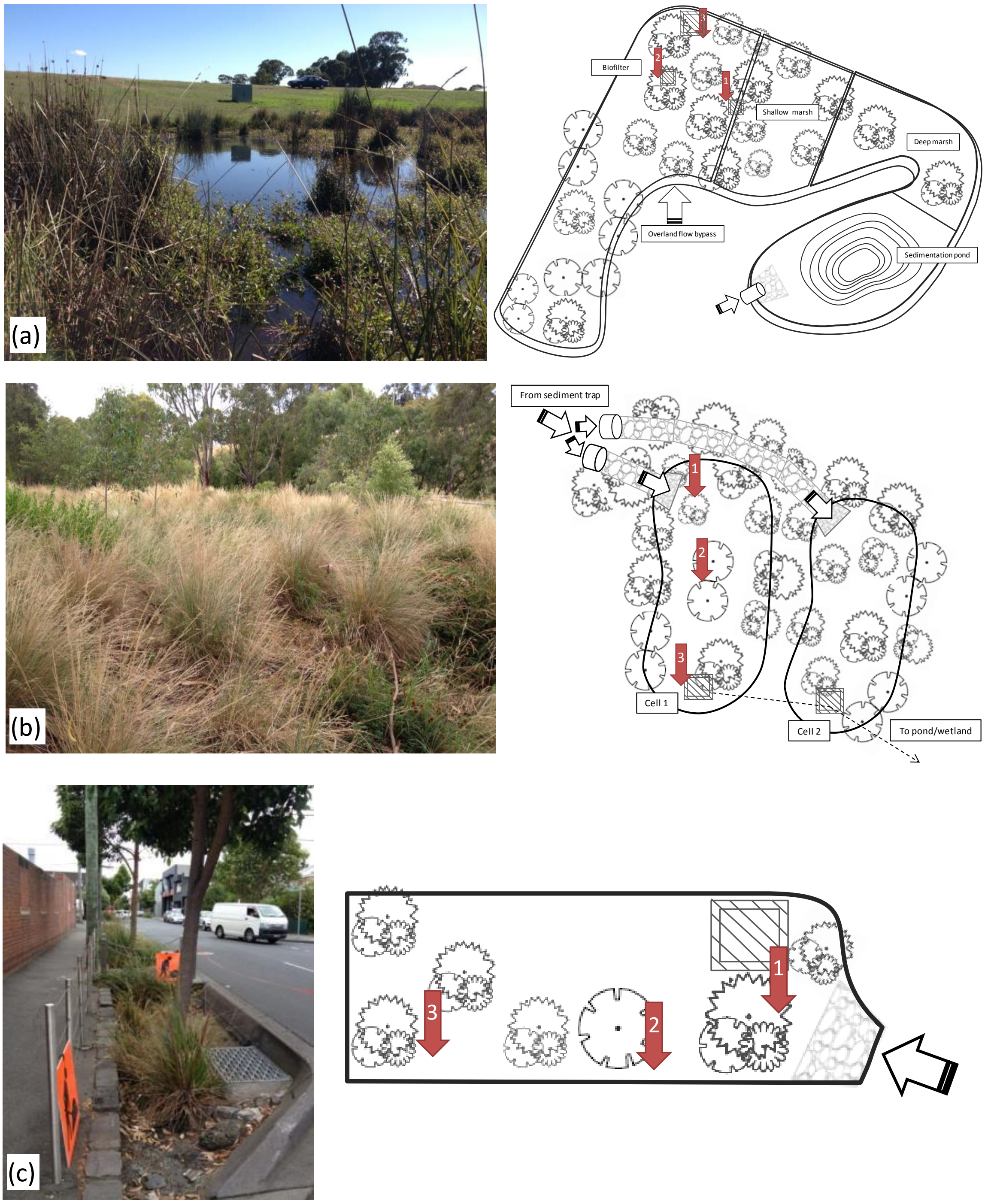

Figure 6.2. Site photos of the (a) Banyan, (b) Clifton Hill and (c) Cremorne St. (outstand Z2) biofilters in Melbourne and schematic diagrams outlining the location of the filter media cores extracted from each system respectively (not to scale) (see Chapter 6 appendix A6.2 for detailed site descriptions).

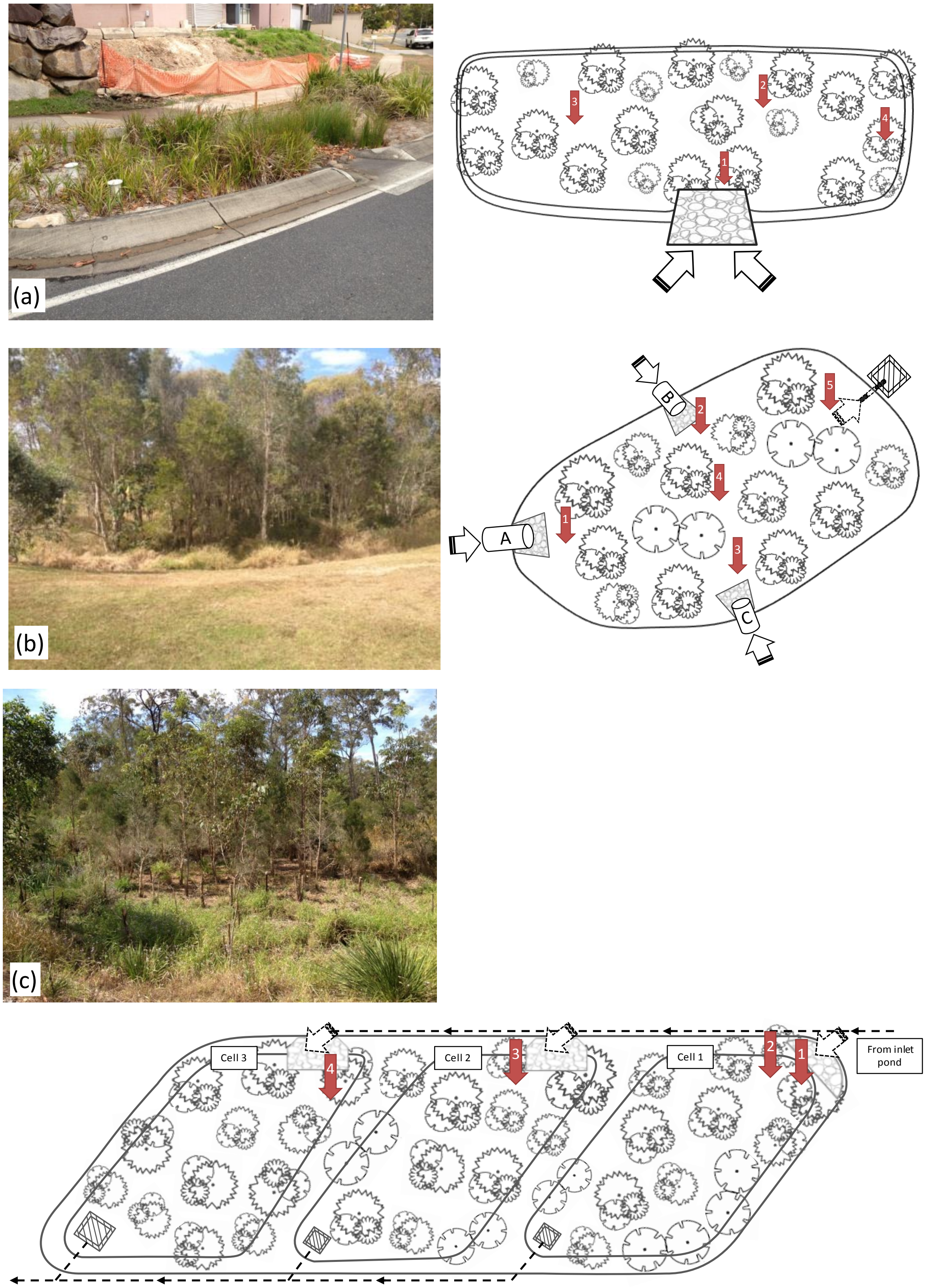

Figure 6.3. Site photos of the (a) Saturn Crescent, (b) Hoyland St. and (c) Wakerley biofilters in Brisbane and schematic diagrams outlining the location of the filter media cores extracted from each system respectively (not to scale) (see Chapter 6 appendix A6.2 for detailed site descriptions).

6.2.3 Field-scale biofilters: filter media sampling and preparation

The Brisbane and Melbourne biofilters were sampled in September 2012 and April 2013 respectively. Filter media cores were manually extracted using 400mm PVC pipes (25mm diameter) (Figure 6.4a) (refer to Chapter 6 Appendix section A6.4 for cross-sectional photos of the filter media cores). The depth of the core void was measured following extraction to account for in-situ compaction. The cores were frozen (-2°C) until such time that the filter media could be extracted (<2 weeks). The filter media cores were segmented and homogenised into the following depth intervals: 0-10mm, 10-20mm, 20-40mm, 40-80mm, 80-120mm, 150-200mm and 300-350mm (Figure 6.4b). Two 0.5g sub-samples from each filter media depth interval were collected to (i) measure the dry weight of the sample (24 hours at 105°C) and (ii) elucidate the concentration and partitioning of P in the filter media.

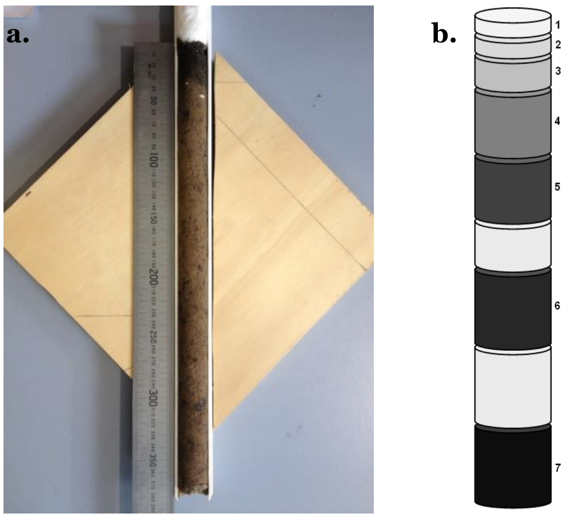

Figure 6.4. (a) example filter media core extracted from field scale biofiltration systems (b) schematic representation of the filter media segments removed from the filter media cores.

6.2.4 Phosphorus sequential extraction scheme

The four step sequential extraction scheme outlined in Table 6.3 was adapted from existing methods (Jensen et al. 1993; Kostka et al. 1994; Ruttenberg 1992) to measure the concentration of P retained in the following phases: 1) loosely sorbed/exchangeable (Bioavailable-P); 2) adsorbed to poorly crystalline (reducible) iron oxyhydroxides (Adsorbed-P); 3) sorbed to or in mineral phase with amorphous iron oxyhydroxides (Mineral-P); and 4) Organic-P. Although this method targets Fe-bound P, P may also be liberated from Al and Mn oxides and carbonate minerals, particularly in the ascorbate and HCl extractions. However, Al and Mn are expected to have relatively minor associations with P compared with Fe, especially in Skye sand (see Chapter 4 Table 4.6 for filter media characterisation).

The first step of the extraction used a 0.5M solution of magnesium chloride ($MgCl_2$) to release loosely sorbed $PO_4^{3}-P$ from the filter media (Bioavailable-P). Next, $PO_4^{3}-P$ sorbed to poorly crystalline or loosely sorbed (reducible) iron oxyhydroxides (Adsorbed-P) was extracted using an ascorbate solution (Step 2). Following this, a 0.5M solution of hydrochloric acid (HCl) was used to extract $PO_4^{3}-P$ sorbed to or in mineral phase with any remaining amorphous Fe(III) oxides or newly formed acid volatile sulfides (AVS) (Mineral-P) (Step 3). Finally, the filter media was furnace ashed then extracted again in a 0.5M HCl acid solution to release the residual organic phosphorus fraction (Organic-P) (Step 4).

Table 6.3. Phosphorus sequential extraction scheme.

Step	P-Fraction	Extractant	Time	Fe-P phase extracted
1	Bioavailable	0.5M $MgCl_2$	Shaking for 2hrs (125RPM)	Dissolved Fe (II) and exchangeable or loosely adsorbed phosphate P: Bioavailable or sorbed P
2	Adsorbed	Ascorbate Solution 4g Ascorbic Acid + 10g sodium citrate + 10g sodium bicarbonate in 200mL milliQ (pH 8)	Shaking for 24 hrs (125RPM) at room temperature	Fe: Poorly crystalline or loosely sorbed (reducible) iron oxyhydroxides P: Adsorbed P (reducible Fe-bound P)
3	Mineral	0.5M HCl Cold Extraction (pH <2)	Shaking for 2 hrs (125RPM)	Fe: Primarily amorphous iron oxyhydroxides (as well as newly formed acid-volatile sulphide) P: Mineral P (sorbed to or in mineral phase with amorphous iron oxyhydroxides)
4	Organic	Ash Sediment 450°C 0.5M HCl (pH<2)	Ash for 4 hrs Shaking for 2 hrs (125RPM)	P: Organic P (associated with the organic phase)

6.2.5 Experimental procedure

Table 6.4 summarises the filter media samples analysed using the phosphorus sequential extraction scheme. A 0.5g sample of each filter media was added to a 50mL Falcon™ tube, along with 10mL of the first extraction solution, then agitated on an orbital shaker table for the designated time period (i.e. Step 1; 2 hours). Following extraction, the samples were centrifuged at 4000rpm for 10 minutes. Thereafter, the supernatant was drawn off, filtered (0.45µm, Sartorius Minisart®) and analysed for $PO_4^{3}-P$ using Flow Injection Analysis (molybdenum blue method)

(APHA/AWWA/WPCF 1998). The next extraction solution (Step 2) was then added to the filter media in the same sample tube and the process repeated for the required time period. This process was repeated again for extraction Step 3. Prior to the final extraction the sediment was ashed in a furnace at 450°C for 4hrs. The leftover filter media was then returned to the sample tube to undergo the last 0.5M HCl extraction (Step 4) before repeating the sample preparation and analysis procedure for the last time.

Table 6.4. Summary of filter media samples analysed

Biofilter scale	Description	# Cores	Depth increments analysed (mm)
Laboratory	LS-V-S	-	0, 25, 50, 75, 200, 300, 450
Laboratory	SS-NV-S	-	0, 25, 50, 75, 200, 300, 450
Laboratory	SS-V-S	-	0, 25, 50, 75, 200, 300, 450
Laboratory	SS-V-NS	-	0, 25, 50, 75, 200, 300, 450
Field	Banyan Reserve	3	0-10, 10-20, 20-40, 40-80, 80-120, 150-200, 300-350
Field	Clifton Hill	3	0-10, 10-20, 20-40, 40-80, 80-120, 150-200, 300-350
Field	Cremorne St.	3	0-10, 10-20, 20-40, 40-80, 80-120, 150-200, 300-350
Field	Saturn Crescent	4	0-10, 10-20, 20-40, 40-80, 80-120, 150-200, 300-350
Field	Hoyland St.	5	0-10, 10-20, 20-40, 40-80, 80-120, 150-200, 300-350
Field	Wakerley	4	0-10, 10-20, 20-40, 40-80, 80-120, 150-200, 300-350

6.3 Results and Discussion

6.3.1 Laboratory-scale biofilter column study

6.3.1.1 Phosphorus accumulation

Short-term P accumulation was quantified in laboratory-scale biofilter columns following 12 months of stormwater dosing. The profiles in Figure 6.5 present the total concentration of P (measured as $PO_4^{3}-P$) in the filter media measured as the sum of the four partitioned P-phases. Consistent with previous laboratory and field studies, P concentrations across all configurations decreased with depth, predominantly in the top 100mm (Hatt et al. 2008; Komlos et al. 2012; Li et al. 2008a; Li et al. 2008b). Below 100mm, P accumulation remained fairly uniform irrespective of biofilter design, suggesting that, over this period of testing, neither filter media type, vegetation nor inclusion of a saturated zone influences P accumulation. However, variation in P accumulation between the configurations is most notable at the filter media surface where P concentrations are highest owing to the sedimentation of particulate-bound P.

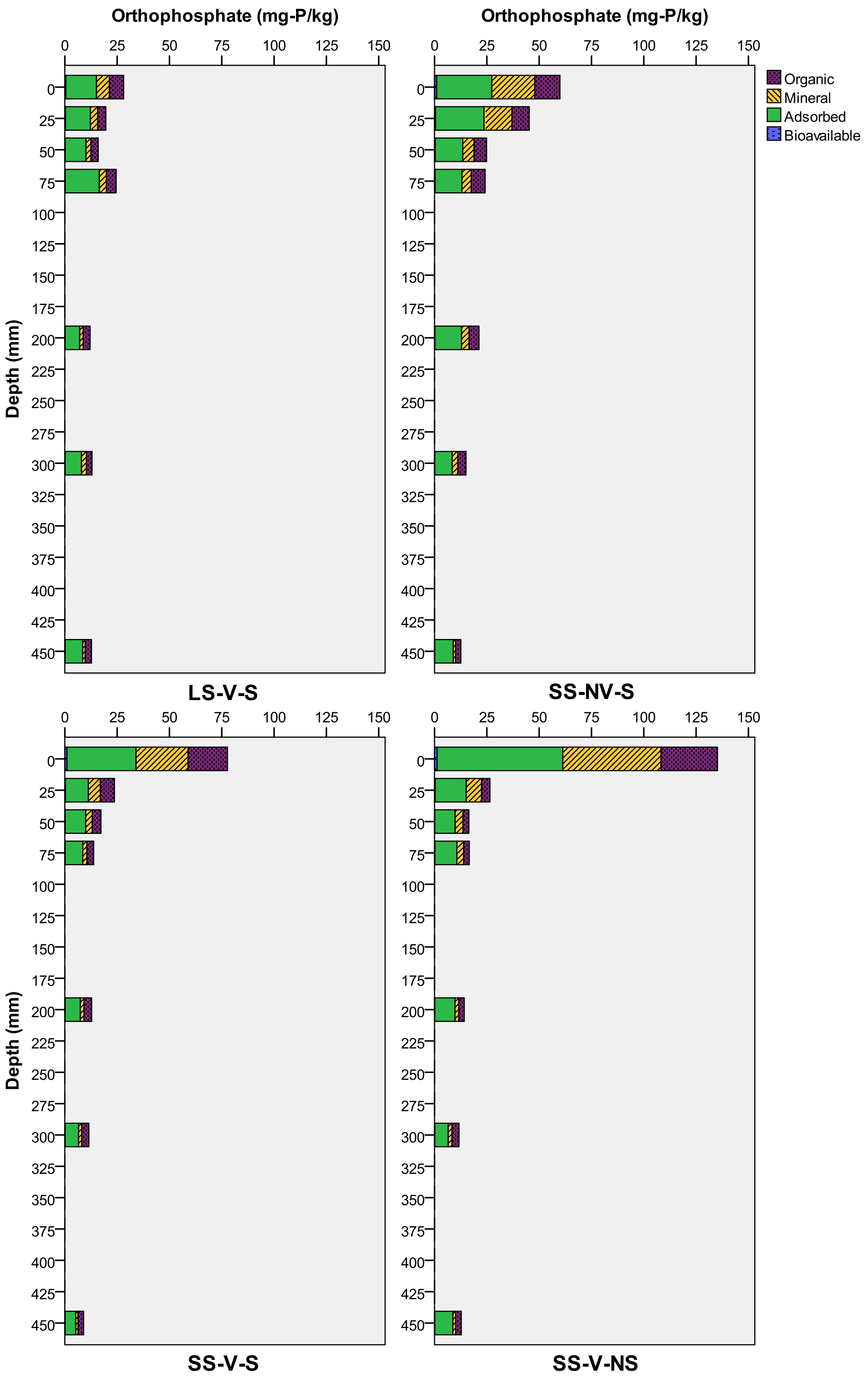

Figure 6.5. $PO_4^{3}-P$ accumulation and partitioning (mg-P/kg) in the stormwater biofilter columns (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone). Data is the mean of five replicates.

Phosphorus concentrations varied mostly between the configurations in the top 100mm of filter. For instance, biofilters containing Skye sand filter media had higher surface layer P concentrations than the loamy sand configuration, suggesting that Skye sand can retain more P than loamy sand. This finding supports previous analyses conducted by the authors, which suggest that Skye sand has the potential to enhance a biofilters capacity for P removal (see Chapter 3).

Phosphorus concentrations in the loamy sand biofilters remained relatively consistent down the column profile and did not exceed 28mg-FRP/kg (n=5) (Figure 6.5). The P sorption capacity of sand, with similar properties to that of loamy sand, was estimated by Hsieh et al. (2007) to be 28mg-FRP/kg. On this basis, these findings could imply that loamy sand is approaching P saturation. Nevertheless, the loamy sand biofilters demonstrated very good P removal (TP and PO_4^3-P) during the 12 month study (Glaister et al. 2014), suggesting perhaps that sorption was not the critical process driving P removal under these testing conditions. Alternatively, after 12 months of operation, the role of loamy sand filter media could perhaps be limited to providing temporary retention of P between events to allow time for P uptake by plants, thereby making rapid sorption sites available for the next event (see Chapter 5). This hypothesis was also posed by (Henderson et al. 2007b) who concluded that rather than providing a long-term sink for nutrients the role of filter media may be to extend the residence time of nutrients in the media so that plants and microbes have the opportunity to mineralise and assimilate P compounds. Therefore, over time, as plants reach maturity or plant-uptake and release (due to senescence) approaches equilibrium, the P-removal capacities of filter media may translate more into stormwater treatment results.

Including a saturated zone reduced the effective rate of infiltration through the vegetated Skye sand biofilters from ~280mm/hr to ~80mm/hr (Glaister et al. 2014). These altered hydraulic properties could be responsible for the markedly higher surface layer P concentrations in the non-saturated zone inclusive biofilters (i.e. SS-V-NS 135mg/kg), however this was not specifically investigated. With the exception of differences at the surface layer very similar P accumulation was observed in the vegetated Skye sand biofilters with and without a saturated zone (i.e. Figure 6.5; SS-V-S and SS-V-NS). The vegetated Skye sand columns showed a distinct decrease in P concentrations in the top 0 to 25mm of filter media, while the non-vegetated columns exhibited a more gradual decline (i.e. Figure 6.5; SS-V-S vs. SS-NV-S). During stormwater dosing, surface layer filter media in the non-vegetated biofilter columns was prone to disruption and resuspension into the ponded stormwater.

Frequent redistribution of filter media prevented the establishment of a stable surface sediment layer, which may account for the difference in P accumulation observed at this depth between the vegetated and non-vegetated systems. This finding emphasises the influence vegetation has on soil-stability and the distribution of P accumulation down the biofilter profile. Below the surface P concentrations were consistently lower in the vegetated biofilters than in the non-vegetated (Figure 6.5; SS-V-S and SS-NV-S), which could reflect the contribution of plants to P uptake. However, since analysis of plant tissue phosphorus content was outside the scope of this study, this unfortunately could not be quantitatively verified.

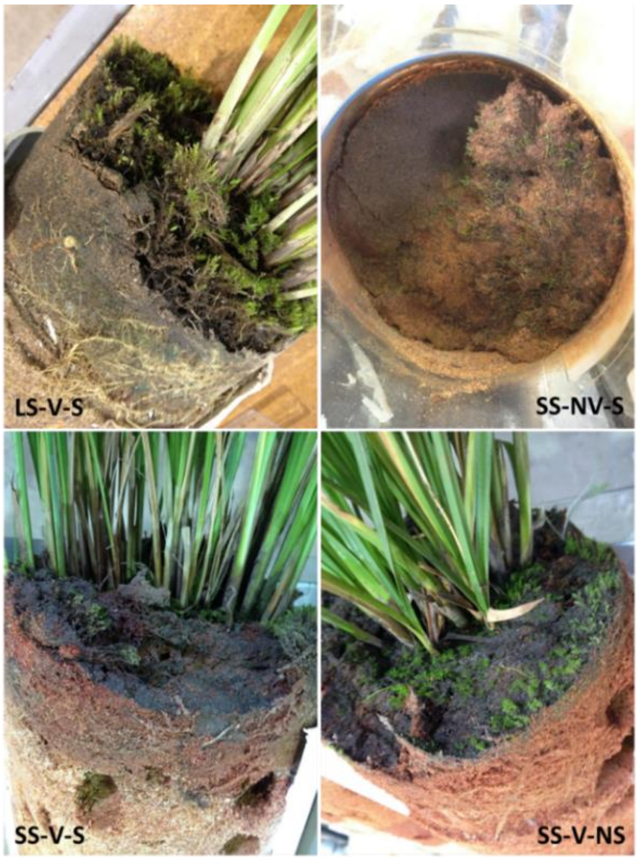

Figure 6.6. Biofilter column surfaces following 12 months of stormwater dosing (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone).

6.3.1.2 Phosphorus partitioning

The concentration profiles in Figure 6.7 illustrate P partitioning in the filter media as determined by a four-step sequential extraction. Partitioning of P in the filter media provides snapshot of a dynamic system wherein transformations of P between the pools occurs continuously. From these observations we can gain insights about the biofilters' capacity to provide short- and long-term P retention.

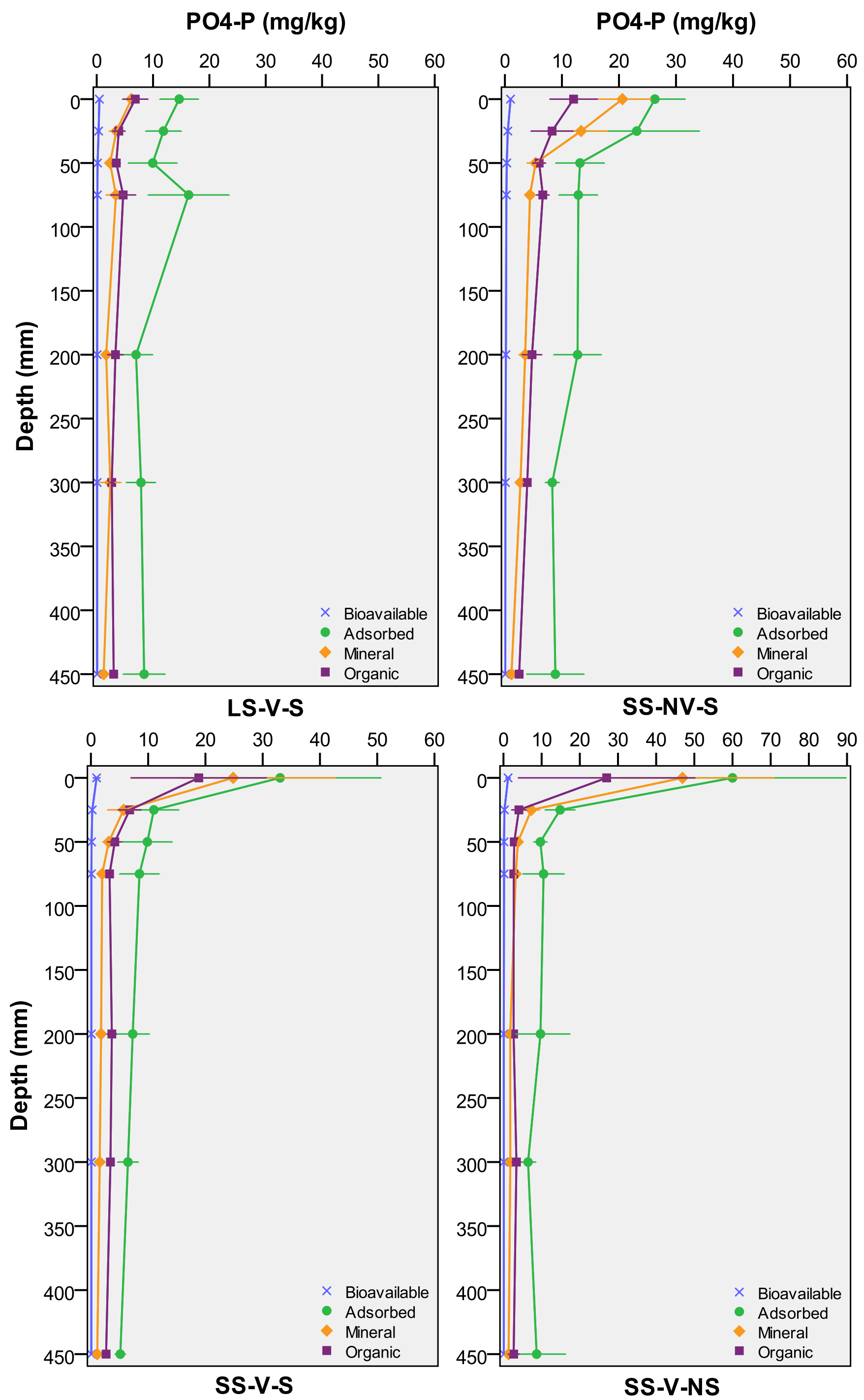

Figure 6.7. Phosphorus (mg-FRP/kg) partitioning in the biofilter columns' filter media (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone). Data is the mean of five replicates. Error Bars: +/- 1 SD. Note change in x-axis scale.

The P-partitioning profiles indicate that in all biofilter configurations the concentration of bioavailable-P in the filter media was less than 1.2mg/kg, accounting for less than 2% of extracted-P (Table 6.5). The average concentration of bioavailable-P was highest (albeit marginally) in the non-vegetated configuration (i.e. SS-NV-S) (0.35mg/kg), indicating perhaps that the absence of a biological uptake pathway increases bioavailable-P accumulation in the filter media. These results represent a positive finding as they indicate that very little labile phosphorus is present in vegetated biofilters, thus, mobilisation of loosely sorbed-P is unlikely to be an issue; at least until filter media approaches P-saturation and/or plant-uptake and release (due to senescence) reaches equilibrium.

The lower surface concentrations in the loamy sand configuration and lower percentage of P associated with mineral and organic P suggests that these columns were less effective at trapping suspended sediment than the Skye sand biofilters. Below the surface layer P concentrations and partitioning were comparable between the LS-V-S and SS-V-S configurations. Figure 6.8 illustrates P-partitioning as a percentage of total P extracted. In all biofilter designs the largest percentage of P in the filter media (approximately 56%) was adsorbed to poorly crystalline or loosely sorbed (reducible) iron oxyhydroxides (i.e. adsorbed-P) (Table 6.5). This was expected given that iron oxyhydroxides are highly reactive with P and adsorption is regarded as the predominant pathway for P removal in biofilters at least in the short term (Henderson et al. 2007b; Lucas et al. 2008; 2011). In each configuration the percentage of P in the adsorbed phase tends to increase with depth (Figure 6.8). Indicative of a decrease in sediment deposition and a greater presence of adsorbed P. Over time, as P becomes more strongly sorbed, this adsorbed-P will be transformed into the mineral phase (Goldberg et al. 1985; Torrent et al. 1992). Thus, the proportion of P in the mineral phase should increase with time. This is an important process since P in the adsorbed phase, which according to these results makes up roughly half the P retained in the filter media, represents potentially reducible P.

Under well-functioning hydraulic conditions the risk of P-desorption from the adsorbed phase is minor, however, if biofilters were to become clogged or oxygen concentrations in saturated zone were to fall within reducing conditions P dissolution from iron-phosphorus complexes may occur (Boström et al. 1988; Jansson 1987; Li et al. 2007). These results therefore emphasise the importance of biofilter maintenance to reduce the risk of such conditions occurring. In biofilters with a saturated zone, anaerobic conditions may also arise following extended dry spells. However, monitoring of dissolved oxygen concentrations in the saturated zone of the biofilter columns indicated that even after long periods of dry weather (i.e. 18 days) reducing conditions did not occur (i.e. dissolved oxygen >1.0mg/L) (Glaister et al. 2014). Anaerobic microsites may exist within the saturated zone (Parkin 1987). However, it is unlikely that desorbed P would be released from the system before being re-adsorbed elsewhere in the filter media or biologically assimilated.

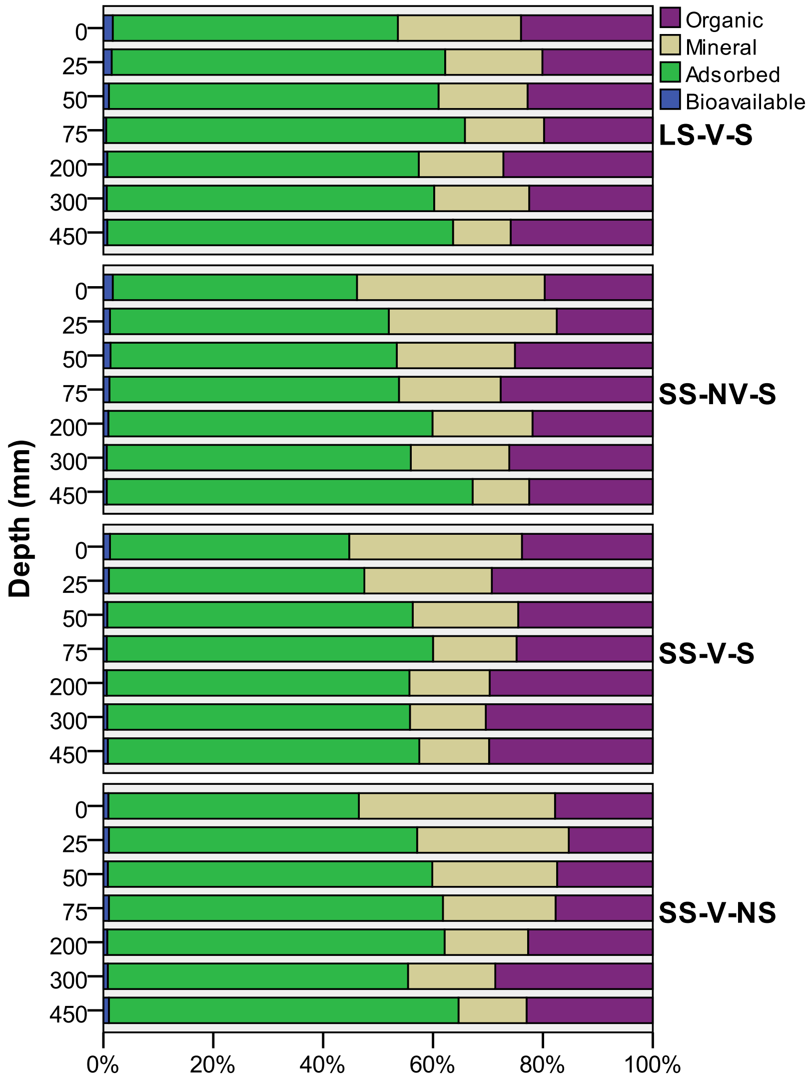

Figure 6.8. Mean (n=5) percentage of P (mg-FRP/kg) extracted from each phase in the four biofilter configurations as a function of depth (mm). Y-axis not to scale.

Table 6.5. Mean (n=5) percentage of P (mg-FRP/kg) extracted from each phase in the four biofilter configurations.

Configuration	Bioavailable	Adsorbed	Mineral	Organic
LS-V-S	1.0%	60%	16%	23%
SS-NV-S	1.1%	54%	22%	23%
SS-V-S	0.8%	53%	19%	27%
SS-V-NS	0.9%	57%	21%	20%
Average	0.9%	56%	19%	23%
Standard Deviation	0.001	0.03	0.03	0.03

The percentage of absorbed P was similar across all depths in the Skye sand biofilter configurations and marginally higher in the loamy sand biofilters, suggesting that there is a slightly greater fraction of reducible Fe in loamy sand than Skye sand.

Mineral-P accounts for approximately 19% of the P extracted from the filter media (Table 6.5). The percentage of P associated with the mineral phase is generally higher in the upper layers of the Skye sand filter media. This could reflect the composition of P associated with trapped runoff particulates. It may also be indicative of slow-sorption reactions occurring between the adsorbed- and mineral-P phases where P has been retained for the longest period (Ryden et al. 1977; Torrent et al. 1992). The ability of Skye sand to retain phosphorus in non-labile mineral forms reduces the likelihood of P-desorption and may prolong the P-removal longevity of the biofilter. Therefore, the suggestion that P is transitioning over time between the adsorbed and mineral phases is a promising finding in terms of long-term P retention.

Organic-P represents P bound to particulate organic matter including, plant-debris, microbes and humus. Organic-P accounted for approximately 23% of the total P extracted from the filter media (Table 6.5). The highest percentage of organic-P was present in the vegetated, saturated zone inclusive, Skye sand biofilters (27%), which also had the highest plant biomass overall (Glaister et al. 2017). Overall, there was negligible difference between the configurations in terms of organic-P partitioning, and thus a very minor influence associated with specific design elements (Table 6.5).

Concentrations of mineral- and organic-P in the filter media were generally similar, except in the top 25mm of the Skye sand filter media configurations, where mineral-P concentrations were somewhat higher. This was most notable in the non-vegetated Skye sand configuration (i.e. SS-NV-S), which may reflect the absence of a plant-uptake pathway to transfer mineral- or adsorbed-P into the organic phase, or simply the composition heterogeneity of captured particulates.

Phosphorus partitioning remained fairly consistent down the loamy sand biofilter column profile (LS-V-S), suggesting that the mechanisms governing P-partitioning in loamy sand are unaffected by the duration of retention in the filter media (i.e. there is little transfer between the P-pools over time) (Figure 6.8). The Skye sand biofilters each demonstrated a gradually increasing percentage of adsorbed-P and decreasing percentage of mineral-P with depth, implying perhaps a transition of adsorbed P into the mineral phase P is taking place, most notably in the upper layers where the P has been adsorbed the longest (Ryden et al. 1977; Torrent et al. 1992).

The non-saturated Skye sand biofilters had the lowest percentage of organic-P overall, suggesting that including a saturated zone facilitates more transition of adsorbed- and mineral-P into organic pools by enhancing biological activity. However, relatively minor differences in the percentage of P associated with each phase were observed between the four biofilter configurations (standard deviation ≤0.03). Implying that under these testing conditions the mechanisms which govern *how* and *where* P is retained by the filter media are not strongly influenced by filter media type nor the inclusion of vegetation or a saturated zone (Figure 6.8). However, these design characteristics do influence P accumulation patterns. Overall, this relatively short term investigation tested limited design variations under uniform treatment conditions. Therefore, further research investigating long-term P retention dynamics in biofilters of varying age and design characteristics is needed to confirm whether the hypotheses developed through this study remain true over time.

Overall, P-partitioning was fairly consistent between the Skye sand biofilters (Figure 6.8). Below the surface, adsorbed-P concentrations were typically lowest in the Skye sand biofilters with both vegetation and a saturated zone (i.e. SS-V-S) (Figure 6.7). This implies that the presence of vegetation and a saturated zone provides greater opportunity for biological assimilation of adsorbed-P. In practical terms, this finding suggests that including vegetation and a saturated zone can prolong the P-removal lifespan of filter media by enabling 'rapid-adsorption' sites in the filter media to be replenished.

6.3.2 Field-scale biofilter study

6.3.2.1 Phosphorus accumulation

Phosphorus concentration profiles of filter media collected from biofilters in Melbourne and Brisbane are presented in Figure 6.9. These profiles indicate that the spatial distribution of P in biofilters varies both areally and with depth. The highest P concentrations typically correlate with filter media collected near stormwater inlets. This is illustrated by the 'Inlet' filter media cores collected from the Saturn Cres., Clifton Hill and Hoyland St. biofilters (Figure 6.9). Of the three stormwater inlets at Hoyland St., P concentrations were highest at 'Inlet A', which conveys stormwater from the largest of three contributing sub-catchments. These findings suggest that P accumulation in filter media is proportional to stormwater loading, which is to be expected. In terms of accumulation with depth, P concentrations were typically highest in the top 100mm of the filter media. This corroborates findings from several other field-scale biofilter studies, which found that TSS, TP and heavy metals accumulate mostly in the top 0 to 100mm of filter media (Feng et al. 2012; Hatt et al. 2007; Komlos et al. 2012; Li et al. 2008b). High surface layer P concentrations are attributed to the filtration of runoff particulates, which account for approximately 70% of total P in stormwater , and adsorption of P to filter media and runoff particulates.

Phosphorus concentrations typically decrease along the filter media profile, which most likely reflects diminishing deposition of runoff particulates. Observing the 'Inlet' concentration profiles in Figure 6.9 in terms of increasing biofilter maturity (i.e. Clifton Hill, Saturn Cres., Hoyland St.) suggests that P concentrations down the filter media profile increase with time, reflecting deeper infiltration of runoff particulates and exhaustion of the upper filter media layer's P-adsorption capacity. The decreasing *then* increasing P concentrations with depth exhibited by the Cremorne St. biofilter, conflicts with the typical P concentration decay relationship found at the other field sites (Figure 6.9). Research has found very high metal concentrations in the Cremorne St. biofiltration system (Al-Ameri et al. 2018), which is located in a high-density urban area with large traffic volumes. The presence of metals in this system may be contributing to the pattern of P accumulation observed here. This will be explored further through P partitioning.

Phosphorus concentrations in the top 30mm were lowest in the Wakerley and Banyan biofilters. These systems both include sediment pre-treatment zones (sedimentation ponds), which substantially reduce the concentration of particulate associated P entering the biofilter (Hatt et al. 2012). Furthermore, these systems have the highest total surface area of those tested, thus the largest surface area across which stormwater is dispersed. Therefore, Wakerley and Banyan would be expected to accumulate less P per kilogram of filter media than smaller systems without pre-treatment. This would also be expected given the age of the biofilters at the time of testing.

With the exception of filter media collected near stormwater inlets and from the Cremorne St. biofilter, which yielded high P concentrations below ~100mm, P concentrations measured in the biofilters were generally comparable down the filter media profiles, irrespective of differences in the biofilters' design, age and catchment characteristics. This finding provides confidence that biofilters are being designed in a way that is effective for P removal, and perhaps more importantly, that P accumulation typically occurs in a uniform way.

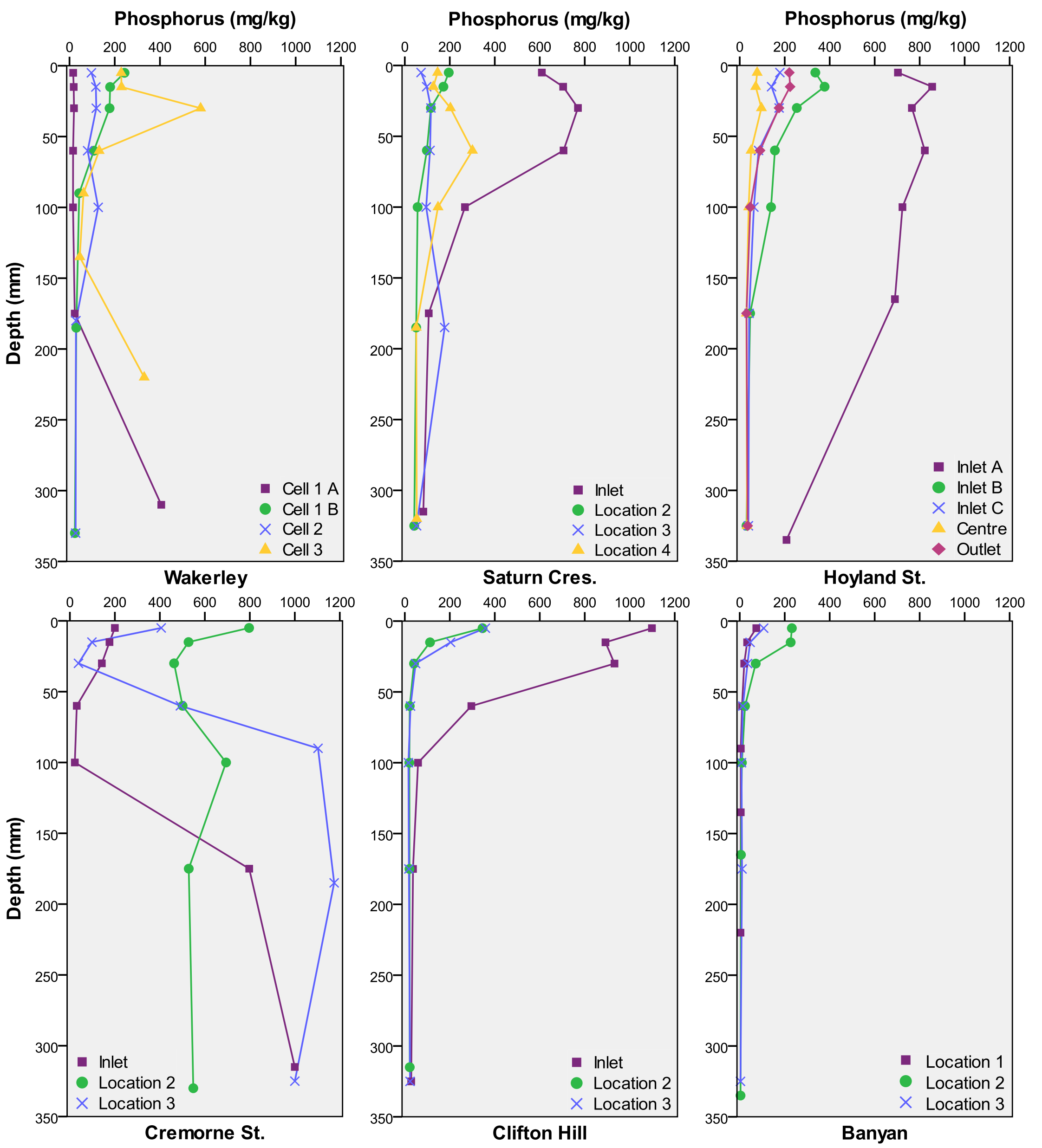

Figure 6.9. Total P (mg-FRP/kg) extracted from the filter media cores. Y-axis values represent the mean depth of the filter media analysed. Data points represent the sum of P extracted through the four step sequential extraction. Refer to Figure 6.2 and Figure 6.3 for core sampling location details.

6.3.2.2 Phosphorus partitioning

Partitioning of P in the filter media gives further insight into the form in which P is retained in biofilters and the consequences for its long-term retention. The P partitioning profiles of the 'Inlet' and 'Outlet' filter media cores collected at Hoyland St. (Location 1; 5), Saturn Cres. (Location 1; 4) and Clifton Hill (Location 1; 3) illustrate that where P concentrations in biofilters are highest (i.e. near stormwater inlets and in the top 0-10cm of filter media), P is predominantly present in mineral forms (Figure 6.10, Figure 6.12). This observation is generally consistent between the biofilters and most likely reflects the composition of particulates trapped in the filter media. Decreasing concentrations of mineral P with depth and distance from stormwater inlets correlates with reduced deposition of runoff particulates and thus supports this hypothesis. The presence of mineral-bound P at these points may also reflect the gradual transition of P from the adsorbed to the mineral phase over time (Ryden et al. 1977; Torrent et al. 1992). Indeed, representing P partitioning in the biofilters as a function of increasing age indicates, arguably, that the mean percentage of total extracted P bound in the adsorbed phase decreases as biofilters mature in favour of an increasing mineral P fraction (Figure 6.11); with the exception of the Cremorne St. biofilter, which exhibits rather different P accumulation behaviour.

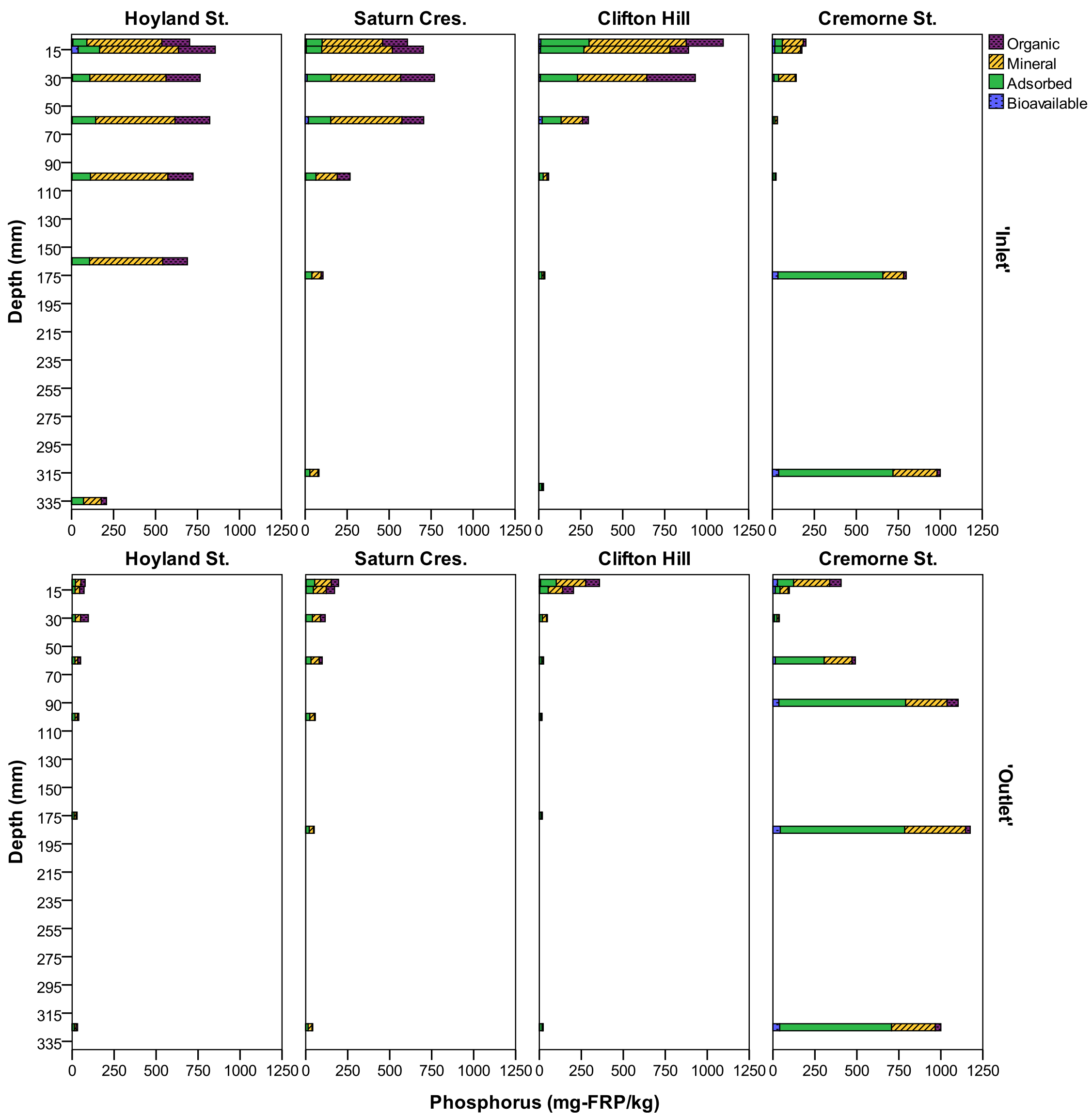

Figure 6.10. Inlet and outlet phosphorus partitioning concentration profiles (mg-FRP/kg) for Hoyland St., Saturn Cres. and Clifton Hill. Y-axis values represent the mean depth of the filter media analysed.

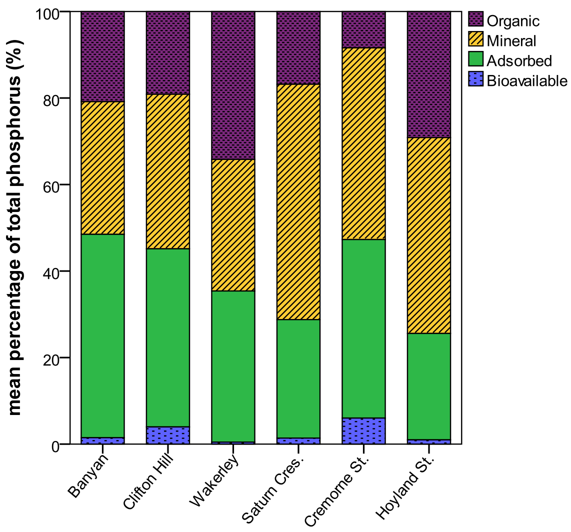

Figure 6.11. Mean percentage of P extracted in each P-fraction as a function of biofilter age (L to R; youngest to oldest).

Under normal operating conditions mineral P would be considered “fixed” and thus in a stable form for long-term retention in biofilters. However, there are several mechanisms through which mineral bound P can become bioavailable (i.e. dissolution of secondary compounds via plant root exudates: organic acids, chelating ions) (Lambers et al. 2009). Once mobilised, bioavailable P in the soil solution will be readily transformed into other P phases via physicochemical and biological processes (i.e. adsorption and plant-uptake). Therefore, it is unlikely that bioavailable P would be released from the biofilter before being re-sequestered in other forms. Indeed, the total P partitioning profiles show that bioavailable P concentrations in the filter media are negligible.

Particularly low bioavailable P concentrations were found at the Brisbane sites (i.e. Hoyland St., Saturn Cres., Wakerley), which may be due to the extended dry period which preceded the sampling (approximately 30 days). Higher fractions of bioavailable P are present in the Clifton Hill and Cremorne St. biofilters (Figure 6.10). Whilst several mechanisms could be responsible this is most likely due to the composition of the filter media, to which bioavailable P is loosely sorbed. Organic P concentrations also decrease with filter media depth (Figure 6.10). Perhaps reflecting reduced build-up of organic detritus from plant die-off and incoming leaf litter, decreasing plant root density, and/or diminishing accumulation of organic P associated with runoff particulates. When bound in living tissue organic P in biofilters would be considered “fixed”. During decomposition, organic P can transform into other organic pools (via assimilation) or into bioavailable forms (via mineralisation). However, unless the filter media has reached P-saturation, leaching of bioavailable P is unlikely to occur before it is re-sequestered. Investigating P partitioning in terms of the percentage of total P extracted shows that the fraction of adsorbed P typically increases with depth, corresponding with decreasing fractions of mineral and organic P (

Figure 6.12). This most likely reflects diminishing accumulation of runoff particulates with depth and thus a higher fraction of P that has been removed via adsorption. However, this could also, at least partially, indicate transfer of adsorbed P into mineral complexes (i.e. secondary compounds: Fe, Al, Mn & Ca phosphates) over time, which is observed in Figure 6.11.

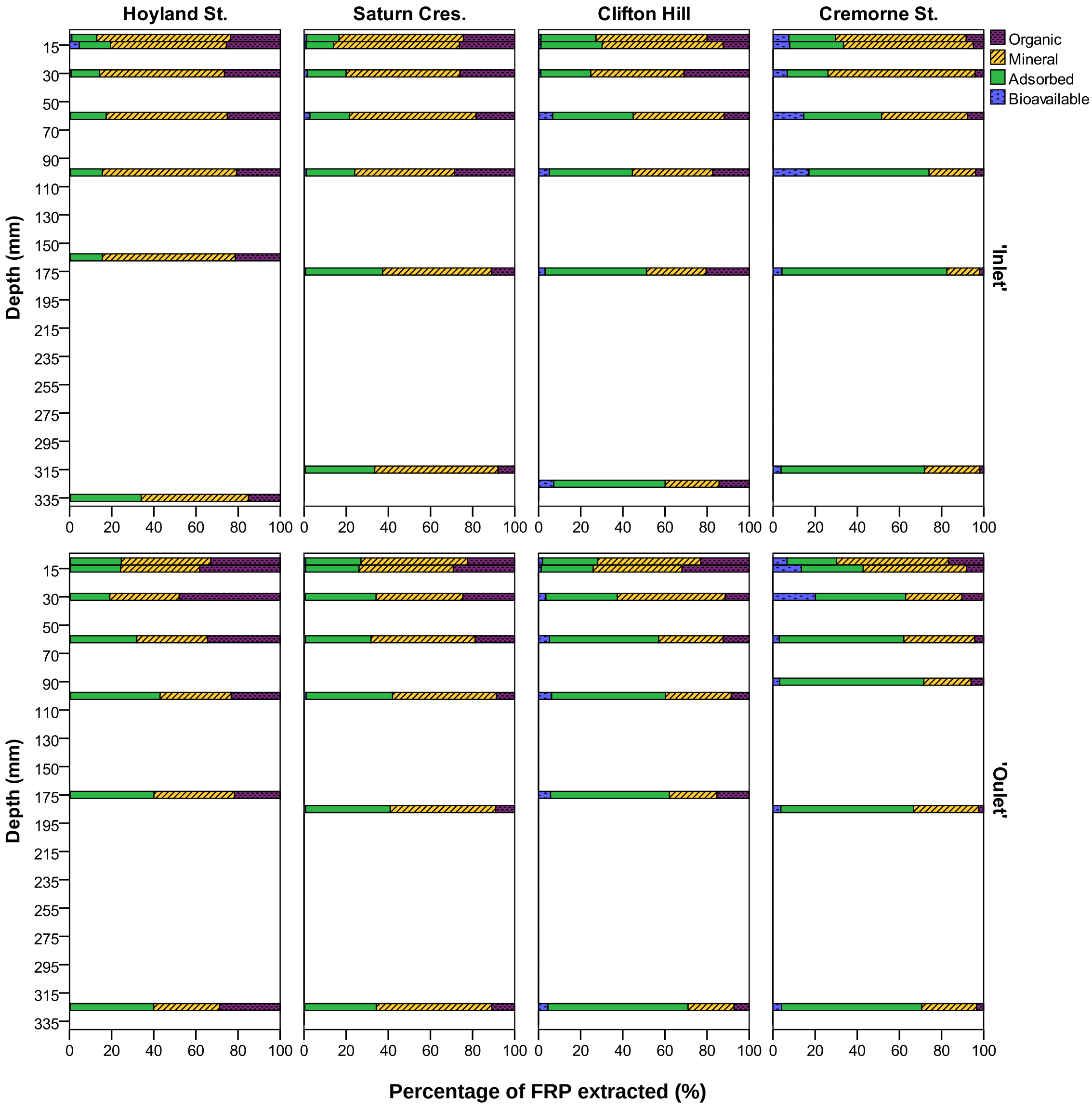

Figure 6.12. Inlet and outlet phosphorus partitioning profiles for Hoyland St., Saturn Cres. and Clifton Hill where P pools are represented as a percentage of FRP extracted (%). Y-axis represents the mean depth of the filter media analysed.

This represents a positive finding in terms of P-retention longevity, since P-bound in mineral forms are less susceptible to desorption due to changes in redox conditions than adsorbed-P. Moreover, transitioning from adsorbed into more "fixed' forms enables long-term retention and replenishes rapid-sorption sites for future P removal. On the other hand, P bound in mineral forms may be more difficult for plants and microbes to acquire. This is unlikely to affect plant health unless biofilters receive infrequent rainfall, under which circumstances the use of drought tolerant plant species would be recommended.

The concentration of adsorbed P retained in the field-scale biofilters' is typically greater than the estimated P-sorption capacity of biofilter media (~30mg/kg) (Glaister et al. unpublished data; Hsieh et al. 2007), particularly in the top 30mm (Figure 6.13). The additional adsorbed-P present at this depth is presumably attributed to the deposition of runoff particulates, to which phosphate has adsorbed either prior to mobilisation into stormwater, during transport through the catchment, or while trapped in the biofilter. As such, adsorbed-P concentrations are typically higher near stormwater inlets (Figure 6.13). This finding infers that the P-adsorption capacity of the filter media alone does not provide a good overall measure of the biofilters P-adsorption capacity. Indeed, runoff particulates are capable of adsorbing much higher concentrations of P than the filter media, if their physico-chemical properties permit. As such, by providing an additional sink for P, runoff particulates may prolong the P removal lifespan of biofilters. The concentration profiles in Figure 6.13 suggest that the filter media at Hoyland St. and Saturn Cres. are approaching P saturation. However, because the depth of the filter media cores analysed was limited to ~300-350mm, we cannot ascertain with certainty whether the P adsorption capacity of these biofilters has been exhausted. In considering this, it is also important to remember that we are observing a snapshot of a dynamic system, wherein transformations between the P-phases occurs continuously.

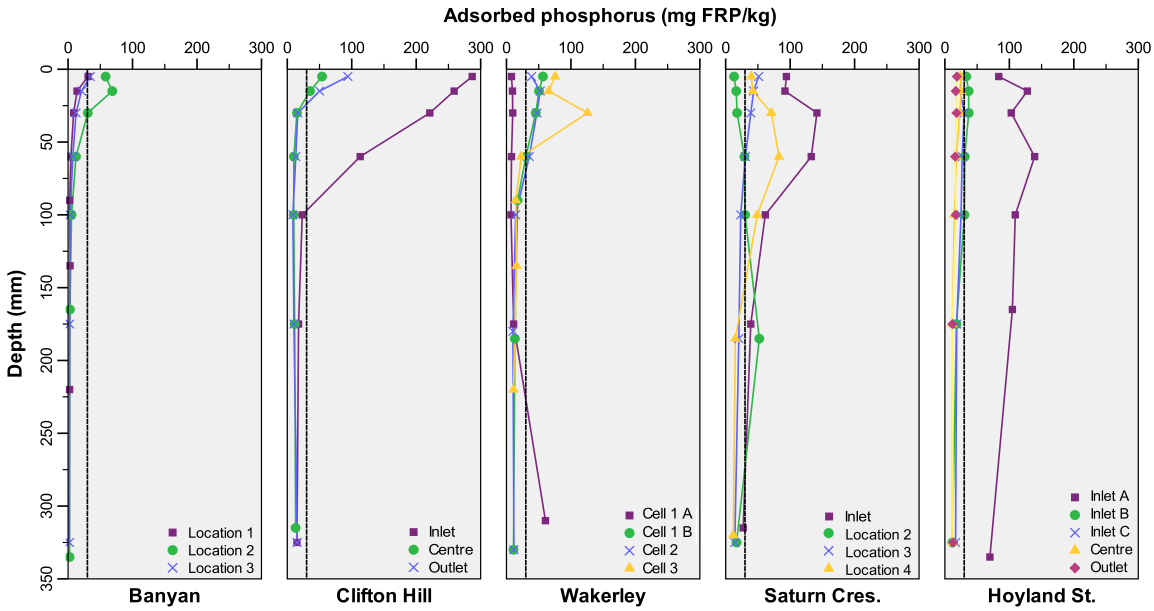

Figure 6.13. Adsorbed P concentration profiles (mg-FRP/kg) of the biofilters tested (Cremorne St. excluded). Y-axis represents the mean depth of the filter media analysed. Reference line represents the approximate sorption capacity of the filter media (~30mg-FRP/kg).

6.3.2.3 Site specific considerations

Banyan

Contrary to the other biofilters, concentrations of adsorbed-P in the Banyan biofilter below 30mm are negligible, reflecting almost no adsorption of P to the filter media (Figure 6.13). This may be attributed to the use of an engineered sand at this site, which has demonstrated relatively poor P-removal compared with typical loamy sand filter media, owing to a lower clay fraction and ion exchange capacity (Bratieres et al. 2009). The P partitioning profile of the Banyan system suggests that sediment associated P is present in the upper layers of the filter media (Figure 6.14). However, these concentrations are lower than expected given that, due to insufficient protection from high-volume flows, sediment clogging has become an issue in the Banyan biofilter, which consequently operates somewhat like an ephemeral wetland. The absence of P in the filter media is also perhaps being driven by prolific macrophyte growth at the site (Figure 6.2a). Increased rates of biological processing may explain how P concentrations in the filter media are able to be so low, while TP and FRP removal in this system has continued to be effective (Hatt et al. 2012).

Phosphorus retained in biofilters through adsorption would be considered “fixed” under well-functioning conditions. However, sediment clogging at the biofilters’ surface can alter the redox potential of underlying filter media, creating conditions under which adsorbed P is susceptible to mobilisation. For example, changes in the redox state of metals to which P is sorbed to (e.g. reduction from Fe^{3+} to Fe^{2+}) will most likely result in P being desorbed into the soil solution as bioavailable P. Unless biologically assimilated or resorbed onto other metal oxides in the filter media, Fe^{2+} and bioavailable-P will migrate through filter media until aerobic conditions recur, at which point Fe^{2+} will oxidise forming Fe^{3+} to which bioavailable P can be readily adsorbed. Therefore, unless the biofilter is completely anaerobic, which is highly unlikely, leaching of bioavailable P is unlikely to occur (Parkin 1987). However, the high concentration of reducible adsorbed P associated with runoff particulates remains a cause for concern, since mobilisation of this P pool could quickly diminish the P-adsorption capacity of the filter media. Maintaining good hydraulic function in biofilters is therefore critical to ensuring that P can remain stably adsorbed to runoff particulates and filter media, and the effectiveness of P removal is not compromised.

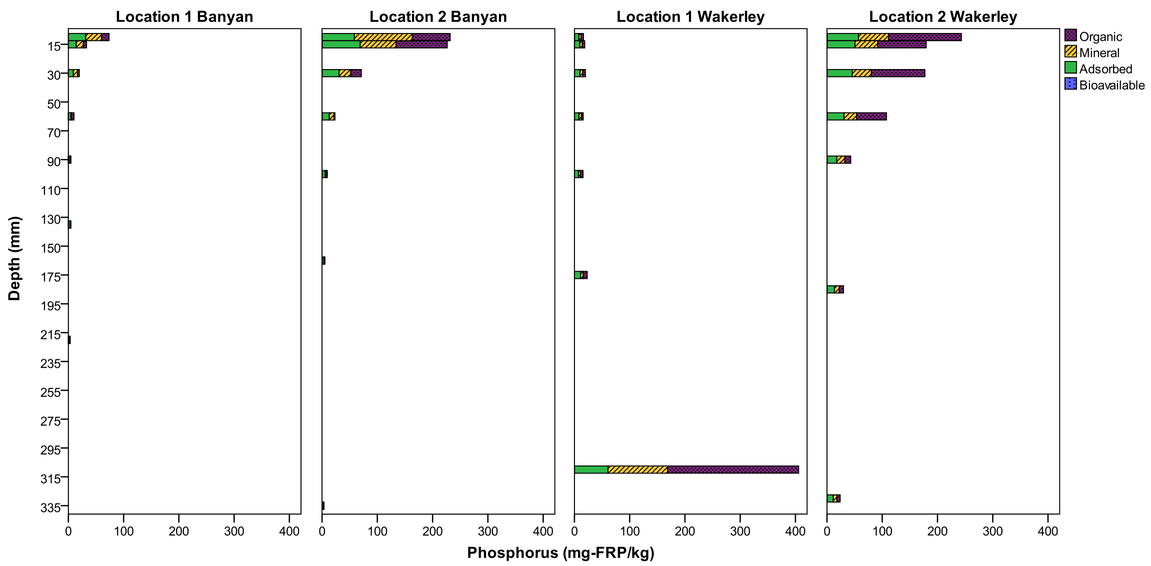

Figure 6.14. Partitioned P concentration (mg-FRP/kg) profiles of the Banyan (Location 1 & 2) and Wakerley (Cell 1 Location 1 & 2) biofilters. Y-axis represents the mean depth of the filter media analysed.

Wakerley

The P concentration profile from the Wakerley biofilter (Location 1 'Cell 1 A'), shows a spike in P concentrations at ~300mm (Figure 6.9). This type of profile is characteristic of P desorption in anaerobic sediments and resorption upon oxidation of the soil, however, further testing would be needed to confirm if this is the mechanism responsible. The Location 1 core was collected from an area near the biofilter inlet where surface clogging and stormwater ponding (~3-5cm deep) had occurred. Comparatively, the Location 2 core ('Cell 1 B'), which was collected nearby (<5m away) in an area without surface clogging, presented a typical P accumulation profile (Figure 6.14), suggesting that surface clogging is perhaps driving the disparity in these profiles. Partitioning of P in the filter media from Location 1 revealed that where the concentration spike occurs (~315mm) P is mostly present as organic P (Figure 6.14). However, if the build-up of P at this depth was attributed to desorption from and resorption to metal oxides we would expect P to be mostly associated with the adsorbed or mineral bound phases, rather than the organic. The presence of organic-P at this depth could indicate transformation of adsorbed- and mineral-P into organic forms via microbial immobilisation or plant uptake. However, given the high concentration at which organic-P is present (>200 mg-FRP/kg) it is more likely that another mechanism is responsible for the organic enrichment in the filter media at this depth (i.e. presence of roots or detritus). Further investigation would be required to understand the cause of organic-P accumulation at this depth. However, this is outside the scope of this study.

Cremorne St.

The decreasing then increasing concentrations of P observed along the filter media profile in the Cremorne St. biofilter could also be the result of P desorption from overlying filter media or trapped runoff particulates. While there was no sign of clogging in the Cremorne St. biofilter at the time of sampling, it cannot be ruled out that surface clogging and redox conditions have occurred in the past. The higher than average fraction of bioavailable P present in the top 25mm of filter media (up to 20% of total P) supports this hypothesis (

Figure 6.12) as do the 'inlet' P concentrations in the top 100m of filter media, which are very low compared with the field scale systems of similar age and catchment to surface area ratio (i.e. Hoyland St. and Saturn Cres. respectively) (Figure 6.10).

Below 100mm, P concentrations in the Cremorne St. biofilter increase substantially, predominantly in the adsorbed phase, accounting for up to 70% of total P at these depths (see Figure 6.10 and

Figure 6.12). The adsorbed P concentrations at these depths are, even for a 10 year old system in a high urban catchment, very high and typically in excess of that observed in this study and others (e.g. Komlos et al. 2012). Moreover, the adsorbed P concentrations are far greater than the estimated sorption capacity of typical biofilter media (~30mg/kg) (Glaister et al. unpublished data; Hsieh et al. 2007). This suggests that the cause of this P accumulation is unlikely to be related to stormwater alone. For instance, errors made at the time of construction (i.e. improper or incomplete system lining or incomplete removal of native soil) may have allowed Fe or P contaminated soil (a product of the site's industrial legacy), to migrate into the biofilter providing a both a source of and sink for P. This may explain, at least in part, why the fraction of adsorbed and mineral-bound P in the Cremorne St. biofilter is higher compared with the other field-scale biofilters tested and consequently, why a lower proportion of organic P is present (Figure 6.11 and

Figure 6.12). Ultimately, the cause of the P accumulation and partitioning observed in the Cremorne St. biofilter is unclear. Further investigation of its underlying cause is thus required but unfortunately is outside the scope of this study.

6.3.3 Comparison of the laboratory- and field-scale studies

There was low variability between replicates in the laboratory study, increasing confidence in the experimental design. Very little difference in P accumulation and partitioning was observed between the biofilter design configurations tested and the differences that were observed were largely limited to the top 100mm of filter media. Although filter media P concentrations in the field-scale biofilters were more variable and far exceeded those in the laboratory-scale columns, similarities in terms of P accumulation and partitioning were observed, indicating that laboratory scale P-partitioning testing translates well to field conditions.

Both the laboratory- and field-scale studies showed P concentrations were typically highest in the top 100mm of the filter media, due mostly to the deposition of sediment. Both studies observed a trend of decreasing P-concentrations with depth. In terms of removal longevity, the relatively young laboratory columns still had a high capacity to remove P. Similarly, there appears to be large remaining capacity for P retention in the field-scale biofilters, with the exception of Cremorne St.

6.3.4 Implications for long-term P retention in biofilters

The increased understanding of P is accumulated and partitioned in biofilters offers greater insight into how biofilters can best be designed and maintained to optimise initial removal and long-term retention of P. Nevertheless, it is important to note that these results are a snapshot of a dynamic system wherein transformations between P-phases occur continuously. Accumulation of P is also transient and can be affected by both external and internal factors, such as: the composition and concentration of P in stormwater; the frequency and intensity of rainfall events; biofilter surface area and gradation/undulation; and the number of stormwater inlets.

The P-partitioning analysis suggests that, even where surface concentrations are highest, such as close to biofilter inlets, previously captured P is unlikely to become labile provided hydraulic functionality is maintained and biological uptake exceeds decomposition. The long-term retention of P may be further secured through the use of a filter medium with a strong affinity for P sorption, such as Skye sand, as this can increase the percentage of P retained in mineral forms, which have far less potential to be re-mobilised than P adsorbed to poorly crystalline iron oxyhydroxides. Nevertheless, the ability of P to transfer between P pools within the biofilter should not be overlooked when designing biofilters and planning biofilter maintenance, in particular plant harvesting and filter media replacement.

Deposition of particulates delivered with stormwater accounted for most of the P accumulated in the field-scale biofilters. This deposition was largely concentrated in the top 100mm of filter media and surrounding biofilter inlets. While stormwater particulates are a source of P, they can also act as a sorption-sink for bioavailable-P. Nevertheless, designing systems to include sediment pre-treatment zones or gross pollutant traps to capture TSS and incoming organic detritus will extend the P-removal lifespan of a biofilter by reduce sediment accumulation on and in the filter media. Pre-treatment also reduces the risk of clogging and thus the potential for dissolution of Fe-P compounds under reducing conditions.

6.4 Conclusions

This study used a four step sequential extraction to analyse phosphorus accumulation and partitioning in six field-scale biofilters of varying age, size and catchment characteristics and twenty laboratory-scale biofilter columns after twelve-months of dosing with stormwater. The results show that phosphorus accumulation varies spatially (areally and with depth) within biofilters. Phosphorus accumulation is most concentrated in the top 0-10cm of the filter media and in areas surrounding the inlet. At the surface phosphorus is mostly associated with TSS and found in the mineral-bound and organic phases. The fraction mineral- and organic-P typically decreased with depth, which is likely representative of reduced accumulation of runoff particulates and decreasing density of plant growth and rhizosphere activity with depth. Alternatively, this may be indicative of transfer of adsorbed-P into more recalcitrant phases over time. Overall adsorbed-P (reducible Fe-bound P) makes up the largest fraction of P retained in the biofilters. This emphasises the importance of maintaining good hydraulic function in biofilters given that this P-pool has the potential to become mobile under oxygen depleted conditions. These results highlight the contribution that Fe-P interactions have in P-retention. Despite the distinctive variation in the design and age of the biofilters tested, the results generally showed consistency in P accumulation and distribution between phases, with some exceptions. No clear signs of P-breakthrough were observed, offering positive reinforcement that the current biofilter design specifications are producing systems which function well in the long-term.

6.5 References

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Chapter 7: Conclusions and Implications for Practice

Foreword

This concluding chapter aims to synthesise the key outcomes of the research and the implications of the work in terms of optimising biofilter design, operation and maintenance for phosphorus removal. The discussion relates the findings back to the research objectives outlined in Chapter 1. The chapter concludes with an assessment of the strengths and limitations of the evidence and opportunities for further work.

7.1 Research outcomes and implications for practice

The present thesis aimed to provide a comprehensive assessment of the processes and properties of design that govern P removal in stormwater biofilters. This research program was delivered through a series of experimental studies which tested biofilter design elements over a range of physical and time scales and under variable operating conditions. The overall outcome of the research is a broader and deeper understanding of the processes that govern P removal in stormwater biofilters and the influence of design elements and operating conditions on these. These new insights can be readily translated into practice and will thus better inform biofilter design and operational dynamics for effective and long-term P removal. To align with the research objectives outlined in Chapter 1 and the chapter structure of this thesis, the discussion of the key findings are grouped as followed: (i) enhancing phosphorus removal using iron-rich filter media (ii) co-optimising biofilter design for N and P removal; and (iii) phosphorus accumulation and partitioning in filter media.

7.1.1 Enhancing phosphorus removal using Skye sand

Substrates and substrate amendments to enhance phosphorus removal have been widely researched in various wastewater treatment and environmental protection applications. Use of such amendments to enhance P removal in biofilters is a growing area of research (Erickson et al. 2010; Lucas et al. 2011; O'Neill et al. 2012). Similar to the findings of studies covered in the literature review (Chapter 2) the use of sand with a natural iron coating, ‘Skye sand’, demonstrated a strong capacity for P-sorption in both batch- and small column-tests (Chapter 3). Substituting loamy sand filter media with Skye sand in vegetated columns achieved better TN removal and similar TP removal under both wet and dry conditions (Chapter 4). Skye sand may also enhance long-term P-retention in biofilters by transforming adsorbed-P into more recalcitrant forms (Chapter 6).

There were a number of concerns regarding the use of Skye sand as a filter media in biofilters. These are discussed below along with recommendations for the use of Skye sand in practice.

Suitability as a substrate for plant growth

Concerns that Skye sand may limit P-bioavailability and affect plant growth were overcome during the twelve-month vegetated column study (Chapter 4). Not only did *C. appressa* grow successfully in biofilters containing only Skye sand filter media, it was found to provide advantageous conditions for the development of morphological traits that have been linked to improved nutrient uptake (Payne et al. 2014b; Read et al. 2010) (Chapter 5). Skye sand, or a sand of similar composition can therefore be recommended for use in combination with *C. appressa*. However, plant species that are not so well adapted to growing in soils where access to nutrients is limited would perhaps struggle to establish in Skye sand.

Interactions with a saturated zone

In order to provide the enhanced N treatment observed in these studies, Skye sand needs to be coupled with a saturated zone (internal water storage) to protect plants and increase retention time for biological nutrient removal. While the saturated zone is less critical for direct P removal, it can mitigate the effect of particle mobilisation following dry periods by protecting biofilters against the effects of drying (e.g. desiccation; cracking; plant die-off) and by acting as a buffer to high-velocity flows. Contrary to the hypotheses proposed, dissolution of Fe-P compounds was not found to be a concern with the inclusion of a saturated zone.

Compliance with soil guidelines

Other concerns regarding the use of Skye sand emerged (quite literally) during the vegetated column study wherein efflux of very fine Skye sand particles were mobilised into the biofilter effluent during events. This was exacerbated by dry weather, particularly in the absence of a saturated zone. Since P sorbed to Skye sand is relatively immobile, washout of P-bound Skye sand particles should not pose a serious threat to the water quality of aquatic environments. Still, these very fine particles may cause discolouration of drains and perhaps more critical issues over time if, following burial of particles in deoxygenated aquatic sediments, dissimilatory iron reduction causes P to be released into the water column.

Analysis of Skye sand's particle size distribution revealed that the sand was 'gap-graded' with a coefficient of uniformity (d_{60}/d_{10}) of 480. The volume of particles 2μm or less constituted approximately 25% of Skye sand's total volume, compared with only 2% for loamy sand. Consequently, Skye sand does not comply with local guidelines for the proportion of silt and clay in biofilter media (<3% w/w, noting that there will be some discrepancy because we are comparing v/v and w/w, Payne 2015). However, the work undertaken in this thesis clearly demonstrates the benefits of using Skye sand as a filter medium, which is intrinsically related to the iron-oxide coating that is responsible for the high fraction of fine particles (Arias et al. 2006; Strauss et al. 1997; Torrent et al. 1990).

Recommendations for the use of Skye sand filter media

Rather than substituting loamy sand with Skye sand, it would perhaps be better to apply Skye sand to biofilters as an amendment (i.e. blending Skye sand with loamy sand). This would improve the grading of the filter media and thus reduce particle efflux from the systems. However, particle size analysis determined that loamy sand has a clay and silt fraction of 7%, meaning that this media is already in excess of the recommended clay and silt fraction (<3% w/w). As such, based on current filter media guidelines, the hydraulic performance of any ratio of blended loamy sand/Skye sand filter media would need to be carefully tested prior to installing in any field-scale biofilters. The results of this testing could inform future revisions of these guidelines e.g. if it is determined that an amended particle size grading can provide optimal P removal whilst also maintaining structural and hydraulic integrity.

7.1.2 Co-optimising biofilter design for N and P removal

Biofilter performance variation

The vegetated column study monitored N and P removal performance over twelve-months of variable wet and dry climates. Four biofilter configurations were designed to compare N and P removal performance between systems with different filter media, with and without vegetation (*C. appressa*), and with and without a saturated zone. The key effects of design and climate were as follows:

- Skye sand biofilters configured with vegetation and a saturated zone maintain very good N and P removal and achieve water quality guidelines for the protection of ecosystem systems under both wet and dry operating conditions.
- Including a saturated zone benefits N removal by (i) extending retention time between events, further enabling N processing to occur; (ii) reducing the effective rate of infiltration

thus increasing opportunity for biological removal during events; and (iii) protecting biofilters against the effects of drying and supporting plant health during dry periods (Payne et al. 2014a).

- With both vegetation and saturated zone biofilters co-optimised N and P can maintained removal under variable climate conditions, irrespective of the filter media type.

Considerations for meeting water quality targets

Biofilters typically aim to reduce pollutant loads by a certain percentage; in Melbourne, for instance, the target for P load reduction is 45%. Load reduction targets are practical in that they can be applied broadly, however, the use of load reduction targets is inherently flawed in that the reduction is measured against conventional stormwater management (i.e. they still allow an increase in N and P inputs to the environment compared with pre-development levels). Assessing biofilter performance using guidelines for ambient water quality in receiving environments is thus likely to provide a stronger link between best-management practice and ecosystem protection.

The results of the biofilter column study demonstrated variable compliance with water quality guidelines for the protection of aquatic ecosystems in South-Eastern Australia. On average, all design configurations met the guidelines for TP and FRP, however only designs that included both vegetation and a saturated zone were able to meet the guidelines for TN and NH_3. Interestingly, only the design that incorporated Skye sand, vegetation and a saturated zone was able to meet the guideline for NO_x. It was somewhat surprising that the Skye sand, which was initially intended to facilitate increased P removal delivered greater benefits for N removal. An extended antecedent dry period compromised the ability of all design configurations to meet the guidelines, however the same trends described were apparent and the design that included Skye sand, vegetation and a saturated zone was most resilient.

7.1.3 Phosphorus accumulation and partitioning in filter media

Using a sequential extraction procedure, P accumulation and partitioning across four P-pools (bioavailable, adsorbed, mineral and organic) was analysed in six field-scale biofilters of varying age, size and catchment characteristics as well as twenty laboratory-scale biofilter columns that had been subjected to twelve-months of dosing with stormwater. The key findings and implications for practice emerging from this research are as follows:

- Deposition of stormwater particulates accounted for most of the P accumulated in the field-scale biofilters. This deposition was largely concentrated in the top 100mm of filter media and surrounding biofilter inlets. Although stormwater particulates are a source of P the partitioning analysis revealed that this P was mostly bound in the mineral- and organic-P phases and therefore are unlikely to become labile provided hydraulic functionality is maintained and biological uptake exceeds decomposition.
- Long-term P retention may be secured through the use of a filter medium with a strong affinity for P sorption, such as Skye sand, which can increase the percentage of P retained in mineral forms, which have less potential to be re-mobilised than P that is adsorbed to poorly crystalline iron oxyhydroxides.
- Addition of a saturated zone increased stormwater residence time and maintained microbial activity through wet and dry cycles, providing optimal conditions for P transformation from less to more stable forms of retention.
- The ability of P to transfer between P pools within the biofilter should not be overlooked when designing biofilters and planning biofilter maintenance. Periodic pruning and harvesting of plants may present a permanent pathway for P removal from biofilters that would also reduce the quantity of P returning to the soil through plant die-off. Regular maintenance can benefit biofilter performance in other ways, for example through detection of operational issues (Hunt et al. 2006; Virahsawmy et al. 2014). Potential issues may include clogging, scouring, ponding, disturbance of surface gravel layer (if present) and sediment build-up, all of which have implications for P accumulation and retention.
- Replacement of filter media in sections of the biofilter where high concentrations of P accumulate (i.e. in the top 100mm of filter media and near inlets) also presents a potential permanent removal pathway. However, filter media replacement is more complicated than plant harvesting. Although undesirable in practical terms, filer media replacement may be the only option available in situations where biofilters have become P-saturated.
- Designing biofiltration systems with sediment pre-treatment zones (e.g. a vegetated swale, coarse sediment forebay or inlet pond) or gross pollutant traps to capture TSS and organic detritus could effectively extend the P-removal lifespan of a biofilter by reducing sediment accumulation on and in the filter media. Pre-treatment also reduces the risk of clogging and thus the potential for dissolution of Fe-P compounds under reducing conditions.

7.2 Strengths and limitations of the research

The major strengths and limitations of the research are discussed in the following sections. In coordination with the thesis logic these are discussed in order of the research program.

7.2.1 P-sorption tests (Chapter 3)

The purpose of the P-sorption tests were to provide proof-of-concept for the use of Skye sand filter media. There were strengths to this approach but there were also several limitations.

- The small-columns provided an effective means of comparing filter media, however, the applicability of this study to P-removal in stormwater biofilters was limited to physico-chemical processes.
- To satisfy particle size distribution guidelines for biofilter media, the materials used in the through-flow column tests were sieved and added in even amounts of each particle size range. However, sieving did not remove surface layer of iron-oxide particles from the Skye sand filter media. Therefore the blend of Skye sand and loamy sand reflected neither the soil guidelines nor the natural particle size distribution of the media.

+ The small-column test used a "compressed time" approach to investigate two years of exposure to stormwater. High P inflow concentrations are typically used in tests of this type so that the point at which filter media becomes P-saturated can be quickly determined, or several years of load rapidly simulated (Hsieh et al. 2007; Lucas et al. 2011). However, this overlooks the important role that equilibrium concentration plays in P-sorption kinetics (Henderson et al. 2007). To maintain conditions realistic to biofilter operation P-concentrations akin to stormwater were utilised. This also allowed outflow concentrations to be compared to water quality guideline targets.
+ While the use of an iron-rich material to improve pollutant retention is not novel in itself, it has not really been applied in the stormwater biofilter context which, as noted previously, are subject to very different influent characteristics and flow dynamics than other water treatment systems. Further, one of the challenges of using a filter media amendment is aligning it with the broader sustainability goals that ultimately drive the quest for better stormwater management. In keeping with the principles of sustainability, this study utilised a locally available, natural material.

7.2.2 Vegetated biofilter column study (Chapters 4 & 5)

Biofilter column studies allow stormwater treatment performance to be quantified under quasi-realistic field conditions with the benefit of being able to control multiple factors. However, there are also limitations that come with being restricted to laboratory conditions. Previous research has demonstrated that many of the limitations of biofilter column studies can be reduced through use of a semi-synthetic stormwater and careful construction of the biofilter columns (Bratieres et al. 2008; Payne 2013). For instance, the PVC columns were scoured prior to filling with filter media to overcome the boundary effects and the risk of side-wall preferential flows (Sentenac et al., 2001). Nevertheless, there remain several limitations to conducting research under laborator-conditions. These issues are well documented by Payne (2013). For brevity, this discussion will focus on the broader limitations of the research and well as the major strengths.

- Time and resource constraints were the most significant limitation of the vegetated biofilter column study.
- Time constraints are typically overcome by performing accelerated-dosing experiments. However, increasing the concentration of nutrients in the stormwater was not an option during this study, since increasing inflow concentrations would affect the physico-chemical processes that govern P removal (i.e. greater removal is achieved when influent concentrations are high) (Henderson et al. 2007). Increasing concentrations would also contradict the objective of studying phosphorus removal at typical stormwater concentrations. As such, the given timeframe for study was not sufficient to measure the point at which the columns reached P saturation.
- The effect of filter media type on PO_4-P removal was not distinctly evident in the monitoring of outflows during the column study, reinforcing the conclusion that twelve-months of stormwater campaign was not long enough for clear distinctions to be made between the PO_4-P removal performance of loamy sand or Skye sand. This could have been overcome by performing a break-through test. However, this would have compromised the experimental design, limiting the usefulness of the biofilters in terms of analysing filter media and plant traits.
- The number of biofilter designs which could be investigated was limited by the resources available. Ideally various configurations of the two media would have been tested (i.e.

blended at different ratios or constructed in layers) since this is most likely how the Skye sand filter media would be applied in the field. Comparison of these filter media should be considered as part of a long-term field scale monitoring program

- The breadth of the vegetated column study was also limited by only being able to test one plant species due to resource limitations. To observe the greatest benefit of including vegetation, the native Australian sedge *C. appressa* was selected. This species has consistently demonstrated excellent nutrient removal performance in biofilter column studies and recommended for use in field scale systems by Australian biofilter guidelines (Payne 2015). It has also been studied extensively in previous research and so provided a point of comparison with the literature. The strength of the study was also limited by not being able to test them once they reached maturity.

+ Discrete sampling of dissolved oxygen concentrations in the saturated zone of the columns provided insight into the potential for denitrification or desorption of iron-bound P to occur in the biofilters. Further monitoring of chemical and physical parameters in-situ and in the biofilter effluent (i.e. soil moisture, pH, temperature) would have provided additional insight into nutrient processing, however, this was not done due to either resource, equipment or time limitations.

+ Skye sand, which has not previously been tested as a P removal enhancing filter media, demonstrated compliance with ANZECC water quality guidelines for N and P under variable operating conditions in conjunction with vegetation and a saturated zone. This level of compliance with Australian water quality guidelines has not been previously demonstrated in biofilter column studies. Moreover, iron-rich filter media has not previously been tested in biofilters with a saturated zone.

+ The influence of iron-rich filter media ‘Skye sand’ on the growth and morphology of plants and N and P removal in biofilters has not previously been investigated.

+ The influence of biofilter design elements on the event ‘pollutograph’ of N and P provided new insight into nutrient removal dynamics and processes occurring between and during rainfall events and opportunities to improve compliance with ecosystem protection guidelines.

7.2.3 Phosphorus accumulation and partitioning (Chapter 6)

– The advantage of studying field-scale biofilters is they provide an opportunity to test performance under real operating conditions and thus provide an important means of validating the accompanying laboratory research. A disadvantage however, is the lack of control of variables and the inherent complexity of a real system. This can make data interpretation challenging.

+ P accumulation and partitioning in biofilters has not, to the best of the author's knowledge, previously been analysed using this four-step sequential extraction method to the extent that was undertaken in this research program. This assessment provided essential insights critical to understanding the long-term stability and effectiveness of P removal in biofilters and verification of the laboratory-scale testing.

+ Although filter media P concentrations in the field-scale biofilters far exceeded those in the laboratory-scale columns, similarities in terms of P accumulation and partitioning were observed, indicating that laboratory scale P-partitioning testing translates well to field conditions.

7.3 Recommendations for future research

Testing of Skye sand at the field scale

Hydraulic and pollutant removal testing of Skye sand blended with loamy sand is needed to determine a suitable ratio that balances particle size distribution, providing sufficient P sorption sites and cost. A preliminary accelerated-dosing study of small, non-vegetated columns similar to that described in Chapter 3 could be undertaken to determine the optimal Skye sand: loamy sand ratio. This could then be further tested in a field-scale system to overcome the limitations of laboratory-scale testing and enable long-term observations. A similar approach is currently being undertaken in Western Australia, in a constructed wetland in Ellenbrook. This system has been ameliorated with Gypsum specifically to remove P from the Ellen Brook which drains an agricultural catchment.

Testing of additional plant species performance in Skye sand biofilters

Further research is needed to verify the suitability of Skye sand filter media in conjunction with a broader range of plant species typically used in biofilters. A comparative study of loamy sand and Skye sand in combination with less effective plant species may provide a greater understanding of the contribution Skye sand makes to pollutant removal. Further, the results of the plant growth and morphology study (Chapter 5) suggest that Skye sand filter media may improve the N and P removal performance of species previously recognised as having a poor capacity for nutrient removal.

Tracing the fate of phosphorus in biofilters

The fate of P in stormwater biofilters could be further understood through a laboratory-scale column study that utilises a tracer study. A method for investigating the partitioning of P amongst storage pools using a radiotracer, 32P, in biofilters was recently trialed in a preliminary study of greywater biofilters (Fowdar et al. 2017). That study revealed that, while the immediate fate of P was sorption, a surprisingly high amount of P was translocated to the above-ground plant parts within 24 hours of the radiotracer being applied. An expansion of this methodological approach could provide further insights into the intermediate and long-term fate of P.

Quantifying P-removal longevity of biofilters

Synthesis of the data collated in this thesis (e.g. P-sorption tests and vegetated column study results) may provide a basis upon which to estimate the P-sorption capacity of the filter media. However, the long-term removal of P by the vegetated columns would be better measured in an additional vegetated column study that utilising smaller columns to reduce the study time frame. This would enable interplay between N and P removal performance and biofilter design to be monitored as the filter media approaches P saturation. Alternatively, expanding the field-scale biofilter study (Chapter 6) could perhaps provide a more resource efficient means of assessing the long-term removal of P by biofiltration.

Determining when to remove vegetation from biofilters to harvest the most phosphorus

Periodic pruning and harvesting of plants is an important part of best practice biofilter maintenance (Hunt et al. 2006; Victorian Stormwater Committee 1999). Scheduling for such maintenance is typically determined by the responsible Local Government authority and does not, to our best knowledge, take into account *when* removing plant matter would benefit most in terms of maximising phosphorus removal. Decision making about periodic pruning and plant harvesting could be better informed and more efficient if dedicated research was undertaken into understanding the dynamics of P-allocation in biofilter vegetation. For instance, seasonal or visual indicators that suggest when is the most advantageous time to remove above-ground biomass, and thus P.

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Appendices

Chapter 3 Appendix

Chapter 4 Appendix

Chapter 5 Appendix

Chapter 6 Appendix

Chapter 3 Appendix

A3.1 Conference Paper: Diffuse Pollution and Eutrophication Conference 2011.

Can stormwater biofilters meet receiving water phosphorus targets? A pilot study investigating metal-oxide enriched filter media

B. Glaister*, T. D. Fletcher[#]*, P.L.M Cook**, B. E. Hatt*

* Civil Engineering, Monash University, Clayton 3800, Victoria, Australia.
Bonnie.Glaister@monash.edu, Belinda.Hatt@monash.edu
[#] School of Land and Environment, The University of Melbourne, 500 Yarra Blvd, Burnley 3121, Victoria, Australia. tim.fletcher@unimelb.edu.au
** Water Studies Centre, Monash University, Clayton 3800, Victoria, Australia.
Perran.Cook@sci.monash.edu.au

Abstract
Urban stormwater is a major contributor of nutrient pollution to receiving waterways. Given the sensitivity of receiving waters to limiting nutrients, in particular phosphorus, stormwater presents a serious challenge. Biofiltration has proven to be a successful technology for the treatment of urban stormwater, being easily integrated into streetscapes to provide flow attenuation and retention, pollution reduction and landscape amenity. Widespread implementation of biofilters has occurred across Australia over recent years and field monitoring of existing systems shows that biofilters are capable of meeting phosphorus load reduction targets. However, the concentration of phosphorus in biofilter effluent still exceeds typical receiving water quality guidelines (e.g. ANZECC & ARMCANZ, 2000). This pilot study investigated how augmenting a traditional filtration medium with various metal-oxide-rich media influences phosphorus removal. The experiments comprised a series of compressed-time, laboratory-scale column tests, from which both effluent and media samples were analysed to determine the fate of influent phosphorus. Of the three metal-oxide-rich media tested (iron ore, goethite and a locally sourced iron-rich sand “Skye sand”), only Skye sand significantly enhanced performance of the filter medium currently recommended by biofilter design guidelines, and achieved effluent concentrations below typical receiving water phosphorus targets. The poor performance of the iron ore- and goethite-augmented filter medium suggests that metal-oxide content alone may not dictate phosphorus removal performance, and that physical structure of filter media may have a greater influence than previously thought. Future work will investigate the performance of Skye sand in a large-scale vegetated biofilter column study to evaluate whether this medium can achieve and maintain phosphorus concentrations below receiving water targets under realistic field operating conditions.

Keywords: Biofilters, Phosphorus, Stormwater

Introduction

Anthropogenic distortion of catchment hydrology and nutrient cycles results in stormwater runoff being highly enriched in nutrients. Discharge of nutrient-rich stormwater into waterways can affect the natural balance of limiting nutrients in an ecosystem. This poses a particularly severe threat to the health of receiving waters through the proliferation of algal blooms and eutrophication. Biofiltration systems (also known as biofilters, bioretention systems, and rain gardens) have been recognised as a potential solution to this problem. These low energy, low maintenance, natural treatment technologies utilise a suite of physical, chemical and biological processes to reduce stormwater pollutant concentrations. Phosphorus removal in particular is facilitated by sedimentation, fine filtration, adsorption, precipitation and biological mineralisation and assimilation (Tiessen, 1995, Hatt et al., 2009). While the importance of vegetation for nutrient removal has been demonstrated (e.g. Read et al., 2008, Read et al., 2010), studies of treatment performance to date have been largely "black box" and our knowledge of the role of filter media in retaining phosphorus is limited and somewhat contradictory. Henderson et al (2007) argue that filter media is unlikely to retain nutrients in the long term, however it may be important for extending the detention time such that plants and microbial assimilation can occur. Others have suggested that filter media could enable complex sorption and precipitation processes which may strongly, or even permanently, bind phosphorus to the filter media (e.g. Arias et al., 2001). In acidic soils, sorption and precipitation processes are facilitated by aluminium and iron oxides and hydroxides, such as gibbsite, hematite, and goethite (Parfitt, 1989). In neutral-to-calcareous soils phosphorus adsorbs to the surface of calcium carbonates and clay minerals, although precipitation reactions dominate phosphorus retention in these environments (Shen et al., 2011). These interactions have long been recognised as important mechanisms for sequestering phosphorus in aquatic sediments (e.g. Sperber, 1958, Boers, 1991, Smolders et al., 2001). Utilising these interactions by incorporating a metal-oxide-rich media into a traditional filter medium may increase uptake of phosphorus, enable more sustainable long-term retention and allow biofilters to achieve receiving water phosphorus targets. Similar approaches have previously proven successful in controlling release of phosphates from aquatic sediments through the application of iron compounds to the overlying water column (e.g. Murphy et al., 2001, Smolders et al., 2001).

This study analysed the phosphorus removal capacity of three metal-oxide ameliorated filter media, through a series of compressed-time, laboratory-scale column tests. The results suggest that augmenting the currently recommended filter medium with metal-oxide-rich Skye sand significantly increases phosphorus removal capacity, and can achieve effluent concentrations below receiving water phosphorus targets. The negligible increase in phosphorus removal performance exhibited by the iron ore and goethite augmented filter media suggests that metal-oxide alone is unlikely responsible for improved performance. These findings represent significant progress towards optimisation of biofilter media to achieve receiving water phosphorus targets.

Materials & Method

Four configurations of filter media were investigated in this study. The materials included three naturally occurring minerals, loamy sand, Skye sand and iron ore, as well as a synthetically produced goethite. Loamy sand, a light brown quartz mineral sand, is the filter medium currently recommended by Australian biofiltration system guidelines (FAWB, 2009). As such, loamy sand was selected to act as the control in this study and as the base medium for each metal-oxide ameliorated media. Skye sand is a red coloured quartz sand mined in Skye, Victoria. It is rich in iron, aluminium and silicon oxides and hydroxides.

Despite the sustainability and cost issues associated with its widespread use, this study also analysed an iron ore augmented filter media. The iron ore was sourced from the Pilbara region in Western Australia. The chemical characteristics of these media are summarised in Table 1.

Table 1. Test media chemical analysis

Media	Fe	Al	P (mg/kg)*	Mn	Ca	Fe_2O_3	Al_2O_3	SiO_2 %w/w#	CaO	Ti	LOI# (%)	Major Mineral^
Loamy Sand	1600	1300	<50	<5	85	0.21	0.58	99.24	<0.01	0.08	0.74	Quartz
Skye Sand	9800	2100	<50	<5	<5	1.77	2.15	94.44	<0.01	0.22	1.6	Quartz
Iron Ore	94000	2500	140	300	<50	86.63	2.07	4.02	0.07	0.14	7.9	Goethite, Hematite

*Analysed using ICP-OES, #Analysed using XRF, ^Analysed using XRD

Goethite is a mineral iron oxyhydroxide formed through natural transformation of ferric hydroxide. Goethite is often used as a model compound for environmental studies (Atkinson et al., 1967). A microcrystalline precipitate of goethite (α-FeOOH) was prepared under standard laboratory conditions using a method adapted from Atkinson et al (1967). Firstly 250g of ferric nitrate $Fe(NO_3)_3$ was added to 4.125L of deionised water. This was then combined with 1L 2.5M potassium hydroxide (KOH) and stirred constantly for 30 minutes. Adjusting the pH of ferric nitrate creates a ferric hydroxide precipitate which slowly changes its form to 'goethite'. The precipitate was placed in an oven (65°C) for 24 hours, and then washed 4 times. The filter media was coated with goethite (15ml) by pumping a diluted suspension through the loamy sand packed columns using a peristaltic pump.

Filter media configuration

The filter media configurations analysed in this study are outlined in Table 2. The quantities of each metal-oxide-rich media required were based on the results of a preliminary chemical characterization (see Table 1). Each metal-oxide-rich media was added to a known quantity of loamy sand to achieve an iron content of approximately 800mg. This enabled comparisons to be made between the configurations without a disproportionate influence of iron, which is arguably the most reactive with dissolved phosphorus. Prior to being used to pack the columns both the loamy sand and Skye sand were oven dried for 12 hours at 60˚C, to remove residual moisture, then sieved to remove any deleterious material.

Table 2. Column configuration summary

Media	Loamy Sand (control)	Loamy Sand + Skye Sand	Loamy Sand + Iron Ore	Loamy Sand + Goethite
Total Mass (g)	118	110	118	118
Fe content (mg) (preliminary analysis)	160±50	800±150	800±50	820±16
Fe content (mg) (post experimental analysis)	160±12	761±43	1699±102#	386±60*

Natural heterogeneity between iron ore samples is attributed to the variance in results
* Goethite columns experienced significant wash-out of the ferric hydroxide precipitate

Experimental design

The experimental apparatus consisted of two 20L influent tanks, rotated daily, six threaded glass columns (Chromaflex, Multi-Lambda Scientific, 25 x 150 mm) and six peristaltic pumps. To ensure even distribution of inflow and minimise migration of particles into effluent, both the inlet and outlet of the columns contained a 20μm nylon mesh. Each filter medium configuration was replicated in triplicate. As only 6 columns were available, the experimentation was conducted in two phases.

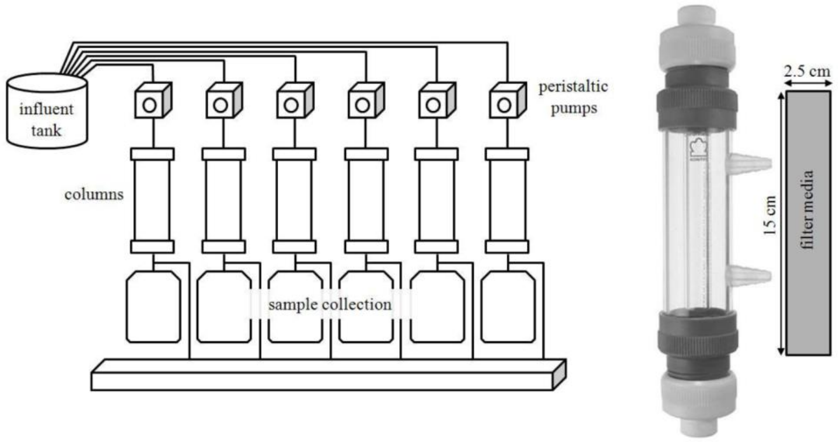

Figure 1. Experimental apparatus and column design

Preparation of synthetic inflow solution

Typical Melbourne stormwater contains a total phosphorus concentration of ~0.3-0.35mg/L, of which orthophosphate or, filterable reactive phosphorus (FRP) makes up approximately 0.12mg/L (Duncan, 2006). A synthetic solution of dissolved phosphorus (1gP/L) was thus prepared by combining 4.386g of potassium dihydrogen orthophosphate (KH_2PO_4) with 1L of deionised water. To reach the desired inflow concentration of 0.1mgP/L, 2ml of this solution was added to 20L of deionised water. This synthetic solution was pumped through the columns (819mm/hr) over a period of 7 days, operating in 12 hour intervals, to reflect fluctuations between saturated and unsaturated conditions. During operation the equivalent of 2.5 years of rainfall-runoff (based on Melbourne average annual rainfall-runoff to a biofilter sized at 2% of its contributing impervious catchment), flowed through each column (~32L). Humic acid (3mg/L) was also included in the inflow solution to account for the presence of organic matter or natural polymeric compounds in stormwater, which may compete with phosphorus for metal-oxide adsorption sites (Hongve, 1997).

Sampling and Analyses

Influent and effluent samples were taken at the beginning of operation and then at intervals equivalent to six months of simulated rainfall until 2.5 years were completed. This resulted in 6 sampling events over the 7 days. Because sampling times were determined by cumulative inflow volume, each sampling event occurred at different times of the day. Samples were analysed for total phosphorus (TP), filterable reactive phosphorus (FRP), total organic carbon (TOC) and total iron (Fe) (to monitor leaching from the columns). The FRP samples were filtered through a 0.45μm cartridge filter (Bonnet Scientific). Upon completion of each experimental phase, the filter media were removed from the columns, sectioned into 3cm depth intervals and then analysed for FRP and Fe. Effluent and media samples were both analysed to determine which media displayed the best phosphorus removal performance. All media and water chemical analyses were undertaken by NATA

(National Association for Testing Authorities) certified laboratories using ICP-MS for metals and ICP-OES for carbon and nutrients.

Results and Discussion

Water Quality analyses: P removal vs. receiving water phosphorus targets

The water sampling analysis results for effluent FRP from this column study are summarised in Table 3. These values represent the average calculated for the three replicates of each configuration type. Both effluent concentration and percentage removal data are displayed for each sampling event over the 2.5 years of rainfall simulated. Results for TP have been omitted as these closely reflect FRP values. The effluent FRP results are also represented in Figure 2.

Table 3. Column effluent FRP concentration (mg/L) and removal (%)

Media	Loamy sand (control)		Skye sand + Loamy sand		Iron Ore + Loamy sand		Goethite + Loamy sand	
Sample (months)	Conc. (mg/L)	Removal (%)	Conc. (mg/L)	Removal (%)	Conc. (mg/L)	Removal (%)	Conc. (mg/L)	Removal (%)
0	0.01	92	0.00	96	0.01	92	0.01	90
6	0.09	11	0.00	97	0.07	30	0.06	44
12	0.10	0	0.01	95	0.08	22	0.07	30
18	0.08	22	0.01	90	0.07	34	0.06	38
24	0.08	14	0.03	68	0.09	14	0.08	18
30	0.09	15	0.05	50	0.09	10	0.09	13

Each filter media configuration exhibits a trend of increasing effluent FRP concentration over the six sampling events. While the iron ore and goethite columns closely followed the effluent FRP concentration trend shown by the loamy sand control columns, the Skye sand columns behaved quite differently, maintaining removal greater than or equal to 90% for the first 18 months of simulated rainfall.

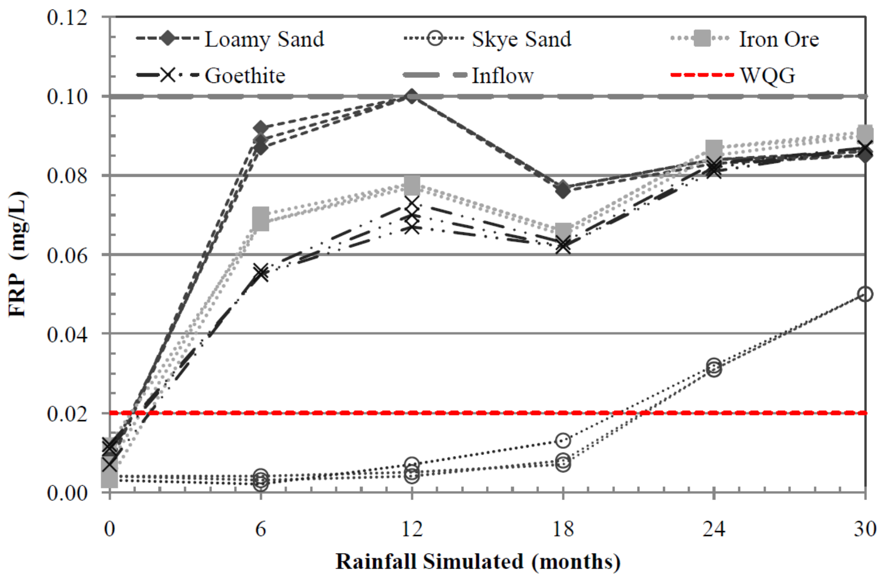

Figure 2. Effluent FRP concentration (mg/L) over 2.5 years of simulated rainfall (WQG represents the ANZECC FRP trigger concentration for lowland rivers).

Each metal-oxide ameliorated filter medium improved the phosphorus removal capacity of the loamy sand control. In the case of iron ore and goethite ameliorated media, this slightly enhanced performance was maintained until the 24th month of simulated rainfall. Given that the performance of the goethite and iron ore ameliorated columns was of negligible difference to the control medium these treatments have shown little benefit overall to FRP removal. The Skye sand augmented filter medium exhibited the best performance overall, having a substantially higher phosphorus removal efficiency compared to the loamy sand control treatment. Furthermore, effluent FRP concentrations from the Skye sand columns remained below receiving water FRP targets until the 24^{th} month of simulated rainfall (see Figure 2).

These results suggest that even under high inflow loading conditions, Skye sand ameliorated filter media can achieve and maintain effluent FRP concentrations below receiving water targets, for a considerably longer period than the currently recommended filter medium. The variability between treatments suggests that the influence of physical characteristics (e.g. specific surface area) may play at least as important a role in phosphorus removal as chemical composition. Further analysis of the Skye sand and loamy sand media is required to ascertain whether performance outcomes can be attributed to physical characteristics. However, it does appear that the Skye sand can increase the phosphorus removal lifespan of standard biofilter media.

Media Analyses: P uptake over the column profile v. Fe content

The results of the analysis of FRP and iron (Fe) concentrations following the experiments over the column profile for each media configuration is outlined in Figures 3a and 3b respectively. The y-axis values correspond to the section of the media profile analysed (i.e. 0-3cm, 3-6cm, 6-9cm, 9-12cm and 12-15cm). The results indicate that of all the media configurations tested, the Skye sand columns had the highest concentration of FRP in the medium following the experiment. This is also confirmed by the FRP mass balance results outlined in Table 4, suggesting 80% of FRP in the inflow was retained in the Skye sand augmented columns. To determine whether FRP uptake was correlated to the metal-oxide content of the media, the samples were also analysed for total Fe. Iron was chosen as the indicator of interactions with metal-oxides in the media as it is arguably the most reactive metal-oxide with FRP. The results revealed that Fe content in the media did not correlate significantly ($p < 0.05$) with FRP uptake. This is particularly evident in the iron ore augmented columns, which despite having significantly higher concentrations of Fe across the media profile, did not greatly improve upon the FRP removal capacity of the loamy sand control.

Analysis of Fe in the media also highlighted a problem with the goethite columns, discovered following the experimentation, which may have impacted significantly on FRP removal performance. It was observed that the goethite experienced some clogging in the first 2cm of the filter media, and therefore the goethite was not evenly distributed through the column profile. The impact of this evident in Figure 3b, where two of the goethite replicate columns recorded double the average Fe content in the first 3cm of the column profile. Upon completion of the experimental run the clogged goethite columns also bore signs of cracking, suggesting that preferential flows had formed, further reducing inflow access to binding sites and thereby affecting FRP removal performance.

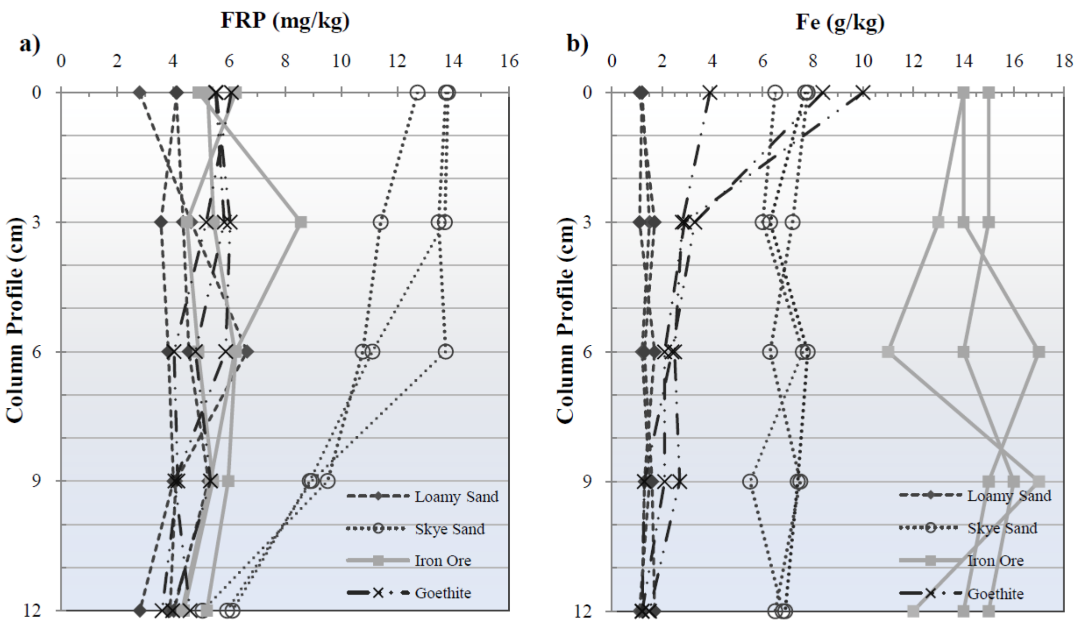

Figure 3. a) FRP concentration (mg/kg) b) Fe concentration (g/kg), over the column profile (cm) for each filter media configuration

Table 4. FRP mass balance

Sample (months)	FRP in inflow (mg)	FRP in effluent (mg)			
		Loamy sand (control)	Skye sand + Loamy sand	Iron Ore + Loamy sand	Goethite + Loamy sand
0	0.39	0.00	0.00	0.00	0.00
6	0.60	0.54	0.00	0.42	0.36
12	0.64	0.64	0.06	0.51	0.45
18	0.64	0.51	0.06	0.45	0.38
24	0.64	0.51	0.19	0.57	0.51
30	0.64	0.57	0.32	0.57	0.57
Total	3.19	2.77	0.64	2.52	2.27
FRP retained (mg)		0.41	2.55	0.66	0.91
FRP retained (%)		12.99	80.00	20.74	28.62

Conclusion

This study investigated how augmenting a loamy sand filter medium with metal-oxide-rich media (iron ore, goethite and Skye sand) influenced phosphorus removal. Overall, the Skye sand was the most effective in improving removal efficiency, significantly improving upon the removal capacity of the loamy sand control and achieving effluent concentrations below typical receiving water phosphorus targets. The iron ore and goethite augmented media showed very similar results to the control medium suggesting that metal-oxide content alone may not dictate phosphorus removal performance. This hypothesis was supported by analysis of the filter media following the column experiments which showed no significant correlation between FRP uptake and Fe content. This disparity may be explained by differences in the surface area of the metal-oxide-rich media tested, although this requires further investigation.

In conclusion, the performance of the Skye sand ameliorated filter media illustrated in this study suggests that incorporating metal-oxide-rich sand into biofilters can significantly improve the uptake of FRP, and potentially enable biofilters to reduce phosphorus concentrations to below receiving water quality targets. Perhaps more importantly, it suggests an ability of media augmented with Skye sand to maintain effective phosphorus removal over a longer lifespan than standard filter media. However, the current trials were conducted without vegetation and it is not yet known whether the augmented media will support plant growth. In fact, vegetation may indeed improve upon removal performance by facilitating additional uptake of phosphorus by plants and rhizosphere microorganisms. Additionally, the consequences of coupling a metal-oxide-rich media and a saturated zone in biofilters remains unknown, as does its influence on nitrogen removal and the broader issue of longevity. The next stage of research will address these remaining knowledge gaps through a large-scale vegetated biofilter column experiment. Once complete, design recommendations will be integrated into stormwater biofiltration system adoption guidelines and treatment predictive models.

This study has provided further knowledge about the fate of phosphorus in filter media and how this is affected by the presence of metal-oxides. This finding represents progress towards the development of a biofiltration system which is optimised for phosphorus removal, and capable of meeting receiving water phosphorus targets.

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A3.2 SEM micrograph of filter media

Scanning electron microscope images of the filter media analysed in the batch- and through flow column-tests are presented in Figure A3.1.

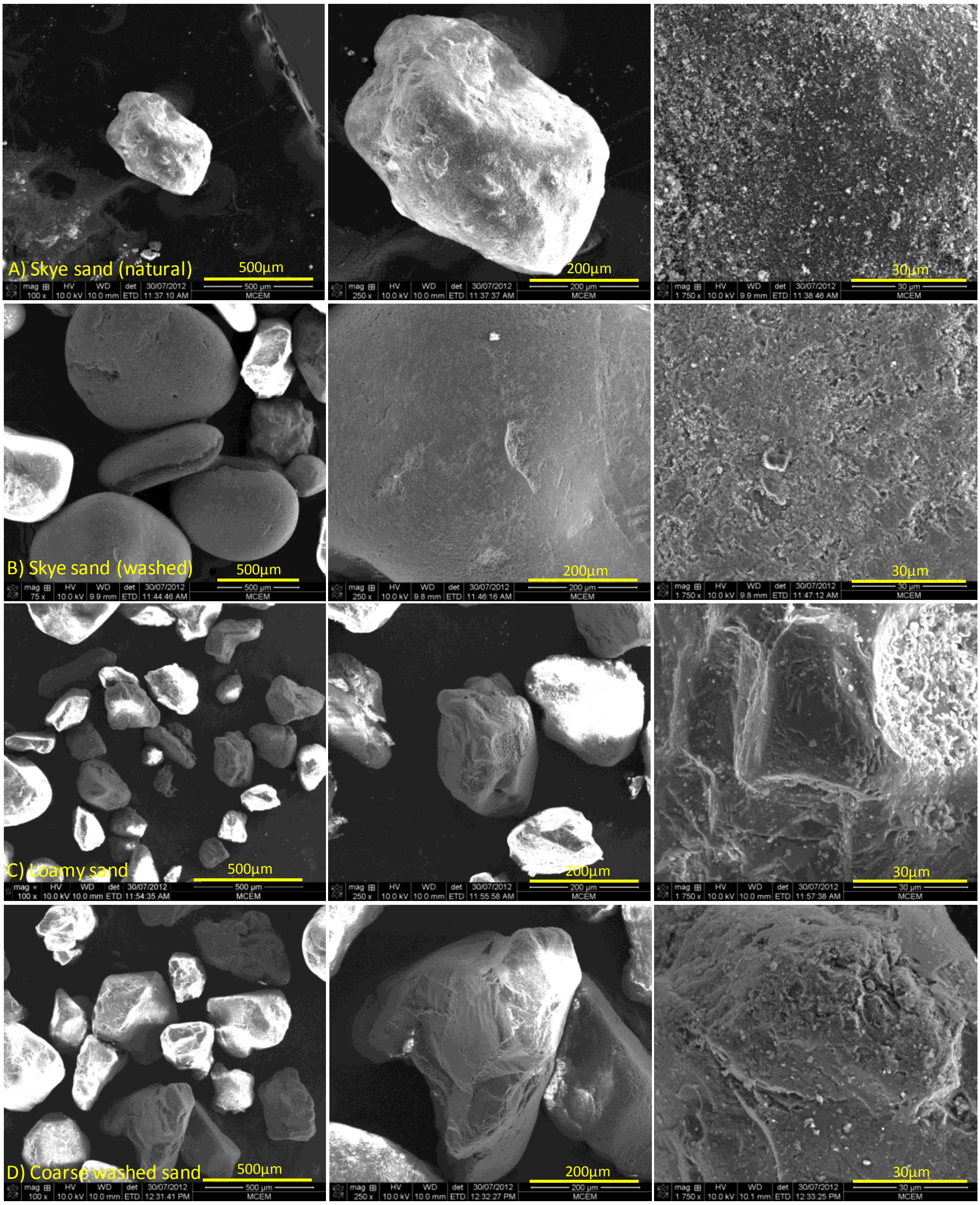

Figure A3.1 Scanning electron microscope images of the filter media a) Skye sand b) washed Skye sand c) loamy sand d) coarse washed sand, at three levels of magnification L-R: 500µm, 200µm and 30µm (Note size of particles in images are not uniform).

A3.3 Energy Dispersive X-ray analysis (EDAX) of Skye sand

Using EDAX the distribution of chemical elements in Skye sand could be visualised (Figure A3.2). The energy spectrum accompanying this analysis determined that for the particles scanned oxygen represented ~50% of the atomic weight, silicon ~30%, iron ~15% and aluminium ~5%.

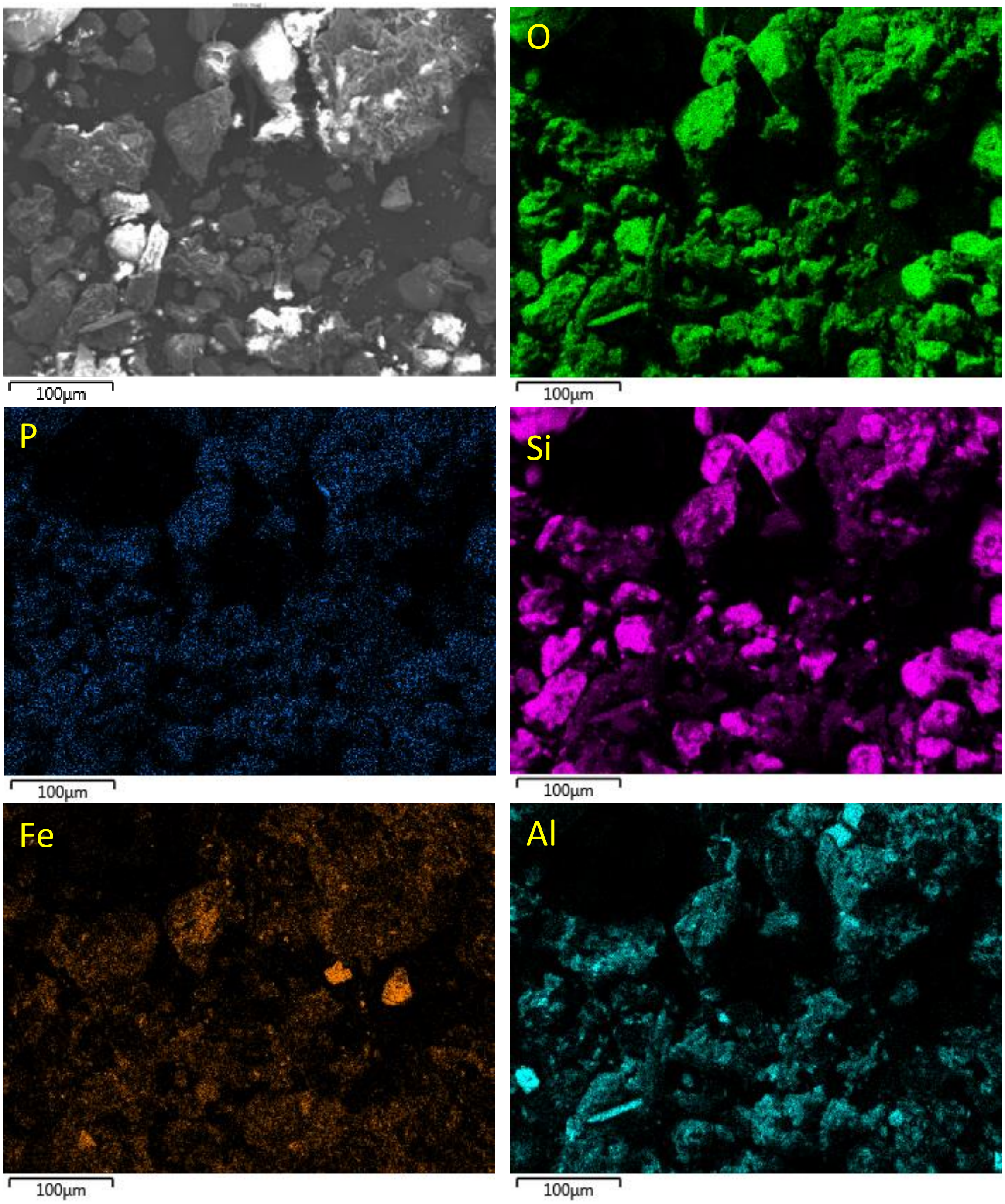

Figure A3.2 Energy Dispersive X-ray analysis (EDAX) of the Skye sand under SEM enabled the distribution of chemical elements in the filter media to be visualised. Each scan is labelled with the corresponding element.

A3.4 Particle size distribution of filter media

Figure A3.3 illustrates the particle size distribution of loamy sand, Skye sand and coarse washed sand filter media.

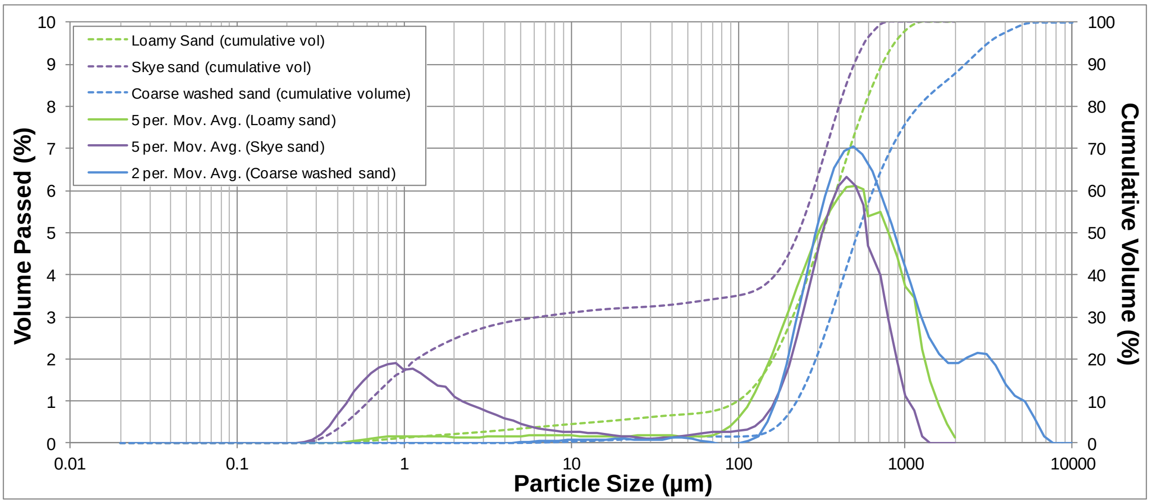

Figure A3.3 Particle size distribution by volume of loamy sand, Skye sand and coarse washed sand.

A3.5 Exchangeable ions batch-test

The results of the exchangeable ions batch-test are illustrated in Table A3.1.

Table A3.1. Equilibrium pH and concentrations of Fe, Al, Ca and Mg released from 1g of filter media after 2h agitation in a 50mL Milli-Q water solution of KNO3 0.1M

Medium	pH	FRP (mg/L)	Fe (mg/L)	Al (mg/L)	Ca (mg/L)	Mg (mg/L)
Blank (0.1M KNO3)	5.7	<0.001	<0.002	<0.005	<0.1	<0.1
Skye sand <75um	5.4	<0.001	0.006	0.005	1.8	6.4
Skye sand (natural)	5.9	<0.001	<0.002	<0.005	0.3	0.3
Skye sand (washed)	6.0	0.001	<0.002	<0.005	0.2	<0.1
Loamy sand (natural)	5.4	<0.001	0.066	0.12	1.0	0.2

Note: loamy sand <75μm and coarse washed sand not analysed.

Chapter 4 Appendix

A4.1 Journal Paper: Water Science & Technology

Declaration for Journal Paper contributing content to Thesis

Chapter 4

In the case of this journal paper (which contributes some but not all content towards thesis Chapter 4), the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Experimental construction and works, data collection, data analysis and interpretation, write-up	75%

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
Tim Fletcher	Ideas and design, data interpretation, manuscript revision and comments	
Belinda Hatt	Experiment initiation, ideas and design, data interpretation, manuscript revision and comments	
Perran Cook	Data interpretation, review of manuscript, comments and revisions	

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		**Date** 26/07/18
Main Supervisor's Signature		**Date** 26/07/18

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

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Co-optimisation of phosphorus and nitrogen removal in stormwater biofilters: the role of filter media, vegetation and saturated zone

Bonnie J. Glaister, Tim D. Fletcher, Perran L. M. Cook and Belinda E. Hatt

ABSTRACT

Biofilters have been shown to effectively treat stormwater and achieve nutrient load reduction targets. However, effluent concentrations of nitrogen and phosphorus typically exceed environmental targets for receiving water protection. This study investigates the role of filter media, vegetation and a saturated zone (SZ) in achieving co-optimised nitrogen and phosphorus removal in biofilters. Twenty biofilter columns were monitored over a 12-month period of dosing with semi-synthetic stormwater. The frequency of dosing was altered seasonally to examine the impact of hydrologic variability. Very good nutrient removal (90% total phosphorus, 89% total nitrogen) could be achieved by incorporating vegetation, an SZ and Skye sand, a naturally occurring iron-rich filter medium. This design maintained nutrient removal at or below water quality guideline concentrations throughout the experiment, demonstrating resilience to wetting–drying fluctuations. The results also highlighted the benefit of including an SZ to maintain treatment performance over extended dry periods. These findings represent progress towards designing biofilters which co-optimise nitrogen and phosphorus removal and comply with water quality guidelines.

Key words | biofilter, nitrogen, phosphorus, saturated zone, Skye sand, stormwater

Bonnie J. Glaister (corresponding author)
Belinda E. Hatt
CRC for Water Sensitive Cities,
Water for Liveability Centre,
Department of Civil Engineering,
Monash University, Victoria 3800,
Australia
E-mail: *bonnie.glaister@monash.edu*

Tim D. Fletcher
Waterway Ecosystem Research Group,
Department of Resource Management and Geography,
Melbourne School of Land and Environment,
the University of Melbourne, Victoria 3121,
Australia

Perran L. M. Cook
CRC for Water Sensitive Cities,
Water Studies Centre,
School of Chemistry, Monash University,
Victoria 3800,
Australia

INTRODUCTION

Urban stormwater runoff has a significant impact on the health and ecological function of receiving waters (Walsh *et al.* 2004). Discharge of nutrient-rich stormwater into waterways can be particularly detrimental, leading to increased biological productivity and eutrophication (Kadlec & Knight 1996). Stormwater biofilters (also known as biofiltration systems, bioretention systems or raingardens) have the potential to reduce this impact. Extensive laboratory and field testing has demonstrated the effectiveness of biofilters for removing nitrogen and phosphorus from urban stormwater, confirming that these systems reliably meet load reduction targets for total suspended solids (TSS) and nutrients (TSS 80%, total phosphorus (TP) 45%, and total nitrogen (TN) 45% in Victoria, Australia). However, N removal rates remain variable and reported N and P concentrations are near or above typical Australian and New Zealand receiving water guidelines (ANZECC & ARMCANZ 2000; Hunt *et al.* 2006; Davis *et al.* 2009; Hatt *et al.* 2009). To provide effective protection for receiving waters, biofilters must be co-optimised for N and P removal, and achieve effluent concentrations below environmental protection guidelines.

N and P removal are governed by a range of biogeochemical processes. N removal relies on either the transformation of N species into a gaseous form (N_2) through the processes of ammonification, nitrification and denitrification or biological assimilation by plants and microbes (Vymazal 2007). Particulate-associated P is removed predominantly by physical straining and sedimentation. Removal of dissolved P is facilitated by sorption, precipitation and biological uptake (Kadlec & Knight 1996; Hatt *et al.* 2007). While it has been suggested that plant uptake represents only a fraction of overall nutrient removal (Dietz & Clausen 2006) the role of plants in supporting nutrient removal processes has been well established in the literature (Browning & Greenway 2003; Vymazal 2007; Read *et al.* 2008) and demonstrated by several studies (e.g. Henderson *et al.* 2007a; Bratieres *et al.* 2008; Lucas &

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Greenway 2008). The importance of plant species selection as well as the influence of inter-species competition and planting regime on nutrient removal performance have also been tested (Read *et al.* 2010; Ellerton *et al.* 2012). Australian biofiltration design guidelines (see FAWB 2009) recommend the inclusion of a saturated zone (SZ) to promote anaerobic conditions between wetting events and thus enhance N removal through denitrification. The inclusion of an SZ has also been shown to support plant health and protect biofilters against drying during dry weather periods (Blecken *et al.* 2009). The variable wetting and drying cycles which biofilters experience dramatically alter oxygen concentrations and the distribution of denitrifying bacteria in the SZ (Korom 1992; Chen *et al.* 2013). Seasonality and antecedent dry weather periods therefore have a significant influence on the effectiveness of the SZ, which has achieved mixed success in both field and laboratory experiments (Dietz & Clausen 2006; Hunt *et al.* 2006; Hsieh *et al.* 2007b; Lucas & Greenway 2008; Zinger *et al.* 2012). Furthermore, if not configured correctly, the SZ may become an internal source of P, for instance if P retained in redox sensitive pools (e.g. Fe-bound P) becomes remobilised under reducing conditions (Boström *et al.* 1988), or if the organic carbon added to facilitate denitrification has a high P content. These are important aspects to consider when incorporating an SZ in terms of co-optimising N and P removal.

Biofilters have a finite P retention capacity (Wild 1950; Del Bubba *et al.* 2003; Hsieh *et al.* 2007a). Factors which influence this include native P concentration, depth, chemical composition, particle size and surface area of the filter media, and the presence of other P removal pathways in the system. Presently, our knowledge regarding the role of filter media in facilitating long-term P retention remains limited. Henderson *et al.* (2007a, b) argue that filter media are unlikely to retain nutrients in the long term, but may provide an important function by extending retention time so plant uptake and microbial assimilation can occur. Others have suggested that filter media could enable complex P sorption and precipitation processes through interactions with P attracting ions, which may strongly, or even permanently, bind P to the filter media (Arias *et al.* 2001; Del Bubba *et al.* 2003; Lucas & Greenway 2008). A recent study by Glaister *et al.* (2011) found that under simple laboratory testing a naturally occurring iron- and aluminium- oxide rich sand, known as Skye sand, demonstrated superior phosphate removal performance compared with loamy sand, which is the filter medium currently recommended by Australian biofiltration system guidelines (FAWB 2009). Configuring biofilters with Skye sand may enhance P removal and facilitate long-term P retention. The present study investigates the role of filter media, vegetation and an SZ in co-optimising N and P removal by comparing the nutrient removal performance of biofilters configured with Skye sand and loamy sand in conjunction with and without vegetation and an SZ. Climatic variability imposed during the experiment also investigates the influence of wet and dry periods on filter media durability and treatment resilience.

METHOD

Experimental design

Column construction and filter media selection

Twenty biofilter columns, shown in Figure 1(a), were constructed using PVC pipe (150 mm diameter) and acrylic to create a 200 mm ponding zone. The columns were designed in accordance with Australian biofiltration system guidelines (see FAWB 2009). Columns without an SZ drained freely from the base, while a riser pipe was attached to the outlet of those with an SZ to maintain a 300 mm pool of water in the lower half of the column; Figure 1(b). Elemental characteristics of the Skye sand and loamy sand filter media are described in Table 1. An organic carbon source mixture of pine woodchips (bark removed) (26.5 g) and pine flour ('sawdust') (9.3 g) was blended into the SZ filter medium to facilitate the denitrification process (total material added was equivalent to 5% of the volume of the SZ). These materials were selected on the basis of their biodegradability and low P content (10.2 mg P/kg). The biofilters were configured into four main layers shown in Figure 1(b): (1) filter media (300 mm) loamy sand or Skye sand planted with *Carex appressa*; (2) sand transition layer (200 mm) coarse washed sand; (3) pea gravel drainage layer (70 mm); (4) gravel drainage layer (30 mm).

Column configuration and establishment

Four design configurations were tested (with five replicates of each). The configurations are described in Table 2. Filter media layers 2, 3 and 4 remained constant between configurations. These configurations enabled three key relationships between design characteristics to be analysed: (i) loamy Sand vs. Skye sand vegetated with SZ; (ii) Skye sand non-vegetated with SZ vs. Skye sand vegetated with

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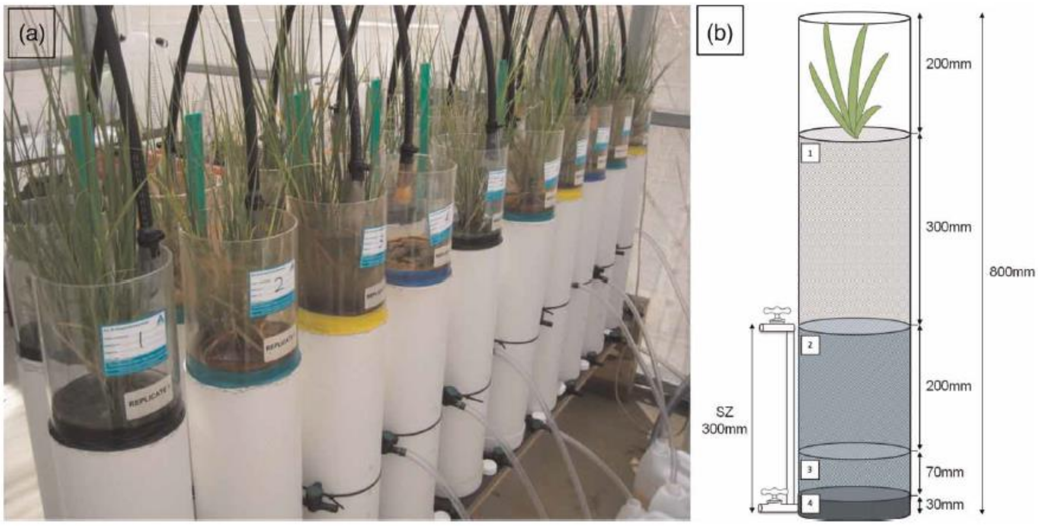

Figure 1 | (a) Experimental set-up of biofilter columns in greenhouse and (b) schematic diagram of the biofilter columns (with SZ riser outlet attached).

Table 1 | Elemental characteristics of loamy sand and Skye sand filter media (parentheses represent range)

Media	Fe[a]	Al[a]	$Fe_2O_3^b$	$Al_2O_3^b$	SiO_2^b
Loamy sand	1,000 (±200)	900 (±100)	0.21	0.58	99
Skye sand	21,000 (±2,000)	1,000 (±100)	1.8	2.2	94

[a]Analysed using inductively coupled plasma mass spectroscopy (ICP-MS; $n = 2$) (mg/kg).
[b]Analysed using X-ray fluorescence (XRF; %w/w).

SZ; and (iii) Skye sand vegetated with SZ vs. Skye sand vegetated without SZ.

The columns were filled manually then compacted using a weighted hammer (as described by ASTM F1815-11 (2011)). The compaction required was determined by the layer thickness and media porosity. Once filled, vegetation was transplanted into the top 100 mm of the columns. The Australian native species *C. appressa* was selected because of its drought tolerance and resilience to climate fluctuations. Previous biofilter column studies have found that this species maintains very good nutrient removal under high loading conditions and inflow concentrations (Bratieres *et al.* 2008; Read *et al.* 2008). Prior to transplanting the plants were matured in a glasshouse (at 25 °C) for 12 weeks. Following construction the columns were placed in a purpose-built ventilated greenhouse and dosed twice weekly for 5 weeks with semi-synthetic stormwater to establish the plants, inoculate the soil microbial community and flush free particles out of the filter media.

Experimental procedure

Semi-synthetic stormwater

Due to limitations associated with the use of real stormwater, a semi-synthetic stormwater mixture was used instead. This approach minimised inflow concentration variability whilst maintaining realistic composition. Several studies have adopted this method and demonstrated

Table 2 | Biofilter column design configurations

Configuration	Filter medium	Vegetation	Saturated zone
Loamy sand, vegetated, saturated zone (LS-V-S)	Loamy sand	*C. appressa*	SZ
Skye sand, non-vegetated, saturated zone (SS-NV-S)	Skye sand	Non-vegetated	SZ
Skye sand, vegetated, saturated zone (SS-V-S)	Skye sand	*C. appressa*	SZ
Skye sand, vegetated, no saturated zone (SS-V-NS)	Skye sand	*C. appressa*	No SZ

consistency in maintaining target concentrations throughout the experimental period (e.g. Hatt *et al.* 2007). Sediment was collected from a nearby stormwater retarding basin and strained through a 1,000 μm sieve. The concentration of solids in the sieved slurry was measured prior to mixing with a known amount of dechlorinated tap water to ensure the target TSS concentration was achieved. Target concentrations for TSS and nutrients were matched with typical values for worldwide and Melbourne urban stormwater quality reported by Duncan (1999) and Taylor *et al.* (2005) respectively. The mixture was topped up using chemicals where necessary to make up the deficit in nutrient concentrations.

Stormwater dosing, sampling and analysis

The stormwater dosing regimen reflected Melbourne average annual rainfall volumes, for a biofilter sized to 2.5% of its contributing catchment area, based on Australian design guidelines (see Hatt *et al.* 2007). The columns received 3.7 L of stormwater during each dosing event. The dosing campaign simulated wet and dry climate conditions by altering the frequency of events (see Figure 2). Each climate reflected typical Melbourne rainfall patterns (Bureau of Meteorology 2013). During the wet periods (April–November) the columns were dosed twice weekly. During the dry period (December–March) the column dosing gradually transitioned from 6 to 18 antecedent dry days to reduce the risk of plant fatality. Sampling took place for 10 select dosing events over the 12-month period from August 2011 to July 2012. Column effluent was collected until flow ceased (approximately 3.0 of the 3.7 L). This bulk sample was mixed thoroughly then sub-sampled for analysis. Samples were analysed for TSS, TN, TP and their dissolved species. Samples analysed for dissolved nutrients were filtered through a 0.45 μm filter (Bonnet Scientific). All water chemical analyses were undertaken by NATA (National Association for Testing Authorities) certified laboratories using standard analysis methods (APHA/AWWA/WPCF 1998). At several points during the campaign discrete water samples were collected from ports installed along the column to measure dissolved oxygen (DO) concentrations in the SZ before and after dosing events using a fibre-optic oxygen meter (PyroScience FireStingO_2).

Data analysis

All statistical analyses were performed using SPSS (version 20. IBM, USA). Analysis of variance (ANOVA) was used to compare performance between biofilter configurations and climate periods, with post-hoc tests used to compare individual pairs (Tukey's HSD where inequality of variance occurred and Tamhane's where not). Data reported below detection limits (e.g. <0.001) were analysed at half the limit of reporting value (e.g. 0.0005). Data from the first sample event (September) were omitted from the analysis because at this stage the columns were still establishing. Additionally, sample data from the SS-V-NS columns were omitted for the eighth event (May), as infiltration had ceased due to sediment clogging of the surface layer. This sediment layer was disturbed manually by gently scraping the surface, allowing regular infiltration to resume.

RESULTS AND DISCUSSION

Phosphorus removal performance of alternative biofilter designs

The influence of filter media

Analysis of TP outflow concentrations from the loamy sand (LS-V-S) and Skye sand (SS-V-S) columns suggests that filter medium type did not significantly influence TP removal (Figure 3). This finding is at least partially attributed to the fact that very effective TSS (86–99%) removal was achieved by both filter media and approximately ~70% of TP is associated with particulates. However, all design configurations also consistently achieved very good removal of PO_4^{3-} (>96%, Table 3) and there were no significant differences between the two filter media types. Perhaps it is not altogether unsurprising that no differences in PO_4^{3-} removal

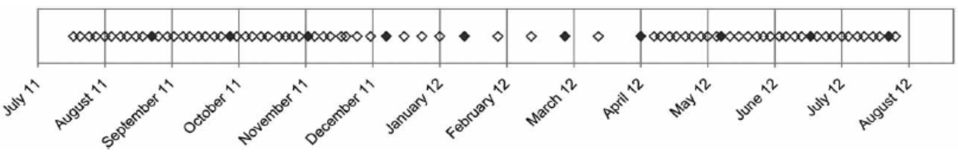

Figure 2 | Stormwater dosing and sampling regime (filled markers denote sampled events).

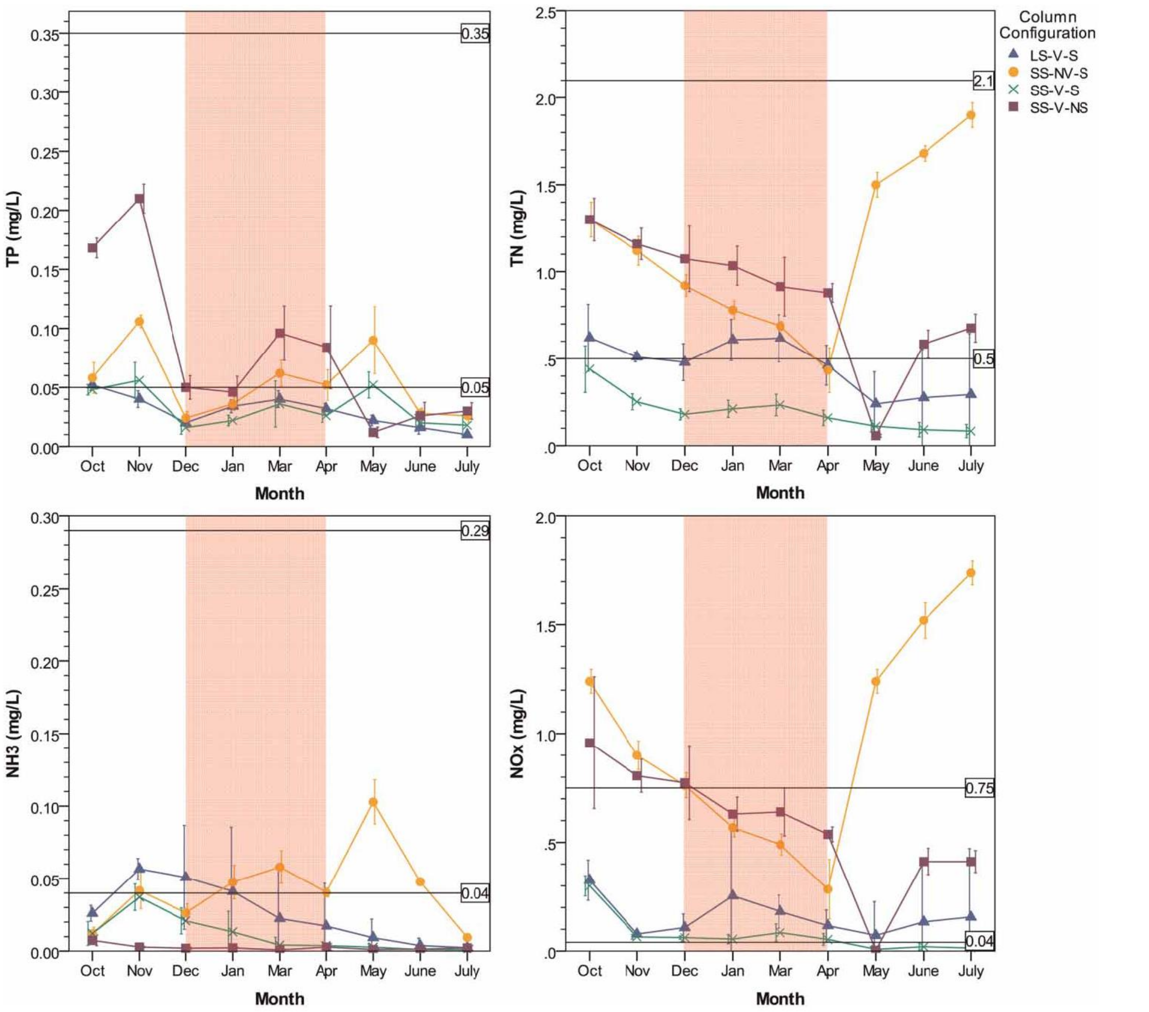

Figure 3 | Biofilter column outflow concentrations (mg/L) from October 2011 to July 2012 (TP, top left; TN, top right; ammonia, NH3, bottom left; and nitrous oxides, NOx, bottom right). Data points represent the mean ($n = 5$) and error bars represent ± 1 standard deviation from the mean. Upper horizontal reference line denotes inflow concentration; lower horizontal reference line represents the water quality guideline concentration for slightly disturbed lowland rivers in South-Eastern Australia (ANZECC & ARMCANZ 2000). Shaded area represents the dry dosing period.

were observed given that the testing period (1 year) was relatively short and neither loamy sand nor Skye were likely to approach PO_4^{3-} saturation during this time. The role of filter media may become more important as plants reach maturity and P uptake and release (due to plant senescence) approach equilibrium. Given that Skye sand has higher concentrations of Fe and Al oxides, to which PO_4^{3-} is readily adsorbed, the sorption capacity and life-span of this medium is expected to extend beyond that of loamy sand (Glaister *et al.* 2011).

Interactions with vegetation and SZ

Vegetation had a significant effect on PO_4^{3-} removal ($p < 0.001$) but not TP. This is perhaps not surprising, given that PO_4^{3-} is chemically and biologically driven, while TP removal is primarily related to removal of TSS. TP removal was improved by the addition of vegetation (Figure 3). Vegetation provides a removal pathway for dissolved nutrients through plant uptake, and supports biological activity in the rhizosphere, which also contributes

Table 3 | Average outflow nutrient concentrations for wet and dry dosing periods (mg/L)

		LS-V-S	SS-NV-S	SS-V-S	SS-V-NS
TP	Wet[a]	0.046 (88)	0.082 (79)	0.052 (87)	0.19 (52)
	Dry	0.032 (92)	0.044 (89)	0.025 (93)	0.069 (82)
	Wet[b]	0.016 (95)	0.048 (86)	0.030 (91)	0.028 (92)
PO_4^{3-}	Wet[a]	0.003 (99)	0.002 (99)	0.002 (99)	0.004 (98)
	Dry	0.002 (99)	0.003 (98)	0.003 (99)	0.003 (98)
	Wet[b]	0.002 (98)	0.002 (97)	0.001 (98)	0.003 (98)
TN	Wet[a]	0.56 (70)	1.2 (35)	0.34 (82)	1.2 (33)
	Dry	0.54 (69)	0.71 (60)	0.20 (89)	0.97 (44)
	Wet[b]	0.27 (85)	1.7 (8)	0.096 (95)	0.63 (66)
NH_3	Wet[a]	0.041 (89)	0.027 (93)	0.026 (93)	0.005 (99)
	Dry	0.037 (88)	0.043 (84)	0.012 (96)	0.002 (99)
	Wet[b]	0.005 (99)	0.053 (85)	0.002 (99)	0.001 (100)
NO_X	Wet[a]	0.20 (80)	1.1 (−10)	0.18 (81)	0.88 (9)
	Dry	0.17 (81)	0.53 (41)	0.064 (93)	0.65 (27)
	Wet[b]	0.13 (86)	1.5 (−59)	0.013 (99)	0.41 (59)

[a]Wet period August–November.
[b]Wet period April–July.
Percentage removed is given in parentheses.

to P removal through microbial assimilation. Furthermore, vegetation improves soil structure, which provides resilience to cracking and the formation of preferential flow pathways during dry periods. The SZ was also found to have a significant influence on P removal (TP and PO_4^{3-}). Inclusion of the SZ reduced the infiltration rate by decreasing the hydraulic head, effectively creating a buffer to high-velocity flow, thereby minimising mobilisation of P-laden particles into the effluent. Retention of stormwater in the SZ also increases detention time between dosing events, allowing P to undergo further biological uptake and chemical complexation. The sustained PO_4^{3-} removal throughout the campaign suggests that biodegradation of the carbon source did not contribute to P leaching and that reduction of Fe-bound P in the filter media did not occur.

Nitrogen removal performance of alternative biofilter designs

The influence of filter media

TN removal trends were similar for LS-V-S and SS-V-S throughout the campaign, although concentrations were consistently lower from the SS-V-S configuration (see Figure 3). ANOVA confirmed this, indicating a significant difference in TN and NH_3 removal between LS-V-S and SS-V-S ($p <$ 0.001). This may be attributed to greater adsorption of ionised ammonia (NH_4^+) in the Skye sand filter medium, which has a higher clay content than loamy sand. Filter medium type did not have a significant influence on NO_x removal, as was discussed in relation to PO_4^{3-}, and this is not surprising, given that NO_x removal is chemically and biologically driven. The very low TN and NO_x concentrations recorded in May (following clogging of the columns) highlights the sensitivity of these systems to changes in hydraulic conductivity and emphasises the influence of detention time on treatment performance. While the clogging may appear to have been beneficial for N treatment it is important to remember that under these conditions the biofilters were not operating within the infiltration rate guidelines of 200–400 mm/h.

Interactions with vegetation and SZ

Vegetation and the inclusion of an SZ had a significant influence on NO_x treatment (and subsequently TN). This was exemplified by the results for the non-vegetated (SS-NV-S) and non-saturated (SS-V-NS) configurations, which both showed poor NO_x removal throughout the experimental period (see Figure 3). Inclusion of vegetation supports biological removal pathways for NO_x captured from incoming stormwater and produced between events through nitrification. Mean DO concentrations in the SZ before (2.1 mg/L) and after (3.7 mg/L) dosing events indicated that conditions were not depleted to the point where denitrification would occur (<0.5 mg/L). However, it is nevertheless possible that anaerobic microsites exist within the SZ where denitrifying bacteria are active (Parkin 1987). The improved NO_x removal demonstrated in the SZ inclusive columns may also be explained by the extended detention time imposed between events, providing further opportunity for biological uptake to occur. NH_3 removal was not affected by the presence or absence of the SZ, presumably because it was retained or nitrified in the upper aerobic layers. However, given the important role which the SZ plays in NO_x removal, its inclusion is recommended to ensure effective overall N removal.

Resilience to variable inflow hydrology

Outflow concentrations from the biofilters during the three climate periods, wet[a] (October–November), dry (December–March), and wet[b] (April–July) are summarised in Table 3. Treatment performance for all nutrients remained relatively consistent between the periods in configurations inclusive of vegetation and SZ (i.e. LS-V-S and SS-V-S). TP concentrations from the SS-V-S columns increased marginally when wet dosing resumed. This was attributed to particulate P mobilisation upon re-wetting. TP concentrations returned to pre-rewetting concentrations in the next sample (June). Therefore, both filter media tested were found to be resilient over extended dry periods when coupled with vegetation and an SZ. The SZ supported nutrient-removal processes during the extended dry period by providing access to a permanent pool of water to sustain plant health, increasing detention time for biological removal processes to occur, and supporting hydro-chemical conditions to facilitate denitrification. The absence of vegetation had a persistent effect on NH_3 removal performance, which gradually declined over the dry and into the second wet period. The vegetated configurations show that NH_3 removal can otherwise be maintained throughout wet and dry periods, with or without the inclusion of an SZ. Vegetation provides a pathway for NH_3 removal under dry conditions, when biological processes slow down and limit nitrification. The impact of wetting and drying in the non-vegetated configuration (SS-NV-S) was most detrimental to NO_x removal (and consequently TN). NO_x removal was maintained over the extended dry period when increased retention time allowed the SZ to become anaerobic and promote denitrification. Extended detention also facilitated advanced biological uptake of NO_x. When regular dosing resumed, the non-vegetated systems responded immediately and began to leach NO_x, which continued for the remainder of the experiment. This suggests that NO_x removal can be maintained over dry periods in non-vegetated SZ inclusive columns, but when dosing frequency increases, oxygen conditions change and detention time in the SZ is reduced, compromising NO_x treatment. Conversely, very good NO_x removal was maintained in the LS-V-S and SS-V-S configurations (>80% removal). This highlights the role of biological uptake in N removal and the importance of coupling vegetation with the inclusion of an SZ.

Performance relative to ecosystem protection guidelines

Table 4 summarises biofilter performance relative to typical Australian and New Zealand receiving water nutrient guideline concentrations (ANZECC & ARMCANZ 2000). TP concentrations less than or equal to the guideline targets were successfully achieved by the SS-V-S and LS-V-S columns throughout the experiment. At the time of the last sampling event all configurations were meeting the TP water quality guideline concentrations. All configurations maintained PO_4^{3-} concentrations below the guideline throughout the experiment. TN concentrations were maintained below guidelines throughout the experiment by the SS-V-S columns. Minimal variation between SS-V-S replicates and consistent results over the sampling events represents a success as studies often cite variability in this regard. LS-V-S outflows also remained close to the TN target concentration, increasing only marginally during the transition into the dry climate. Conversely, TN concentrations from the non-vegetated (SS-NV-S) and non-saturated (SS-V-NS) configurations remained above the guideline for the duration of the experiment. Similar trends were apparent in terms of NO_x removal, although only the SS-V-S configuration achieved the target values. The non-vegetated columns (SS-NV-S) did not achieve the NH_3 targets, although the non-saturated, vegetated configuration (SS-V-NS) achieved this target consistently. The SS-V-S and LS-V-S began to meet the NH_3 target concentration halfway through the experiment, most likely coinciding with the growth of plant roots into the SZ where trapped NH_3 could be accessed.

Table 4 | Summary of success in achieving Australian and New Zealand Environment Conservation Council water quality guideline concentrations (based on trigger guideline values for lowland rivers) (ANZECC & ARMCANZ 2000)

Column	TP	PO_4^{3-}	TN	NO_x	NH_3
LS-V-S	✓	✓	✓	✗	✓
SS-NV-S	✓	✓	✗	✗	✗
SS-V-S	✓	✓	✓	✓	✓
SS-V-NS	✓	✓	✗	✗	✓

CONCLUSIONS

This study investigated nutrient removal performance of biofilter columns under the influence of design modifications (filter media type, vegetation and SZ) and variable climate conditions. The results demonstrated that a vegetated biofilter configured with Skye sand and an SZ can maintain very good N and P removal, and achieve receiving water protection targets in wet and dry climates. The importance of vegetation and an SZ to maintain co-optimised N and P removal under variable climate conditions was also highlighted. However, this experiment was undertaken over a relatively short time period, during which the plants experienced substantial growth. The nutrient removal performance exhibited by these biofilter columns should therefore be verified by research quantifying N and P removal performance as system establishment stabilises and as filter media approach P saturation. In practice, these results may have significant relevance when designing biofilters in areas which experience prolonged dry periods, or where the protection of receiving waters is a priority.

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Co-optimisation of Phosphorus and Nitrogen Removal in Stormwater Biofilters: the Role of Filter Media, Vegetation and Saturated Zone

La co-optimisation du rendement épuratoire de l'azote et phosphore dans les biofiltres; le rôle du matériau filtrant, de la végétation et de la zone saturée

Bonnie J Glaister[1], Tim D Fletcher[2], Perran L M Cook[3], Belinda E Hatt[1]

[1] Department of Civil Engineering, Monash University, Clayton, Victoria, 3800, Australia (bonnie.glaister@monash.edu; belinda.hatt@monash.edu)
[2] Department of Resources Mgt & Geography, The University of Melbourne, Burnley, Victoria, 3121, Australia (tim.fletcher@unimelb.edu.au)
[3] Water Studies Centre, Monash University, Clayton, Victoria, 3800, Australia (perran.cook@monash.edu)

RÉSUMÉ

La performance des biofiltres en termes de de traitement des nutriments est encore mitigée, atteignant rarement le niveau recommandé pour la protection des milieux aquatiques. Par ailleurs, la conception des biofiltres n'est généralement pas optimisée pour le double traitement de l'azote et du phosphore. Cette étude a pour objectif de mesurer l'influence de trois paramètres de conception, le matériau filtrant, la végétation et la présence d'une zone saturée, sur le traitement des nutriments par les systèmes de biofiltration. Nous présentons les résultats d'une expérience réalisée sur 20 colonnes pendant une année, ayant alterné la fréquence de dosage afin d'examiner l'impact des variations climatiques. Un très haut niveau de traitement a été démontré pour une configuration incluant de la végétation, une zone saturée, et un matériau filtrant novateur riche en oxyde métallique. La réduction en concentration des nutriments dans les effluents était conforme aux recommandations locales, et ce pendant tout la durée de l'expérience, indiquant une résilience à la variabilité climatique. Les résultats ont également démontré le rôle de la zone saturée, permettant le maintien des conditions de traitement pendant les périodes de sècheresse. Les résultats de cette étude représentent un progrès important vers une conception des biofiltres explicitement pour la protection des milieux aquatiques.

ABSTRACT

Biofilters have been shown to effectively treat stormwater to achieve nutrient load reduction targets. However, effluent concentrations typically exceed nitrogen and phosphorus targets for receiving water protection. This study investigates the influence of filter media, vegetation and a saturated zone on nutrient removal in biofilters, in order to co-optimise nitrogen and phosphorus removal. Twenty biofilter columns were monitored over 12 months; dosed with semi-synthetic stormwater. The frequency of dosing was altered seasonally to examine the impact of climate variability. Very good nutrient removal could be achieved by incorporating vegetation, a saturated zone and a novel metal-oxide rich filter media. This design maintained nutrient removal at or below water quality guideline concentrations throughout the experiment, demonstrating resilience to climate fluctuations. The results also highlighted the benefit a saturated zone in order to maintain treatment performance over extended dry periods. These findings represent significant progress towards designing biofilters which can meet the water quality concentration requirements of receiving waters.

KEYWORDS Biofilter, Nitrogen, Phosphorus, Stormwater, Saturated Zone

1. INTRODUCTION

Urban stormwater runoff has a significant impact on the health and ecological function of receiving waters (Walsh et al., 2004). Discharge of nutrient-rich stormwater into waterways can be particularly detrimental, leading to algal bloom proliferation, dissolved oxygen depletion and biodiversity loss (Duncan, 1999, Kadlec and Knight, 1996). Stormwater biofilters (also known as biofiltration systems, bioretention systems or raingardens) have the potential to reduce this impact.

Extensive laboratory testing has demonstrated the effectiveness of biofilters to remove nitrogen and phosphorus from urban stormwater, confirming that these systems reliably meet load reduction targets for total suspended solids and nutrients (TSS 80%, TP 45%, and TN 45% in Victoria, Australia). However, nitrogen removal rates are variable and may compete with phosphorus removal. Furthermore, the concentrations to which TN and TP are reduced exceed typical environmental protection guidelines, and thus may still pose a threat to receiving waters. In order to provide effective protection for receiving waters, biofilters must be co-optimised for nitrogen and phosphorus removal, and able to achieve concentrations below typical environmental protection guidelines.

The efficacy of biofilter processes is significantly influenced by the physico-chemical properties of the filter media, hydrochemical characteristics of the biofilter, and hydrologic flow regime. The importance of biological interactions (e.g. plant uptake), in particular for nitrogen removal, has been demonstrated by several studies (e.g Bratieres et al., 2008). The importance of plant selection and the influence of competition and planting regime on performance have all been tested (Ellerton, 2012, Read et al., 2008, Read et al., 2010). Australian biofiltration design guidelines also recommend inclusion of a saturated zone (see FAWB, 2009a). The saturated zone design modification has demonstrated very good results for nitrogen removal (Kim et al., 2003, Davis et al., 2009), in particular nitrate, while also protecting biofilters against drying during dry weather periods (Blecken et al., 2009, FAWB, 2009a).

While the role of biological interactions has been demonstrated, our knowledge of the role of filter media in facilitating long-term nutrient removal, in particular phosphorus, remains limited and somewhat contradictory. Henderson et al. (2007a, 2007b) argue that filter media is unlikely to retain nutrients in the long-term, however, it may provide an important function by extending retention time so plant uptake and microbial assimilation can occur. Others have suggested that filter media could enable complex phosphorus sorption and precipitation processes through interactions with phosphorus attracting ions (i.e. Fe, Al), which may strongly, or even permanently, bind phosphorus to the filter media (e.g. Arias et al., 2001, Del Bubba et al., 2003). The results of a recent study by Glaister et al. (2011a) found that a natural metal-oxide coated filter media, demonstrated better phosphorus removal and retention than the typical loamy sand filter media. These findings however are yet to be validated by a large-scale study.

The present study investigated the nutrient removal performance of biofilters configured with a traditional loamy sand filter media and a novel metal-oxide coated sand filter media, known as Skye sand. The Skye sand was tested in conjunction with and without design modifications shown to improve nutrient removal (vegetation and saturated zone). Climatic variability was imposed during the experiment to evaluate the influence of drying and wetting on filter media durability and treatment performance. The main objective of the study was to develop a biofilter design, co-optimised for nitrogen and phosphorus removal, and capable of achieving effluent concentrations below typical environmental protection guidelines. This study also aimed to improve our understanding of the role of filter media and saturated zones in biofilters, particularly in relation to resilience over extended dry periods. The results demonstrate that biofilters configured with Skye sand, vegetation and a saturated zone can maintain nutrient removal at or below water quality guideline concentrations in wet and dry climates. The results also revealed that vegetation and saturated zone play a crucial role in achieving co-optimisation of nitrogen and phosphorus removal. These findings represent significant progress towards co-optimising nutrient removal in stormwater biofilters and achieving environmental protection objectives.

2. METHOD

2.1. Experimental set-up

2.1.1. Column construction & filter media selection

Twenty biofilter columns (Figure 2.1a) were constructed to compare nutrient removal performance and durability of two filter media, under the influence of design modifications (vegetation and saturated zone) and variable climate conditions. The columns were designed in accordance with Australian biofiltration system guidelines (see FAWB, 2009a). The columns were constructed using PVC pipe (150mm diameter) and Perspex to create a 200mm ponding zone. The saturated zone columns were modified by attaching a riser pipe (300mm) to the outlet tap in order to maintain a constant head at this depth. Sampling ports were drilled at 70mm intervals across the saturated zone to monitor dissolved oxygen concentrations. The filter media selected were, locally sourced and consistent with biofiltration soil guidelines (FAWB, 2009a). The filter media was configured into four main layers (see Figure 2.1b):

1. Filter medium (300mm): Loamy sand or Skye sand planted with *Carex appressa*;
2. Sand transition layer (200mm): Coarse washed sand;
3. Pea gravel drainage layer (70mm);
4. Gravel drainage layer (30mm).

Figure 2.1. (a) Experimental set-up of columns in greenhouse (b) Schematic diagram of the biofilter columns (with saturated zone riser outlet attached)

Loamy sand is the filter media currently recommended by Australian biofiltration system guidelines (FAWB, 2009a). Previous biofilter column studies have demonstrated that loamy sand provides effective removal of both TN and TP when coupled with vegetation (Bratieres et al., 2008, Henderson et al., 2007a). However, reported effluent concentrations of these nutrients are near or above typical Australian receiving water guidelines (ANZECC & ARMCANZ, 2000). Testing of this media with a saturated zone also produced good results, demonstrating that loamy sand can maintain nitrogen removal during dry periods (Zinger et al., 2007a). In this study, loamy sand acted as a control against which the novel Skye sand media could be compared. Skye sand, a red coloured quartz sand from Skye, Victoria (Australia) has a natural coating of metal-oxides (iron and aluminium oxides and hydroxides; Table 2.1). Its has demonstrated a strong affinity for phosphate removal under simple laboratory testing (Glaister et al., 2011a), but this experiment investigates Skye sand under quasi-realistic hydrologic conditions and in conjunction with typical biofilter design features.

Table 2.1. Chemical characterisation of loamy sand and Skye sand filter media

Media	Fe*	Al*	Mn*	Ca*	Mg*	Fe_2O_3#	Al_2O_3#	SiO_2#
Loamy Sand	1183 (±320)	940 (±269)	<5	63 (±15)	<50	0.21	0.58	99.24
Skye Sand	13245 (±9402)	1640 (±717)	9 (±8)	<50	59 (±40)	1.77	2.15	94.44

*Analysed using ICP-OES (n=4) (mg/kg), #Analysed using XRF (%w/w)

2.1.2. Carbon source selection

Between stormwater dosing events water in the saturated zone becomes depleted of dissolved oxygen, thereby providing an anaerobic environment which promotes denitrification. Adding organic matter to the saturated zone provides a carbon source to facilitate the denitrification process. However, care must be taken when configuring the saturated zone, as a P-rich carbon source may cause P leaching, particularly if reducing conditions lead to the release of phosphorus from sorption sites (e.g. iron-phosphates) (Jansson, 1987). With respect to these issues, pine woodchips (bark removed) and pine flour ('sawdust') were determined to be the best available carbon sources, on the basis of their biodegradability and low phosphorus content (10.2 mg P/kg). A mixture of pine woodchips (26.5g) and pine flour (9.3g) was blended into the coarse sand layer of the saturated zone (total material added was equivalent to 5% of the volume of the saturated zone).

2.1.3. Column configuration

Four design configurations were tested (five replicates of each), as described in Table 2.2. Filter media in layers 2, 3 and 4 remain constant between configurations.

Table 2.2. Biofilter column design configurations

Configuration	Filter Medium	Vegetation	Saturated Zone
LS-V-S	Loamy Sand	*Carex Appressa*	SZ
SS-NV-S	Skye Sand	Non-vegetated	SZ
SS-V-S	Skye Sand	*Carex Appressa*	SZ
SS-V-NS	Skye Sand	*Carex Appressa*	No SZ

These configurations enabled three key relationships between design characteristics to be analysed:
1) **Loamy** Sand vs. **Skye** sand: vegetated with SZ
2) Skye Sand: **non-vegetated** with SZ vs. Skye sand: **vegetated** with SZ, and;
3) Skye Sand: vegetated **with** SZ vs. Skye sand: vegetated **without** SZ

2.1.4. Column establishment

The columns were filled manually by measuring the required amount of media for each layer (volume and weight) then compacted using a weighted hammer dropped from 100mm onto the surface of the media (as described by ASTM Standard F 1815 – 06, Standard Test Method for Specific Gravity of Soils). The compaction required was determined by the layer thickness and media porosity. Once filled, vegetation was transplanted into the top 100mm of the vegetated columns. The Australian native species *Carex appressa* was selected for this study because of its drought tolerance and resilience to climate fluctuations. Previous biofilter column studies have found that this species maintains very good nutrient removal under high loading conditions and inflow concentrations (Bratieres et al., 2008, Read et al., 2008). Prior to transplanting into the columns the plants were matured in a glasshouse (at 25°C) for 12 weeks. Following transplantation, columns were dosed twice-weekly with semi-synthetic stormwater, to help establish the plants, inoculate the soil microbial community and flush free particles from the filter media. Five weeks after dosing commenced the first sampling event occurred.

2.2. Experimental procedure

2.2.1. Semi-synthetic stormwater

Due to limitations associated with the collection of a real stormwater a semi-synthetic stormwater mixture was used instead. This approach minimised inflow concentration variability whilst maintaining realistic composition. Several studies have adopted this method and demonstrated consistency in maintaining target concentrations throughout the experimental period (e.g. Blecken et al., 2010, Bratieres et al., 2008, Hatt et al., 2007b). Sediment was collected from a nearby stormwater retarding basin and strained through a 1000µm sieve. The concentration of solids in the sieved slurry was measured prior to mixing with a known amount of dechlorinated tap water to ensure the target total suspended solids (TSS) concentration was achieved. Target concentrations for TSS and nutrients were matched with ‘typical’ values for worldwide and Melbourne urban stormwater quality reported by Duncan (1999) and Taylor et al. (2005) respectively. To make up the deficit in nutrient concentrations where necessary the mixture was topped up using chemicals.

2.2.2. Stormwater dosing, sampling & analysis

The stormwater dosing regime over the twelve month period reflected Melbourne average annual rainfall volumes, for a biofilter sized to 2.5% of its contributing catchment area, based on Australian design guidelines (see Hatt et al., 2007b). The columns received 3.7L of stormwater during each dosing event (delivered in two applications of 1.85L). During application the stormwater was constantly stirred to ensure even distribution of suspended solids and maintain dissolved oxygen saturation. The dosing campaign simulated “wet” and “dry” climate conditions by altering the frequency of events (see Figure 2.2). Each climate reflected typical Melbourne rainfall patterns (Bureau of Meteorology, 2011). During the “wet” periods (April - November) the columns were dosed twice-weekly. During the “dry” (December - March) the column dosing transitioned from 6 to 18 antecedent dry days. Transitioning gradually from wet to very dry conditions was necessary to reduce the risk of plant fatality.

Sampling of the biofilter columns took place for 10 select dosing events over the 12 month period from August 2011 to July 2012 (Figure 2.2). Following dosing, samples were collected from the column outlet until flow ceased (approximately 3 of the 3.7 L). This bulk sample was mixed thoroughly then subsampled for analysis. Samples were analysed for total nitrogen (TN), total phosphorus (TP) and their dissolved species. Samples analysed for dissolved nutrients were filtered through a 0.45µm filter (Bonnet Scientific). All water chemical analyses were undertaken by NATA (National Association for Testing Authorities) certified laboratories using standard analysis methods (APHA/AWWA/WPCF, 1998). Discrete water samples were collected through ports in the saturated zone and analysed for dissolved oxygen (DO) using a DO probe (Hach Company).

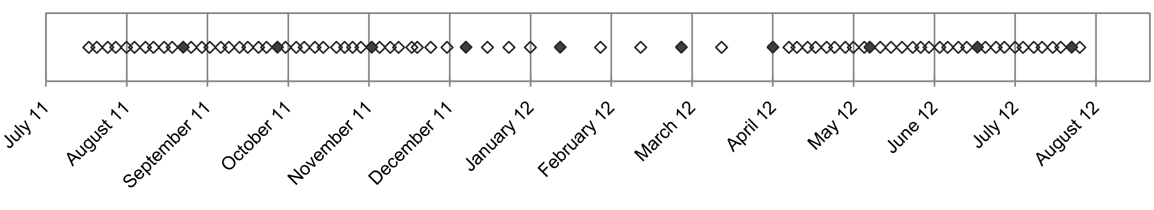

Figure 2.2. Stormwater dosing and sampling regime (filled markers denote sampled events).

2.2.3. Data analysis

All statistical analyses were performed using SPSS (version 20. IBM, USA). ANOVA was used to compare performance between biofilter configurations and climate periods, with post-hoc tests used to compare individual pairs (Tukey's HSD where inequality of variance occurred and Tamhane's where not). Data reported below limits (e.g. <0.001) were analysed at half the LOR value (e.g. 0.0005). Data from the first sample event (September) were omitted from the analysis because the columns were still establishing. Additionally, sample data from the SS-V-NS columns were omitted for the eighth event (May), as infiltration had ceased due to sediment clogging of the surface layer. This sediment layer was disturbed manually by gently scraping the surface, allowing regular infiltration to resume.

3. RESULTS AND DISCUSSION

3.1. Phosphorus removal performance of alternative biofilter designs

3.1.1. The influence of filter media

Total phosphorus (TP) outflow concentrations from the loamy sand (LS-V-S) and Skye sand (SS-V-S) columns were not significantly different (Figure 3.1). This suggests that modifying the filter media did not greatly influence TP removal performance. Only once did the trend deviate, after the wet period was resumed in May, when TP concentrations from the SS-V-S columns increased marginally. This was most likely attributable to particulate phosphorus mobilisation upon re-wetting, since phosphate (PO_4^{3-}) removal was not affected, and concentrations returned to pre-rewetting values in the next sample (June). Very good removal of PO_4^{3-} was maintained for all configurations throughout the experiment (>96%) (see Table 3.1). Similarly TP, PO_4^{3-} removal did not differ significantly between the loamy sand (LS-V-S) and Skye sand (SS-V-S) columns, meaning that removal performance is not attributed to the metal-oxide coated filter media. Notwithstanding, the role of filter media may become more important later in the biofilter lifetime, when plants reach maturity and when availability of sorption sites decline as filter media reaches the equilibrium concentration (Henderson et al., 2007b).

3.1.2. Interactions with vegetation and saturated zone

The presence of vegetation had a significant effect on PO_4^{3-} removal ($p<0.001$) but not TP. This is perhaps not surprising, given that PO_4^{3-} is chemically and biologically driven, while TP removal is primarily related to removal of total suspended solids (TSS), which account for ~70% of TP (Duncan, 1999). Vegetation provides a removal pathway for dissolved nutrients through plant uptake, and supports biological activity in the rhizosphere, which also contributes to PO_4^{3-} removal through microbial assimilation. Furthermore, vegetation improves soil structure, which provides resilience to cracking and the formation of preferential flow pathways during dry periods. For these reasons, vegetation may have important secondary effects on TP removal, and should not be overlooked. The saturated zone (SZ) design modification was also found to have a significant influence on phosphorus removal (TP and PO_4^{3-}). Inclusion of the SZ reduces the infiltration rate by decreasing the hydraulic head, effectively creating a buffer to high velocity flow, thereby reducing the risk of phosphorus laden particle mobilisation. Furthermore, retention of stormwater in the SZ increases detention time between dosing events, allowing the stormwater to undergo advanced treatment through biological removal processes. The sustained efficacy of PO_4^{3-} removal suggests that biodegradation of the SZ carbon source has not contributed to phosphorus leaching. Moreover, this continued removal performance implies that reduction of iron-phosphates, which may have become a concern if complexes formed in the filter media migrated into the oxygen depleted SZ, has not occurred.

3.2. Nitrogen removal performance of alternative biofilter designs

Analysis of total nitrogen outflow concentrations indicates that there is significant difference between all biofilter configurations for TN removal. This suggests that design modifications play an important role in facilitating nitrogen removal. Figure 3.1 shows the TN outflow concentrations for each biofilter configuration over the experimental period.

3.2.1. The influence of filter media

Total nitrogen removal trends are similar for LS-V-S and SS-V-S throughout all sample events, although concentrations are consistently lower from the SS-V-S configuration (Figure 3.1). An analysis of variance confirmed this, indicating that there is a significant difference between the LS-V-S and SS-V-S for TN and ammonia (NH_3). The variation in treatment between these filter media may relate to a number of factors. Firstly, Skye sand has a large portion of very fine particles (20% of total volume <1.2μm) and this portion is much less in loamy sand (10% of total volume <100μm), potentially resulting in an improved capacity for Skye sand to remove TSS and thus sediment bound nutrients. The superior performance of Skye sand may also be attributed to the lower organic matter content of the filter medium, reducing the likelihood of nitrogen leaching, especially following an extended dry period. Additionally, while the organic content of loamy sand may provide better conditions for microbial population growth, supporting bioremediation processes, it may over long dry periods cause lysis, and result in an efflux of nutrients from the system (Zinger, 2012).

3.2.2. Interactions with vegetation and saturated zone

While the influence of filter media was significant for TN and NH_3 this was not the case for NO_x. This indicates that processes relating to filter media are not governing NO_x removal. However, both vegetation and saturated zone modification do have a significant influence on NO_x (and subsequently TN). This is exemplified by the results for the non-vegetated (SS-NV-S) and non-saturated (SS-V-NS) configurations. These these columns showed poor NO_x removal, compared to those with the combined vegetated, saturated zone design, continued throughout the experimental period. These results imply that vegetation and saturated zone are most important in NO_x removal. Vegetation also had a significant effect on ammonia (NH_3) treatment. This result once more highlights the importance of plant-uptake to remove dissolved nutrient species, and suggests that this is the main pathway for their removal. However, nitrification is also important. This was demonstrated by the excellent removal maintained by the vegetated, non-saturated configuration (SS-V-NS) throughout the experiment. While coupling plant-uptake and aerobic conditions provided optimal conditions for NH_3 removal, the results suggest that NH_3 removal was not significantly affected by the presence of a SZ. Indeed, even with the inclusion of a saturated zone very good NH_3 removal was maintained (see Figure 3.1). Therefore, to achieve overall nitrogen removal optimisation a saturated zone modification would be recommended.

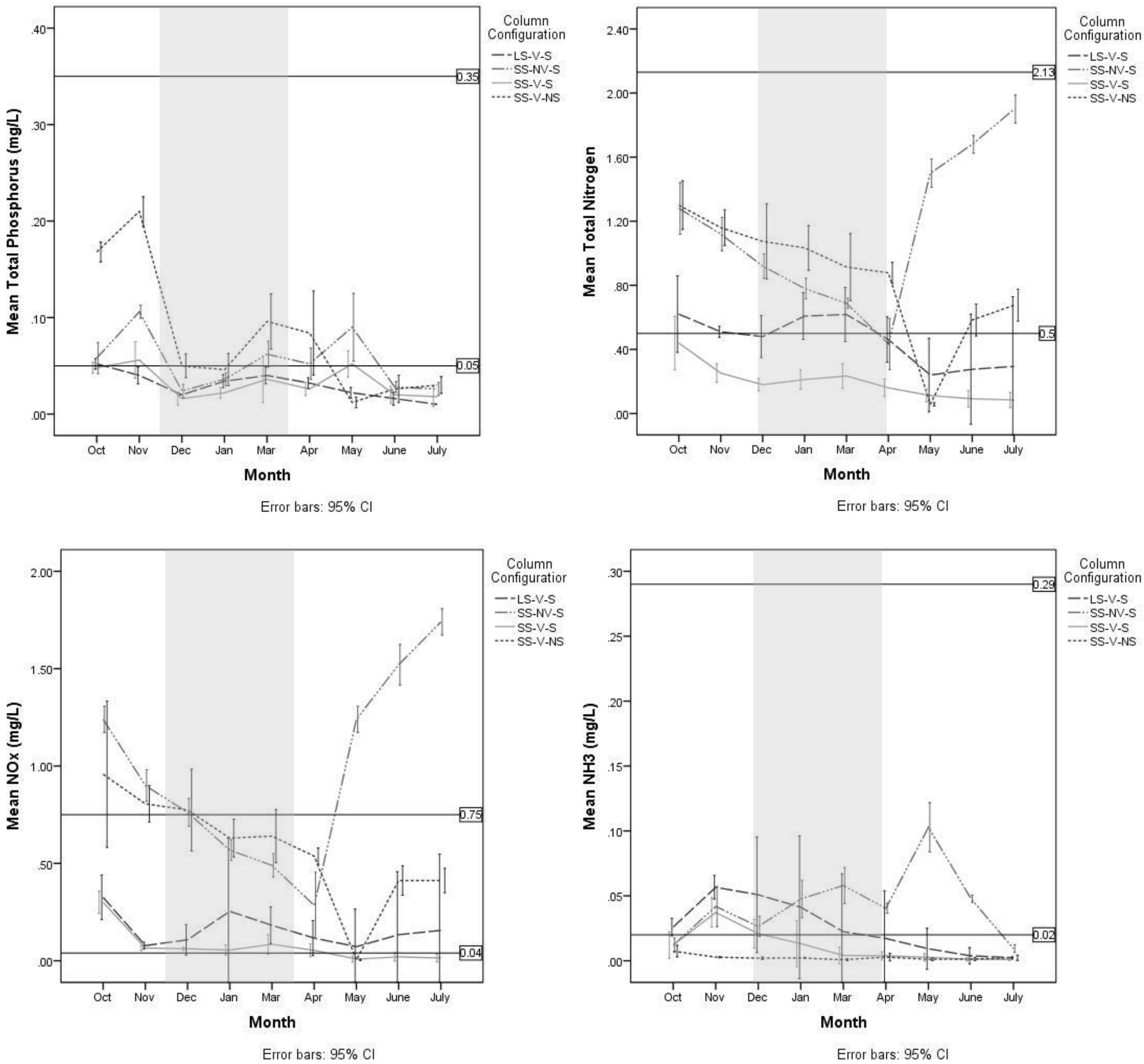

Figure 3.1. Biofilter column outflow concentrations (mg/L): total phosphorus (top left); total nitrogen (top right); nitrous oxides (NO_x) (bottom left); and ammonia (NH_3) (bottom right); from October 2011 to July 2012. Data points represent the mean (n=5) and error bars cover the 95% confidence interval. Upper reference line represents the inflow concentration; lower reference line represents typical Australian water quality target concentrations. Shaded area represents the dry dosing period. Note that the May results for SS-V-NS were omitted from data analysis due to system clogging.

3.2.3. Resilience to changing climate conditions

Outflow concentration from the four design configurations are summarised in Table 3.1, for the three climate periods: Wet[1] (October-November); Dry (December-April), and; Wet[2] (May-July). Treatment performance for all nutrients remained relatively consistent between the wet and dry periods in configurations inclusive of vegetation and saturated zones (i.e. LS-V-S and SS-V-S). Therefore, both filter media tested (loamy sand and Skye sand) were found to be resilient over extended dry periods when coupled with vegetation and a saturated zone. Nutrient removal processes are supported in the saturated zone by: providing access to a permanent pool of water to sustain plant health (especially during extended dry periods); increasing detention time for biological removal processes to occur, and; providing hydro-chemical conditions to facilitate nitrogen removal through denitrification. These benefits are all demonstrated by the results shown here over the three dosing periods.

Table 3.1 Average outflow phosphorus concentrations for wet and dry dosing periods (mg/L). Percent removal is given in parentheses.

	TP			PO_4^{-3}		
	Wet[1]	**Dry**	**Wet[2]**	**Wet[1]**	**Dry**	**Wet[2]**
LS-V-S	0.046 (88)	0.032 (92)	0.016 (95)	0.003 (99)	0.002 (99)	0.002 (98)
SS-NV-S	0.082 (79)	0.044 (89)	0.048 (86)	0.002 (99)	0.003 (98)	0.002 (97)
SS-V-S	0.052 (87)	0.025 (93)	0.030 (91)	0.002 (99)	0.003 (99)	0.001 (98)
SS-V-NS	0.189 (52)	0.069 (82)	0.028 (92)	0.004 (98)	0.003 (98)	0.003 (98)

	TN			NO_X			NH_3		
	Wet[1]	**Dry**	**Wet[2]**	**Wet[1]**	**Dry**	**Wet[2]**	**Wet[1]**	**Dry**	**Wet[2]**
LS-V-S	0.560 (70)	0.542 (69)	0.270 (85)	0.202 (80)	0.165 (81)	0.134 (86)	0.041 (89)	0.037 (88)	0.005 (99)
SS-NV-S	1.20 (35)	0.706 (60)	1.69 (8)	1.07 (-10)	0.526 (41)	1.50 (-59)	0.027 (93)	0.043 (84)	0.053 (85)
SS-V-S	0.338 (82)	0.196 (89)	0.096 (95)	0.183 (81)	0.064 (93)	0.013 (99)	0.026 (93)	0.012 (96)	0.002 (99)
SS-V-NS	1.23 (33)	0.975 (44)	0.63 (66)	0.882 (9)	0.645 (27)	0.412 (59)	0.005 (99)	0.002 (99)	0.001 (100)

Without vegetation (SS-NV-S), TP, TN, NH_3 and NO_x removal responded poorly to changing climate, revealing the importance of plant uptake in long-term nutrient removal, despite modification with a saturated zone to facilitate denitrification. The impact of twice weekly dosing resumption after four months of dry was minor and only temporary for TP, suggesting that any preferential flows which may have formed during dry periods disappear soon after dosing resumes. The absence of vegetation had a more persistent effect on NH_3 removal, which gradually declined over the dry and into the second wet period. The vegetated columns show that NH_3 removal can otherwise be maintained throughout the wet and dry periods. Including vegetation provides a pathway for removal under dry conditions when biological processes slow down, and NH_3 removal through nitrification is limited. When inflow is frequent, especially following an extended dry period, complete removal through nitrification may not necessarily occur; once again vegetation provides a pathway for removal.

The impact of wetting and drying in the non-vegetated configurations (SS-NV-S) was most detrimental to NO_x removal and (and consequently TN). When twice-weekly dosing resumed after the dry period the non-vegetated systems responded immediately and began to leach NO_x which continued for the remainder of the experiment. This suggests that while NO_x removal can be maintained over the dry period through denitrification, when dosing is infrequent and dissolved oxygen (DO) levels in the saturated zone deplete to anoxic concentrations, once dosing frequency increases the SZ no longer has the retention time necessary for DO levels to reduce and denitrification reactions to complete, confirming the importance of providing a source of plant uptake for nitrogen.

3.2.4. Performance relative to ecosystem protection guidelines

Table 3.2 summarises biofilter performance relative to typical Australian nutrient guideline concentrations (ANZECC & ARMCANZ, 2000). TP concentrations less than or equal to the guideline targets were successfully achieved by the SS-V-S and LS-V-S columns throughout the experiment. Results from the non-saturated (SS-V-NS) and non-vegetated (SS-NV-S) columns fluctuated around the target, although, at time of the last sample all configurations were meeting TP guideline concentrations. All configurations maintained PO_4^{-3} concentrations below the guideline throughout the experiment. This most likely relates to the age of the systems, and may change as the biofilters mature, and the role of filter media becomes more critical. TN concentrations were maintained below guidelines throughout the experiment by the SS-V-S columns. The minimal variation between the SS-V-S replicates and consistent results over the sampling events represents a success as studies often cite variability in this regard. The LS-V-S outflows also remained close to the TN target concentration, increasing only marginally during the transition into the dry climate. Conversely, TN concentrations from the non-vegetated (SS-NV-S) and non-saturated (SS-V-NS) configurations remained above the guideline for the duration of the experiment. Similar trends were apparent in terms of NO_x removal although only SS-V-S achieved the target values. The non-vegetated columns (SS-NV-S) were not very successful in achieving the NH_3 targets, however, the non-saturated, vegetated configuration (SS-V-NS) achieved this target consistently. The saturated, vegetated configurations (SS-V-S, LS-V-S), began to meet the NH_3 target concentration roughly halfway through the experiment. This most likely coincided with growth of the plant roots into the saturated zone where trapped NH_3 could be accessed.

Table 3.2. Summary of success in achieving typical ANZECC water quality guideline concentrations.

Column	TP	PO_4^{-3}	TN	NO_x	NH_3
LS-V-S	✓	✓	✓	×	✓
SS-NV-S	✓	✓	×	×	×
SS-V-S	✓	✓	✓	✓	✓
SS-V-NS	✓	✓	×	×	✓

4. CONCLUSIONS

This study compared nutrient removal performance and durability of two filter media, under the influence of design modifications (vegetation and saturated zone) and variable climate conditions. The main objective of the study was to develop a biofilter design, co-optimised for nitrogen and phosphorus removal, and capable of achieving effluent concentrations below typical environmental protection guidelines. The results achieved this, by demonstrating that a vegetated biofilter configured with Skye sand and a saturated zone can maintain very good removal of nitrogen and phosphorus concentrations, and achieve receiving water protection targets in wet and dry climates. The role of vegetation and a submerged zone in maintaining nitrogen removal under variable climate conditions was also highlighted in the results. Further research is necessary to gain a better understanding of role of filter media, particularly in relation to phosphorus removal, as biofilters mature. In practice, these results may have a significant impact when designing biofilters in areas where prolonged dry periods are common, and when protection of receiving waters is a priority.

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Intra-event nutrient removal dynamics in stormwater biofilters: the influence of system design

Les dynamiques intra-événementielles de l'abattement des nutriments dans des biofiltres ; l'influence de la conception

Bonnie J. Glaister[1], Tim D. Fletcher[2], Perran L. M. Cook[3] and Belinda E. Hatt[1]

[1] CRC for Water Sensitive Cities, Monash University, Australia (bonnie.glaister@monash.edu; belinda.hatt@monash.edu)

[2] Waterway Ecosystem Research Group, the University of Melbourne, Australia (timf@unimelb.edu.au)

[3] CRC for Water Sensitive Cities, Monash University, Australia (perran.cook@monash.edu)

RÉSUMÉ

Le rendement épuratoire d'un ouvrage de biofiltration est normalement calculé en termes de la concentration moyenne évènementielle (CME). Par conséquent, la variation temporelle du traitement et le rôle des facteurs de conception sur cette variation sont encore peu connus. Nous avons donc mené une étude en laboratoire afin de mieux comprendre l'effet des paramètres de conception (substrat, végétal et présence ou non d'une zone saturée) et les conditions de fonctionnement sur les concentrations de nutriments rejetées par des biofiltres. Les résultats montrent que la présence du végétal et d'une zone saturée améliorent le rendement épuratoire du système, et réduisent la variation temporelle des concentrations. La zone saturée est également primordiale pour minimiser le flux des matières en suspension (et les nutriments qui s'y trouvent). L'inclusion d'un sable riche en fer dans le substrat était capable de stabiliser le traitement de l'azote après des périodes sèches. La complexité du comportement de différentes espèces de nutriments met en évidence la difficulté d'optimiser un biofiltre pour tous types de polluant. Les résultats montrent que la performance d'un biofiltre dépende surtout du choix du substrat et du végétal et de la présence d'une zone saturée, mais que la même performance peut être atteinte avec un système simple sans drain.

ABSTRACT

Treatment performance of stormwater biofilters is typically reported as an event mean concentration. Consequently, little is currently understood about how pollutant removal fluctuates during events or how biofilter design features affect intra-event treatment. To investigate how design characteristics (filter media, vegetation and a saturated zone) and operational conditions influence intra-event nutrient removal nutrient concentrations from 20 laboratory-scale stormwater biofilter columns were monitored during two simulated rainfall events. The results demonstrate that inclusion of vegetation and a saturated zone enhances nitrogen removal and reduces intra-event treatment variability. Including a saturated zone also minimises mobilisation of particulate-bound nutrients. Nutrient species responded differently to changes in inflow volume and dry weather antecedence, making nutrient removal optimisation a challenge. Biofilters containing iron-rich filter media, 'Skye sand', exhibited greater intra-event nitrogen removal resilience following dry periods than loamy sand. These findings demonstrate that biofilters designed with appropriate filter media, vegetation and a saturated zone can satisfy nutrient treatment objectives with relatively good consistency during rainfall events, which is critical for biofilters servicing ecosystems sensitive to changes in nutrient concentrations. However, these objectives could perhaps be more easily achieved by constructing biofilters without an underdrain.

KEYWORDS

Biofilter, intra-event, nitrogen, phosphorus, saturated zone, Skye sand, stormwater

1. INTRODUCTION

Urban stormwater runoff has been shown to have a detrimental impact on the water quality and hydrology of receiving waterways (Walsh et al., 2005). Nutrient-rich stormwater poses a particularly severe threat to aquatic ecosystems, causing excessive plant growth, depleted oxygen concentrations and eutrophication (Smith et al., 1999). Biofiltration systems (also known as bioretention systems, biofilters, and rain gardens) are recognised as an effective technology for the interception and treatment of stormwater (Davis et al., 2009, Hatt et al., 2009). Previous laboratory and field-scale research has demonstrated that biofilters are capable of achieving effective and reliable phosphorus (P) removal (80-90%) (Davis et al., 2001). However, reported nitrogen (N) removal continues to be variable (Davis et al., 2006, Bratieres et al., 2008), particularly following dry weather periods (Zinger et al., 2007a, Hatt et al., 2007a).

Inter-event fluctuations in N removal and instances of N leaching have often been attributed to NO_x production within biofilters due to nitrification of retained ammonium (Cho et al., 2009, Hsieh et al., 2007). Maintaining robust nutrient treatment following dry periods is a critical objective for biofilters, particularly in semi-arid climates like Australia. Inclusion of suitable vegetation and a saturated zone has been shown to enhance N removal, diminish the effects of drying, and reduce inter-event N removal variability (Zinger et al., 2007b, Payne et al., 2014b, Glaister et al., 2014, Kim et al., 2003), but this is sometimes achieved to the detriment of P removal (Zinger et al., 2013). Further, reported effluent concentrations of total nitrogen (TN), total phosphorus (TP) and their dissolved species from biofilters typically exceed Australian water quality guideline trigger levels for aquatic ecosystem protection (ANZECC/ARMCANZ, 2000). Whether nutrient concentrations in biofilter effluent remain above guideline levels during part of or throughout events is unclear, since concentrations are typically reported in terms of an event mean concentration (EMC) (Davis, 2007). While this method provides a good overall estimation of mass load reduction, it does not give insight into the mechanisms that govern nutrient processing or how effluent concentrations fluctuate during events. Intra-event fluctuations in nutrient concentrations have the potential to significantly impact small streams or disturbed ecosystems that are sensitive to concentration changes. As such, determining the extent to which nutrient concentrations fluctuate during events is critical to designing biofilters that provide optimal nutrient processing and protection for urban waterways and predicting how changes in operational conditions influence treatment. Whilst monitoring of consecutive events has been used to examine the influence that previous events have on internal nutrient removal processes (Brown et al., 2013), studies monitoring intra-event fluctuations in nutrient removal are limited (Hatt et al., 2009, Davis, 2007). Moreover, the influence of biofilter design characteristics, such as a saturated zone, on intra-event nutrient removal behaviour is yet to be investigated.

2. METHODS

2.1. Biofilter column design

2.1.1. Column configuration

Four biofilter configurations were designed to compare nutrient removal performance between systems with different filter media, with and without vegetation (*Carex appressa*), and with and without inclusion of a saturated zone and carbon source (see Table 1). Two filter media were tested: loamy sand, currently recommended for use in biofilters (FAWB, 2009b), and ‘Skye sand’, a naturally occurring iron-coated sand. Previous testing has indicated that Skye sand has a greater capacity to adsorb dissolved P than loamy sand (Glaister et al., 2011b) and can achieve enhanced N removal in conjunction with vegetation and a saturated zone (Glaister et al., 2014).

Table 1 Biofilter column design configurations

Column ID	Filter Medium	Vegetation (Y/N)	Saturated Zone (Y/N)
LS-V-S	Loamy Sand	Y	Y
SS-V-S	Skye Sand	Y	Y
SS-NV-S	Skye Sand	N	Y
SS-V-NS	Skye Sand	Y	N

2.1.2. Column construction

Twenty biofilter columns, five replicates of each configuration, were constructed using PVC pipes (150mm x 600mm) joined to a transparent Perspex pipe to provide a 200mm ponding zone. The filter media (300mm) was underlain by a coarse washed sand transition zone (200mm) and pea gravel (70mm) and a gravel drainage layer (30mm). A cross section of the columns is shown in Figure 1. Effluent drained freely from the base outlets of the non-saturated columns while a riser pipe was attached to the outlet of those with a saturated zone to maintain a 300mm internal ponding zone in the lower part of the columns.

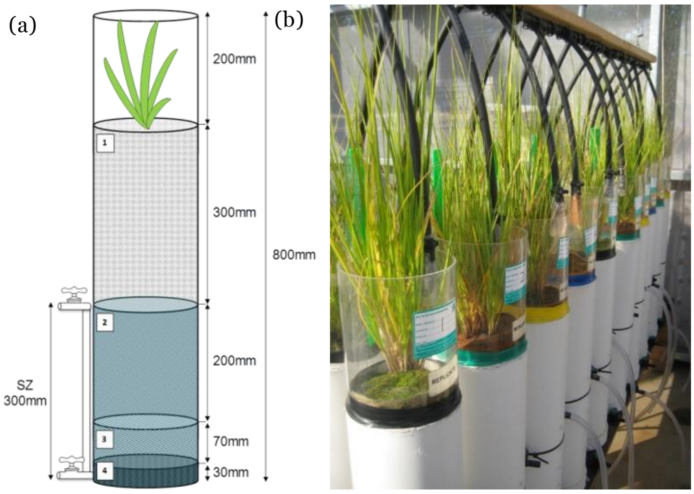

Figure 1 (a) Schematic diagram of the biofilter columns (with SZ rise outlet attached) and (b) experimental set-up of biofilter columns in greenhouse

2.2. Stormwater preparation, dosing and sampling

Because of the uncertainty and inconsistency associated with the use of natural stormwater, this study utilised methods described by prior studies (e.g. Glaister et al., 2014, Hatt et al., 2007b) to produce a semi-synthetic stormwater of a quality consistent with reported stormwater pollutant concentrations (Duncan, 1999, Taylor et al., 2005). Stormwater dosing occurred over a 12 month period with volumes designed to reflect rainfall received by a biofilter sized to 2.5% of its catchment area in Melbourne, Australia, where the annual effective rainfall is approximately 540mm. During the 12 month dosing period two sequential sampling experiments were conducted to measure intra-event nutrient concentration variability in biofilters' effluent. Samples were collected sequentially in order to capture the transition in biofilter effluent from 'old' stormwater retained in the system from the previous dosing to 'new', freshly applied stormwater. The first experiment took place in 8 months after column establishment following 18 antecedent dry days (ADD). This experiment utilised twenty biofilter columns (n=5) and represented a standard stormwater dosing volume (3.7L) equivalent to 5mm of rainfall (where the biofilter surface area represented 2.5% of its contributing catchment). Three consecutive effluent samples of approximately 1L were collected during the first experiment. The second experiment was conducted after 12 months of dosing and following 2 ADD. In this instance, 12 biofilter columns were sampled (n=3) after dosing with 7.4L of stormwater (representative of a 10mm rainfall event). At least 12 consecutive 500mL samples were collected from the columns, of which every second was analysed; approximately 6.0-6.5L of stormwater was recovered overall. This sampling regime enabled an event 'pollutograph' to be produced, providing greater insights into intra-event fluctuations in effluent nutrient concentrations.

2.3. Water quality testing and data analysis

The effluent samples were analysed for TP, TN, total dissolved phosphorus (TDP) and nitrogen (TDN), ammonia (NH_3), nitrate and nitrite (NO_x) and filterable reactive phosphorus (FRP) using flow injection analysis (Lachat, QuikChem® 8000). Concentrations of dissolved and particulate organic nitrogen (DON, PON) and particulate phosphorus (PP) were determined from these results. Samples for dissolved nutrient analysis were filtered immediately following collection (0.45µm Bonnet Scientific). Water analyses were undertaken in a NATA (National Association for Testing Authorities) certified laboratory using standard methods and quality control procedures (APHA/AWWA/WPCF, 2001). Treatment performance between the biofilter configurations was evaluated statistically using a 2-Independent sample non-parametric test (Mann Whitney), where significance was defined as $p \leq 0.05$.

3. RESULTS AND DISCUSSION

3.1. Standard-volume stormwater dosing event

Nutrient concentrations in the biofilter effluent collected during the standard-volume dosing event are illustrated in Figure 2removal as the systems mature.

Figure 2. The three-stage sampling scheme revealed that nutrient concentrations in biofilter effluent fluctuate during events. Excellent FRP removal (>98%) was exhibited by each of the biofilter configurations throughout the event (data not shown), which consistently achieved the water quality targets for ecosystem protection (<0.02mg/L) (ANZECC/ARMCANZ, 2000). Total dissolved phosphorus (TDP) concentrations were consistently below detection limits (<0.1mg/L) in all configurations (data not shown). This performance emphasises the capacity of these recently constructed systems to readily remove phosphate. However, this capacity will diminish as the systems age, at which point the influence of filter media type on phosphate removal will likely become more apparent. Illustrating the results in terms of TP constituents shows that the phosphorus in biofilter effluent is largely particulate associated (PP), and that fluctuations in phosphorus removal are driven by variations in the efflux of particulates (Figure 2). The results for TP suggest that this variability can be reduced by inclusion of vegetation and a saturated zone. Inclusion of these design elements reduces the mobilisation of phosphorus-bound particulates from the biofilters upon rewetting, which is particularly apparent following dry periods. These design elements also maintain effluent TP concentrations below ecosystem protection guideline concentrations (0.05mg/L). Total phosphorus removal was largely unaffected by the choice of filter media. Although, as discussed with regard to FRP, filter media is likely to have more bearing on TP removal as the systems mature.

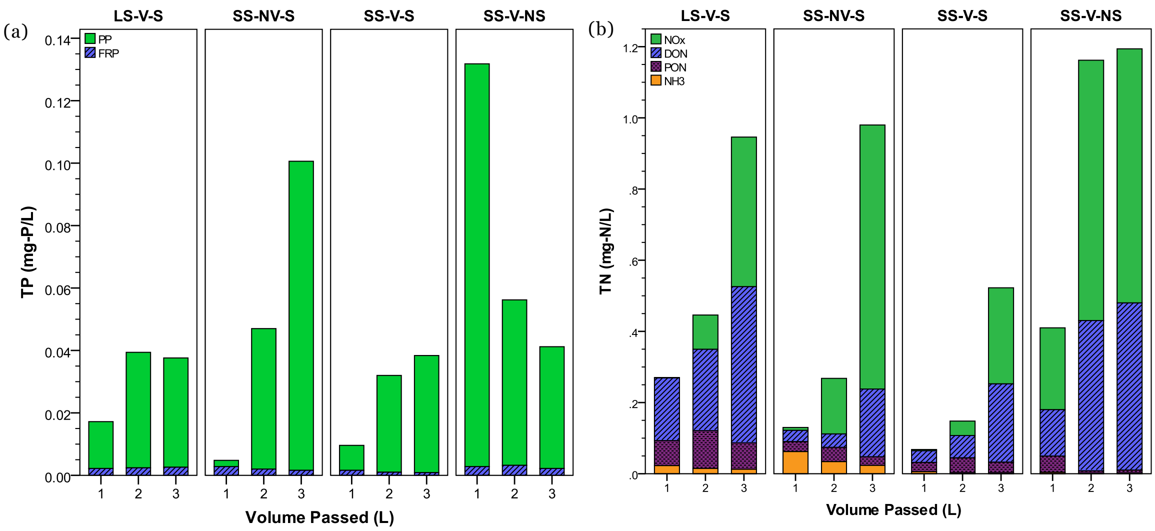

Figure 2 (a) TP (mg/L) and (b) TN (mg/L) concentrations in consecutive effluent samples (L) collected from the biofilter columns after a standard-volume dosing event represented in terms of constituent species. Particulate phosphorus (PP) concentration measured as TP-FRP. Bars represent the mean of five replicates. Panels left to right represent the biofilter configurations (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone).

Total nitrogen concentrations varied considerably during the standard dosing event. The inclusion of vegetation and a saturated zone maintained TN and NO_x concentrations below the water quality guideline concentration initially (0.5mg/L and 0.04mg/L respectively), although all configurations exceeded these values after 2L of effluent had passed. Total nitrogen removal variability was attributed mostly to increasing NO_x concentrations in the effluent. The presence of a saturated zone significantly improved NO_x removal (Table 2), reflecting the benefit of having an internal water storage to provide prolonged retention and enhanced treatment between events, in this instance 18 days. However, once the water retained in the saturated zone was exhausted and effluent transitioned to fresh stormwater, NO_x removal performance declined rapidly. At this point the effect of vegetation on NO_x treatment became more evident. Indeed, ongoing monitoring of the biofilters after recommencement of regular dosing (every 2-3 days) showed that without a plant uptake pathway, or sufficient time between events for microbial processes to occur, leaching of internally produced NO_x quickly becomes an issue in non-vegetated biofilters (Glaister et al., 2014). This leaching of NO_x from the non-vegetated systems implied that complete denitrification was not occurring. On this basis we hypothesise that plant-uptake is the primary pathway for NO_x removal. This conclusion is supported by the findings of Payne et al. (2014a) who determined through the application of an N tracer that NO_x uptake is predominately facilitated by assimilation. These findings suggest that NO_x retained in biofilters, or produced within the system between events, can almost be completely removed through biological assimilation prior to the next dosing event, provided there is sufficient retention time between events. Therefore, in order to achieve optimum NO_x removal and minimise intra-event variability in effluent concentrations, biofilters should be vegetated and include a saturated zone large enough to capture inflow of a standard size rainfall event.

The presence of a saturated zone affected DON removal in a similar way to NO_x, whereby the extended retention time in the system allowed DON stored in the saturated zone to undergo further treatment via biological assimilation or biochemical processing (i.e. ammonification, nitrification, and denitrification). The use of Skye sand filter media also affected DON removal significantly, providing enhanced treatment compared to loamy sand filter media (Table). This was also the case for PON, for which the best removal consistency was maintained in the Skye sand filter media columns with a saturated zone included. Indeed, effluent concentrations of all nitrogen species were lower from the vegetated, saturated zone Skye sand biofilters (SS-V-S) than the loamy sand biofilters (LS-V-S), suggesting that Skye sand provides better N removal, or perhaps better resilience to the effects of drying than loamy sand. Ammonia (present in stormwater as ammonium NH_4^+) was the only nitrogen species for which the presence of vegetation had a significant influence on treatment performance during the standard dosing event (Table). Each of the vegetated biofilter configurations maintained excellent NH_3 removal throughout the event, with effluent concentrations consistently remaining below the ecosystem protection guideline target of 0.02mg/L. However, without vegetation NH_3 concentrations fluctuated somewhat, and despite decreasing, consistently remained above the guideline target. These findings emphasise the critical role plants play in providing a removal pathway for nutrients, particularly during dry periods, when microbial processing slows down.

Table 2 Identification of design elements which had a significant influence on nutrient removal in the biofilter columns during the standard-dosing event as determined by the Mann-Whitney U test for 2-independent non-parametric samples. Significant values (*p<0.05*) are presented in bold.

Configurations	TP	FRP*	TN	NH_4^+	NO_x	DON	PON
LS-V-S v. SS-V-S	0.377	**<0.001**	**0.001**	**0.016**	0.780	**<0.001**	**<0.001**
SS-V-S v. SS-NV-S	0.290	**0.001**	0.057	**<0.001**	0.112	0.425	0.561
SS-V-S v. SS-V-NS	**0.001**	**<0.001**	**<0.001**	0.683	**<0.001**	**<0.001**	0.158

* Statistical significance may be due to there being almost zero error between the results

3.2. High-volume stormwater dosing event

Total phosphorus and total nitrogen concentrations in the biofilter effluent collected during the high-volume stormwater dosing event are illustrated in Figure 3 in terms of their constituent species. This event occurred 4 months after the standard-dosing event, since which regular stormwater dosing (every 2-3 days) had been reinstated. Similar trends in TP removal were observed in the all the Skye sand filter media biofilters during the event. In the Skye sand configurations with a saturated zone (SS-V-S, SS-NV-S) TP concentrations increased until 2.5L of effluent had passed then decreased until the cessation of outflow. This occurred sooner in the Skye sand biofilters without a saturated zone (SS-V-NS) as fresh stormwater containing P-associated particulates mobilised upon rewetting entered the effluent more quickly. As such, including a saturated zone diminished the peak TP concentration and more evenly spread the event pollutograph. The presence of vegetation also reduced particle migration thereby increasing TP removal by approximately 20% overall. However, neither vegetation nor inclusion of a saturated zone was found to have a significant effect on TP removal, suggesting that the influence of filter media is the driving TP removal (Table 3). Visual examination of the biofilter effluent samples indicated that fluctuations in TP concentrations correlated with increasing turbidity of the effluent. This relationship was not surprising since Skye sand has a strong affinity for P-sorption and a high concentration of very fine particles (25% clay) compared with loamy sand (2% clay) (Glaister et al., 2011b). Wash-out of phosphorus associated Skye sand particles may explain why TP removal was better and less variable in the loamy sand biofilters (LS-S-V) during the high-volume event. Because mobilisation of particulates is exacerbated by drying (Blecken et al., 2009, Hatt et al., 2007a) it follows that higher TP effluent concentrations were observed during the standard-dosing event, which occurred after an 18 day dry period. However, the additional establishment time between the events (4 months) could also have influenced the extent of particulate mobilisation. Evidently, mitigating particulate migration is critical to reducing effluent TP concentrations. Measures should therefore be taken to mitigate filter media mobilisation and wash-out during events. For example, filter media should be well graded and strategies to reduce the effects of drying should be considered (i.e. inclusion of a saturated zone or allowing for treatment of other wastewater sources during dry weather periods). Drying of filter media between events also affects the extent to which particles are mobilised upon stormwater dosing. Other than when fresh stormwater containing resuspended particles initially entered the effluent, the Skye sand biofilters maintained TP concentrations below ecosystem protection guidelines concentrations (<0.05mg/L) during the high-volume event. The loamy sand filter media biofilters however maintained concentrations below the target throughout. Excellent FRP removal (>98%) was observed during the high-volume dosing event, indicating that neither of the filter media has reached phosphate saturation and is not likely to some time. Water quality targets for FRP (<0.02mg/L) were also achieved by all configurations throughout.

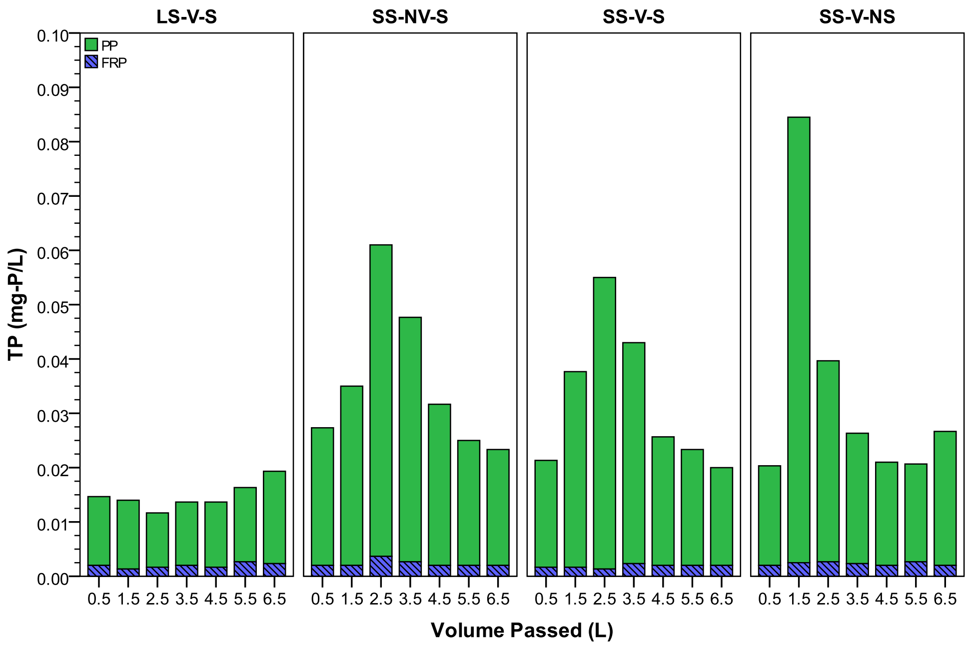

Figure 3 TP (mg/L) concentrations in consecutive effluent samples (L) collected from the biofilter columns after a high-volume dosing event represented in terms of constituent species. Particulate phosphorus (PP) concentration measured as TP-FRP. Bars represent the mean of five replicates. Panels left to right represent the biofilter configurations (LS: loamy sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone).

Consecutive effluent sampling during the high-volume stormwater dosing event revealed that intra-event nitrogen removal variability was greatest in the absence of vegetation and a saturated zone. These design elements were also found to significantly affect overall TN removal performance (Table 3). Throughout the event, NO_x concentrations in the non-vegetated configuration's effluent exceeded the inflow (0.82mg/L) and were well in excess of the water quality guideline concentration

(0.04mg/L). The NO_x leaching was particularly evident in the first 3.5L of effluent, due to the release of NO_x produced between events through nitrification, which without a plant uptake pathway is retained in the system until being flushed out by the next dosing event. The inverse was apparent for NH_3, which gradually increased in concentration during the event as the supply of water retained in saturated zone was exhausted and fresh stormwater, which has had limited time for treatment, entered the effluent (approx. >2.5L). This is however of limited practical importance, considering that all biofilter configurations demonstrated excellent NH_3 removal during the high-volume event (>85%) and achieved water quality guideline targets throughout (0.02mg/L). Nevertheless, these results emphasise the importance of a plant uptake pathway to reduce TN concentrations, in particular NO_x, and maintain an effective level of treatment throughout events.

Dissolved organic nitrogen removal was not significantly affected by absence of vegetation (Table 3) and was almost completely removed in the first 2.5L of outflow from the non-vegetated Skye sand columns (SS-NV-S). This illustrates that in the absence of vegetation, which can be a source of DON, DON can almost be completely removed between events in non-vegetated biofilters when a saturated zone is included. However, as fresh stormwater passes through the biofilter (>2.5L), effluent concentrations increase as there is insufficient time for DON turn-over to be completed. In the vegetated Skye sand biofilter columns with a saturated zone (SS-V-S) DON concentrations also increased with the outflow of ‘new’ stormwater, although the peak DON concentration in the effluent from this configuration was lower and the pollutograph more evenly spread than that of the non-vegetated system. Concentrations of DON from the loamy sand configuration showed the least intra-event variability, although this configuration did not achieve DON concentrations as low as the Skye sand columns with a saturated zone did in the first 2.5L. In the absence of a saturated zone DON concentrations decreased marginally over the event, suggesting that if we were to extend the pollutograph we would perhaps see DON concentrations in the saturated zone inclusive systems start to decrease.

Particulate organic nitrogen removal was more variable during the high-volume event in the non-saturated configuration, emphasising again the role the saturated zone plays in mitigating particle efflux. Removal of PON was otherwise consistent throughout the high-volume event with similar concentrations being achieved regardless of filter media type or the presence of vegetation. Interestingly, several of the nutrient species found to be significantly affected by filter media type in the standard-volume stormwater dosing event were not in the high-volume event (e.g. NH_3, FRP and PON). This suggests that the influence of design characteristics on nutrient treatment is dynamic, and can become more or less critical under certain operational or environmental conditions than others. For example, NH_3 and FRP removal via sorption to the filter media appears to become more critical during dry periods when plant-uptake and microbial processing slows down.

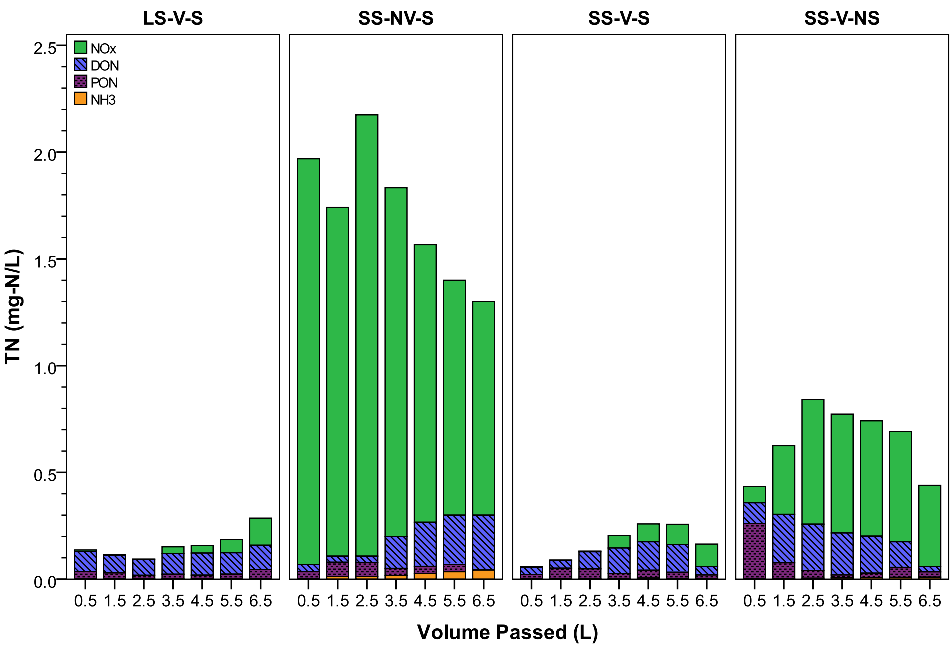

Figure 4 TN (mg/L) concentrations in consecutive effluent samples (L) collected from the biofilter columns after a high-volume dosing event represented in terms of constituent species. Particulate phosphorus (PP) concentration measured as TP-FRP. Bars represent the mean of five replicates. Panels left to right represent the biofilter configurations (LS: loamy

sand, SS: Skye sand, V/NV: vegetated/non-vegetated, S/NS: saturated zone/no saturated zone)

Table 3 Identification of design elements which had a significant influence on nutrient removal in the biofilter columns during the high-dosing event as determined by the Mann-Whitney U test for 2-independent non-parametric samples. Significant values (*p<0.05*) are presented in bold. See Table 1 for configuration IDs.

Configurations	TP	FRP	TN	NH_3	NO_x	DON	PON
LS-V-S v. SS-V-S	**<0.001**	0.737	0.403	0.957	0.207	0.037	0.109
SS-V-S v. SS-NV-S	0.225	**0.013**	**<0.001**	**<0.001**	**<0.001**	0.272	0.182
SS-V-S v. SS-V-NS	0.574	**0.012**	**<0.001**	**0.006**	**<0.001**	0.023	0.251

3.3. Recommendations for the use of Skye sand in stormwater biofilters

Based on the results of this study it would be recommended that rather than full substitution of loamy sand with Skye sand it would be better to apply Skye sand to biofilters as an amendment (i.e. blending Skye sand with loamy sand). This would improve the grading of the filter media and thus reduce particle efflux. Nevertheless, since P sorbed to Skye sand is relatively immobile, washout of P-bound Skye sand particles should not pose a serious threat to the water quality of aquatic environments. These very fine particles may however cause discolouration of drains and perhaps more critical issues over time if, following burial of particles in deoxygenated aquatic sediments, dissimilatory iron reduction causes P to be released into the water column.

4. CONCLUSIONS

Using a sequential effluent sampling method, this study assessed the intra-event variability of effluent nutrient concentrations from laboratory-scale biofilter columns following a standard-volume and high-volume stormwater dosing event. The results demonstrated that nutrient concentrations in biofilter effluent vary during events and that the extent of this variation was affected by system design, particularly the absence of vegetation or a saturated zone, and the antecedent dry period. These findings suggest that biofilters can achieve co-optimised intra-event N and P removal and maintain effluent concentrations close to or below water quality guideline values for ecosystem protection under varying hydrologic conditions, provided that suitable vegetation, filter media and a saturated zone are included. However, the best way to ultimately address the challenge of intra-event variability and satisfy the water quality guidelines is to wherever possible use infiltration-based systems that extend detention times by infiltrating water into underlying soils, such that the biofiltration process continues.

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Advancing biofilter design for co-optimised nitrogen and phosphorus removal

B. Glaister*, T. D. Fletcher**, P. L. M. Cook*** and B. E. Hatt*

** Department of Civil Engineering, Monash University, Wellington Rd, Clayton, Victoria, 3800, Australia (E-mail: Bonnie.Glaister@monash.edu; Belinda.Hatt@monash.edu)*
***School of Land and Environment, The University of Melbourne, 500 Yarra Blvd, Burnley, Victoria, 3121, Australia (E-mail: tim.fletcher@unimelb.edu.au)*
**** Water Studies Centre, Monash University, Wellington Rd, Clayton, Victoria, 3800, Australia (E-mail: Perran.Cook@ monash.edu)*

ABSTRACT
This study investigates the influence of several design parameters; vegetation, filter media type (loamy sand, Skye sand – a locally available iron rich sand) and saturated zone, on the nutrient removal performance of biofilters to develop a design which is "co-optimised" for nitrogen and phosphorus removal. Twenty laboratory-scale biofilter columns were constructed to compare four design configurations (five replicates of each). Over a period of twelve months the columns are dosed with semi-synthetic stormwater, with volumes reflecting both wet and dry weather periods, based on average Melbourne rainfall. Water quality samples collected at five week intervals were analysed for total nitrogen, total phosphorus and their species. Dissolved oxygen concentration in the saturated zone, plant growth and infiltration rate measurements were also collected. Preliminary results indicate that the vegetated, Skye sand filter medium, configuration incorporating a saturated zone, demonstrates the best "co-optimised" nitrogen and phosphorus removal. The present results reaffirm the importance of vegetation and the inclusion of a saturated zone to promote nitrogen removal. The results also identify the saturated zone as an important measure to reduce infiltration rate and minimise migration of fine particles into effluent. The results of this study will provide guidance towards designing biofilters optimised for nitrogen and phosphorus removal.

KEYWORDS
Biofiltration; Nitrogen; Phosphorus; Saturated Zone; Skye Sand; Stormwater

INTRODUCTION

Anthropogenic distortion of catchment hydrology and nutrient cycling has significantly increased the concentration of nutrients present in urban stormwater. Discharge of this nutrient-rich stormwater into receiving waterways can upset the balance of limiting nutrients in an ecosystem, posing a severe threat to their health through algal bloom proliferation, dissolved oxygen depletion, biodiversity loss and eutrophication (Duncan, 1999, Kadlec and Knight, 1996). Biofiltration systems (also known as biofilters and bioretention systems) have proven to be an effective technology for the treatment of stormwater by a range of laboratory and field studies (e.g. Davis et al., 2001, Fletcher et al., 2007). These systems reflect the principles of Water Sensitive Urban Design (WSUD) and offer benefits such as reducing pollutant export, attenuating storm flows and improving urban landscape amenity (Wong, 2001).

Biofilters target fine particulates and dissolved pollutants and are well suited to reduce nutrient loads (Fletcher et al., 2006, Henderson et al., 2007). A typical biofilter design generally incorporates a shallow excavated trench or basin filled with a porous filter medium and planted with vegetation (Hatt et al., 2007, Henderson et al., 2007). Stormwater flows over the vegetation and may be subject to temporary ponding, allowing suspended particles to settle, the stormwater then percolates through the filter media where pollutants are removed through physical, chemical and biological processes such as sedimentation, adsorption and biological assimilation (Hatt et al., 2007). The effluent is then either collected through a perforated pipe and channelled to a drainage network or waterway, or allowed to exfiltrate into the surrounding substrate and groundwater (Davis et al., 2001, Hatt et al., 2007, Read et al., 2010). Incorporation of a submerged zone has been shown to be a promising design modification for enhancing nitrogen removal (Zinger et al., 2007), however this can be detrimental to phosphorus removal if not configured appropriately (Dietz and Clausen, 2006).

Monitoring of existing systems indicates that biofilters are capable of meeting typical Australian phosphorus load reduction targets. However, effluent phosphorus concentrations are still in excess of typical Australian receiving water quality guidelines (e.g. ANZECC & ARMCANZ, 2000). Results of a recent study conducted by Glaister et al. (2011) found that Skye sand, a locally sourced naturally ferric oxide coated sand, improved the phosphorus removal capacity of the traditional loamy sand biofilter medium, and was able to achieve receiving water quality phosphorus targets.

The current study continues the investigation of Skye sand, with the aim of developing a biofilter which is “co-optimised” for nitrogen and phosphorus removal. This involves testing the Skye sand filter medium in conjunction with design characteristics known to improve nitrogen removal, specifically, vegetation and the inclusion of a saturated zone to enhance denitrification. Results from this study will inform decision making when designing biofilters to target nutrient stormwater and further our understanding of the processes and design characteristics which drive or inhibit nutrient removal.

METHODS

To compare the treatment performance of Skye sand under alternative conditions we developed four column design configurations (see Table 1). Twenty laboratory-scale biofilter columns were constructed to compare these (five replicates of each). Figure 1 describes the generic column design. The columns were constructed using PVC pipe and Perspex (150mm diameter), and were fitted with outlet taps to collect samples. To create the saturated zone in configurations A, B and C the outlet tap was raised to 300mm using HDPE pipe. In addition to enhancing denitrification the saturated zone will also protect against drying during dry weather periods (FAWB, 2009). To facilitate the denitrification process a source of carbon (pine woodchips and sawdust) was blended into the saturated zone filter media (total material added was equivalent to 5% of the volume of the saturated zone). This organic matter was selected due to its biodegradability and low phosphorus content (10.2 mg P/kg).

Table 1. Summary of experimental biofilter column design configurations

Configuration	Filter Medium	Vegetation	Saturated Zone
A (LS-V-S)	Loamy Sand	*Carex Appressa*	SZ
B (SS-NV-S)	Skye Sand	Non-vegetated	SZ
C (SS-V-S)	Skye Sand	*Carex Appressa*	SZ
D (SS-V-NS)	Skye Sand	*Carex Appressa*	No SZ

These configurations were selected in the interest of making three primary comparisons, namely;

1) **Loamy** Sand vs. **Skye** sand: vegetated with SZ

2) Skye Sand: **non-vegetated** with SZ vs. Skye sand: **vegetated** with SZ, and;

3) Skye Sand: vegetated **with** SZ vs. Skye sand: vegetated **without** SZ

Column layout (see Figure 1b)

1. Filter medium (300mm): Loamy sand or Skye sand
2. Sand transition layer (200mm): Triple-washed sand
3. Coarse washed sand drainage layer (70mm)
4. Gravel drainage layer (30mm)

a. b.

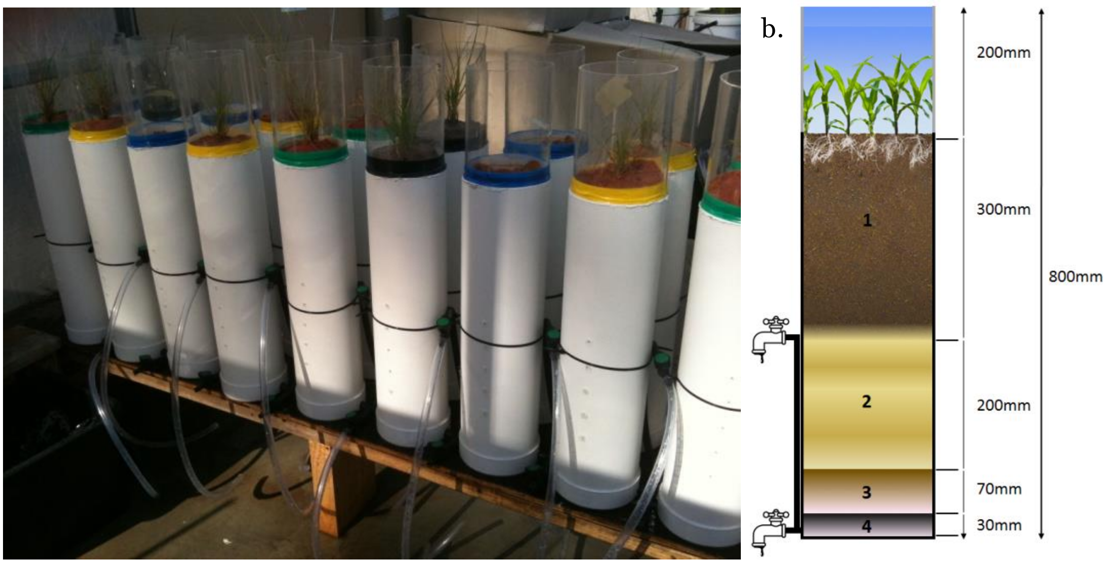

Figure 1. (a) Laboratory set-up and (b) example column schematic

The loamy sand filter medium configuration was included as a control to compare the performance of Skye sand against a traditional biofiltration media. Previous research has investigated the performance of loamy sand with and without vegetation and a saturated zone; as such these comparisons were omitted from this study. *Carex appressa* was the plant species selected for the vegetated biofilter columns. This species is a widespread Australian native which is drought tolerant and resilient to fluctuations in climate. Previous research has shown that this tall sedge is efficient in nutrient removal under high loading conditions and pollutant concentrations (Bratieres et al., 2008, Read et al., 2008). The plants were matured in a glasshouse (maintained at 25°C) for 12 weeks prior to planting in the columns.

The columns were manually filled by firstly measuring out the required amount of media in each layer (by volume and weight) then compacting these using a "compactor" (a weighted hammer dropped from 100mm onto the surface of the sample, as described by ASTM Standard F 1815 – 06, Standard Test Method for Specific Gravity of Soils). The compaction required was determined by the thickness of the media layer and its porosity. Using this method maintained consistency between replicates and minimised the risk of over-compaction which may result in a loss of permeability of the biofilter. Once the columns were filled, the vegetation was transplanted into the top 100mm of column configurations (A, C, and D). The columns were set-up on custom built benches in a shade house designed to protect the columns from rainfall. During a five week establishment period, prior to the first sampling run, the columns were dosed twice weekly with semi-synthetic stormwater. This allowed inoculation of the soil microbial community and flushing of the filter media to remove free particles.

Column dosing and sampling

Over a period of twelve months the columns are dosed with semi-synthetic stormwater (reflecting a 6 month ARI storm for a biofilter of 2.5% of its contributing catchment area based on Australian design guidelines; see Hatt et al., 2007). The dosing regime comprises a "wet" (twice weekly dosing of 3.7L from April to November) and "dry" period (dosing of 3.7L every 15 days from December to March) to reflect typical Melbourne rainfall patterns (Bureau of Meteorology, 2011). Preparation of the semi-synthetic stormwater required adding a known concentration of sediment (collected from a nearby stormwater retention basin and strained through a 1000µm sieve) to a known volume of water, then topping up with synthetic chemicals, to match typical stormwater nutrient concentrations (see Table 2).

Table 2. Typical Melbourne stormwater nutrient concentrations (based on concentrations reported by Duncan (2003) and Taylor et al. (2005).

Pollutant	Concentration (mg/L)	Chemical additives
Total Suspended Solids (TSS)	150	Sediments
Total Nitrogen (TN)	2.13	From N additives
Ammonia (NH_3)	0.29	Ammonium chloride (NH_4CL)
Oxidized Nitrogen (NO_x)	0.74	Potassium nitrate (KNO_3)
Organic N (ON)	1.1	Sediments and DON
Dissolved ON	0.6	Nicotinic acid ($C_6H_5O_2N$)
Total Phosphorus (TP)	0.35	Sediments and FRP
PO_4- (Phosphate ortho=FRP)	0.12	Potassium phosphate (KH_2PO_4)

Water quality samples collected at five week intervals were analysed for total nitrogen (TN), total phosphorus (TP) and their dissolved species, along with total iron. Samples analysed for dissolved nutrients were filtered through a 0.45μm cartridge filter (Bonnet Scientific). All water chemical analyses were undertaken by NATA (National Association for Testing Authorities) certified laboratories using standard analysis methods (APHA/AWWA/WPCF, 1998). Additional water quality data was measured using a Horiba U10 multiparameter probe (2-point calibrated). Discrete water samples were withdrawn from the saturated zone, using ports installed prior to filling the columns, and analysed for dissolved oxygen (DO) using a DO probe (Hach Company). Plant growth and infiltration rate measurements were also collected during the experiment.

RESULTS AND DISCUSSION

Since establishment of the biofilter columns, two nutrient sampling runs have occurred. These preliminary results have identified some significant differences between the design configurations. These are presented and discussed in the following sections.

Nitrogen removal. The results for TN and its species for sampling runs 1 and 2 are summarised in Table 3. Concentrations of the influent stormwater are given in the first row and column outflows thereafter.

Table 3. Summary of nitrogen results for sampling runs 1 and 2 (mg N/L). Each data point is the mean of five replicates.

Sample Description	**TN**		**TDN**		**NH_3**		**NOx**	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Inflow	2.30	2.30	2.00	2.00	0.37	0.36	0.99	1.00
A (LS-V-S)	1.50	0.61	1.04	0.48	0.05	0.02	0.70	0.33
B (SS-NV-S)	1.56	1.28	1.56	1.30	0.28	0.01	1.14	1.24
C (SS-V-S)	1.16	0.42	1.16	0.39	0.18	0.01	0.84	0.30
D (SS-V-NS)	1.90	1.30	1.84	1.13	0.21	0.01	1.36	0.96

Total nitrogen removal has shown improvement between the two samples for each design configuration. However, this result is not so pronounced for the non-vegetated (B) or non-saturated columns (D), except in terms of NH_3 removal, which indicates that nitrification is occurring.

Nitrogen removal, particularly NO_x and TN, is clearly affected by both the absence of vegetation and a SZ, as demonstrated by the net leaching of NO_x from column configurations B and D. Conversely, column configurations A and C, which are vegetated and SZ inclusive show good removal of NO_x, increasing between runs 1 and 2 from 35% to 77% in configuration A (LS-V-S), and from 15% to 70% in configuration C (SS-V-S). These findings support those reported in previous studies (e.g. Bratieres et al., 2008, Read et al., 2008).

Discrete sampling of dissolved oxygen (DO) from the saturated columns (A, B, and D) revealed similar DO concentrations in each of these configurations (2.20mg/L, 2.28mg/L, and 2.29mg/L respectively). While it is possible that pockets of very low, possibly, anaerobic, DO concentrations occur throughout the saturated zone, it is unlikely that the reduction in NO_x can at this stage be attributed to denitrification (which requires anaerobic conditions to occur <1.0mg/L). More likely, this data is mainly a demonstration of importance of vegetation to facilitate NO_x removal directly and through the facilitation of microbial uptake.

Phosphorus removal. The results for TP and its species for sample runs 1 and 2 are summarised in Table 4. What is immediately evident is that, at this stage, all biofilter configurations are facilitating greater than 98% removal of FRP and 95% removal of TDP. However, this is not the case for TP. Approximately 50% of TP present in the inflow is in particulate form. This portion was most likely removed by filtration processes. Nonetheless, the loamy sand filter media configuration (A) showed less than 50% removal in the first sampling run. We hypothesise that this could be attributed to the migration of fine loamy sand particles from the filter media into the effluent. Turbidity monitoring has shown a decrease in the release of fines from this configuration since the first sampling run, from on average 600NTU to 80NTU, which is reflected in the run 2 results for TP. Conversely, the Skye sand filter media columns have experienced a slight increase in TP concentration in the effluent over this time. This has been recognised as a consequence of very fine Skye sand particle migration through the column and into the effluent, which was not evident during the first sampling run. These results, while potentially simply an artefact of the relatively short monitoring time so far, do confirm that careful attention must be paid to the use of transition layers to prevent or reduce migration of fines.

Table 4. Summary of phosphorus (mg P/L) & iron (mg Fe/L) results. Each data point is the mean of five replicates.

Sample Description	**TP**		**TDP**		**FRP**		**Fe**
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 2
Inflow	0.40	0.40	0.21	0.24	0.20	0.20	0.91
A (LS-V-S)	0.23	0.05	<0.01	<0.01	0.002	0.002	1.77
B (SS-NV-S)	0.02	0.06	<0.01	<0.01	0.002	0.002	3.67
C (SS-V-S)	0.02	0.05	<0.01	0.01	0.002	0.002	2.70
D (SS-V-NS)	0.06	0.17	<0.01	<0.01	0.002	0.003	16.0

The inclusion of a saturated zone in configurations A, B and C appears to minimise the outflow of fines most probably due to the fact that it acts like a sedimentation basin in the base of the biofilter. The reduction in effective infiltration rate, due to the decrease in hydraulic gradient caused by the saturated zone, may also play a role in minimising the migration of fines. The average infiltration rate of the columns is currently 340mm/hr, 580mm/hr, 290mm/hr and 900mm/hr for configurations A, B, C and D respectively. This is demonstrated by the TP results for the non-saturated column (configuration D), which had a concentration of TP 50% higher than the SZ inclusive configurations (A, B, and C).

The presence of Skye sand fines in the outflow was confirmed by an analysis of total iron. These results, also displayed in Table 4, show that the outflow from the non-saturated columns has a much greater concentration of iron than the other configurations. Analysis of effluent iron concentration and TSS will continue to monitor Skye sand particle migration during the experiment. The loss of these fines could have ramifications for the on-going treatment of phosphorus, as it is hypothesised that this particle size fraction is important for phosphorus sorption and straining of fine particulates in the stormwater influent itself (Glaister, 2011).

Overall, the vegetated, Skye sand, SZ inclusive configuration (C) currently demonstrates the best nutrient removal rates. This represents a significant finding in terms of the use of Skye sand as a biofilter medium. Inclusion of a saturated zone has also demonstrated several benefits, including accelerated plant growth. Over the past two months the presence of this permanent water supply in the saturated columns (A and C) has resulted in a 72-74mm increase in longest shoot length, compared to only a 9mm increase for plants grown in the non-saturated columns (D). The columns will next be subjected to the “dry” conditions described above, where it is expected that the saturated zone will play an even more important role in supporting plant health and providing additional resilience to the effects of drying.

CONCLUSIONS

This study investigated the influence of several biofilter design parameters; vegetation, filter media type (loamy sand, Skye sand) and saturated zone, to develop a biofilter design which is co-optimised for nitrogen and phosphorus removal. Results to date show that vegetation, the inclusion of a saturated zone, and choice of filter media each affect the nutrient removal capacity of the biofilters. Currently, the vegetated, Skye sand filter medium, saturated zone inclusive biofilter (configuration C) provides the best “co-optimised” nitrogen and phosphorus removal performance. Additionally, the results suggest that a permanent saturated zone can promote plant growth and reduce migration of fine particles from biofilters by altering the hydraulic properties thereby reducing infiltration rates. Continued monitoring of these columns will further address key remaining knowledge gaps surrounding the use of Skye sand in a saturated zone inclusive biofilter, particularly in regard to the reductive dissolution of iron, retention of phosphorus, and nutrient removal performance following a prolonged drought.

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A4.5 Supplementary data: Intra-event N & P removal variability

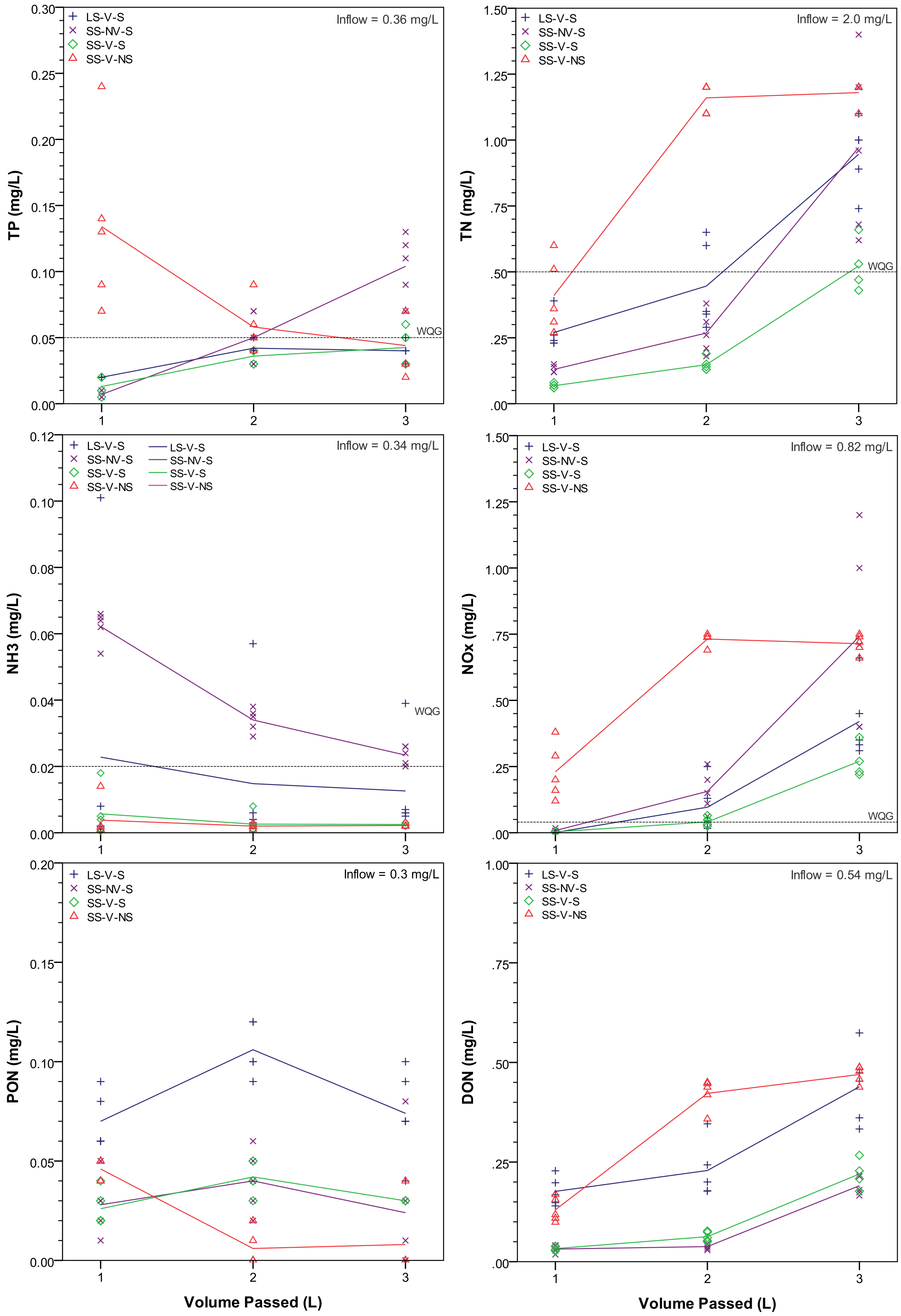

Figure A4.3. Nutrient concentrations (mg/L) in the biofilter outflow during April sampling event. Lines represent the mean of 5 replicates. Note changes to y-axis scale. Dashed reference lines represent the water quality guideline concentrations (ANZECC/ARMCANZ 2000).

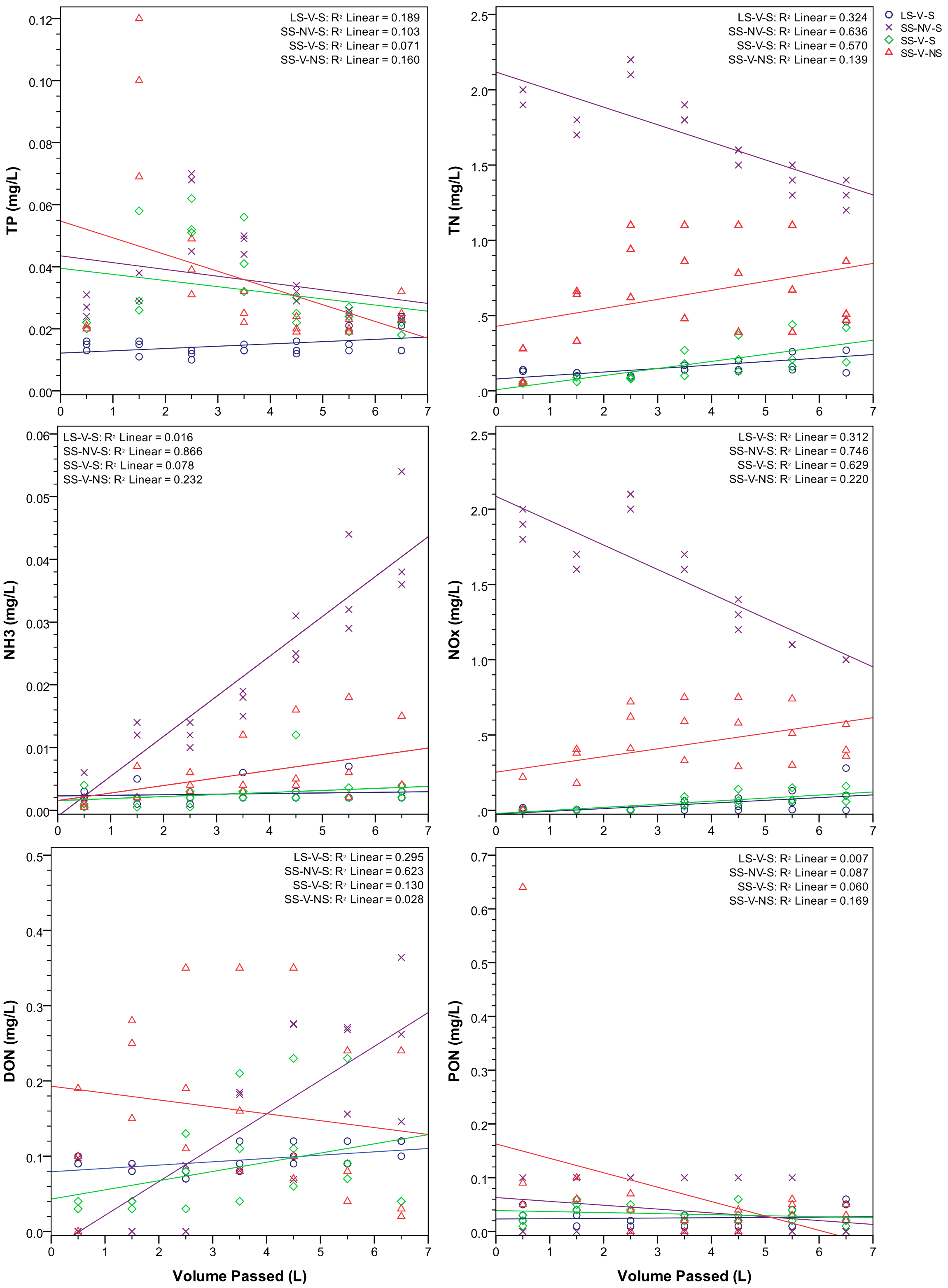

Figure A4.4. Nutrient effluent concentrations from the biofilters during the August dosing event after a 2 day dry period. Regression line is based on the mean of 5 replicates. Note changes to y-axis scale.

Chapter 5 Appendix

A5.1 Journal Paper: Ecological Engineering

Declaration for Journal Paper contributing content to Thesis

Chapter 5

In the case of this journal paper, which contributes all content towards thesis Chapter 5, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Experimental construction and works, data collection, data analysis and interpretation, write-up	85%

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
Tim Fletcher	Data interpretation, manuscript revision and comments	
Belinda Hatt	Data interpretation, manuscript revision and comments	
Perran Cook	Data interpretation, review of manuscript, comments and revisions	

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature		**Date** 26/07/18
Main Supervisor's Signature		**Date** 26/07/18

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

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Research paper

Interactions between design, plant growth and the treatment performance of stormwater biofilters

Bonnie J. Glaister[a,*], Tim D. Fletcher[b], Perran L.M. Cook[c], Belinda E. Hatt[a]

[a] Department of Civil Engineering, Monash University, Victoria, 3800, Australia
[b] Waterway Ecosystem Research Group, School of Ecosystem & Forest Sciences, Faculty of Science, the University of Melbourne, Victoria, 3121, Australia
[c] Water Studies Centre, School of Chemistry, Monash University, Victoria, 3800, Australia

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ABSTRACT

Plants play a critical role in the nutrient removal performance of stormwater biofilters. However, the influence of biofilter design on plant growth and subsequent implications for treatment performance are not well understood. A 12 month, laboratory-scale biofilter column experiment was conducted to investigate the response of *Carex appressa* to variations in biofilter design and implications for nutrient removal performance. Plant growth in Skye sand, a natural iron-coated sand with a strong capacity to immobilize phosphorus, was evaluated against a typical loamy sand filter media in biofilters with and without a saturated zone. Plant biomass correlated strongly with nutrient removal and was significantly greater in biofilters with a saturated zone, suggesting that inclusion of a saturated zone facilitates nutrient uptake. In the presence of a saturated zone, plants grown in Skye sand had a significantly higher specific root length, surface area and volume than plants grown in loamy sand, illustrating *C. appressa's* ability to adapt root morphology to maintain growth under nutrient limited conditions. These root traits also correlated strongly with nutrient removal, suggesting that use of Skye sand in biofilters rather than loamy sand would be advantageous for nutrient removal. However, root adaptations, in particular increased etiolation, can make plants vulnerable to stressful environments (e.g. prolonged drying). Therefore, it is critical that a saturated zone be included in stormwater biofilters to increase growth and protect against drying.

1. Introduction

Stormwater biofilters provide passive treatment of urban runoff by harnessing the natural bioremediation properties of plant-soil systems (Fletcher et al., 2006; PGC, 2002). Extensive research in laboratory- and field-scale settings has demonstrated that plants play a critical role in facilitating stormwater treatment, particularly nutrient removal (Bratieres et al., 2008; Davis et al., 2006; Lucas and Greenway, 2008; Payne et al., 2014a; Read et al., 2008). Nevertheless, achieving co-optimised nitrogen and phosphorus (P) removal (particularly phosphate) remains a challenge for biofilters, as does meeting nutrient removal objectives for ecosystem protection (Davis et al., 2006; Glaister et al., 2014). Whilst nitrogen removal relies predominately on biological processes, which has been shown to improve with the inclusion of an internal water storage or 'saturated zone' (Zinger et al., 2013), the predominant mechanism by which phosphate is removed in plant-soil systems is through sorption to filter media (Erickson et al., 2007; Reddy et al., 1999).

The endeavour to improve the effectiveness of P removal in biofilters, among other stormwater and wastewater treatment systems, has led to many alternate filter media types being investigated (Bachand, 2003; Ballantine and Tanner, 2010; Lucas and Greenway, 2011; Vohla et al., 2011). The affinity of iron-rich soils and sediments for P sorption (Goldberg and Sposito, 1985) has motivated numerous researchers to test how augmenting the filter media of stormwater and wastewater treatment systems with iron-rich materials affects the P removal performance and retention capacity (Arias et al., 2006; Ayoub et al., 2001; Boujelben et al., 2008; Dobbie et al., 2009; Erickson et al., 2012). Recent research has shown that using 'Skye sand', a natural iron-coated filter media with a strong affinity for phosphorus (Glaister et al. unpublished data), in conjunction with a saturated zone, can improve N and P removal and enable biofilters to achieve ecosystem protection

* Corresponding author.
E-mail addresses: bonnie.glaister@monash.edu (B.J. Glaister), tim.fletcher@unimelb.edu.au (T.D. Fletcher), perran.cook@monash.edu (P.L.M. Cook), belinda.hatt@monash.edu (B.E. Hatt).

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0925-8574/

Table 1
Biofilter column configurations.

Configuration ID	Filter Medium	Saturated Zone (Y/N)
Loamy sand (S)	Loamy Sand	Y
Skye sand (S)	Skye Sand	Y
Skye sand (NS)	Skye Sand	N

objectives (Glaister et al., 2014). However, while success in ameliorating N and P removal has been demonstrated, the influence of Skye sand on plant growth in biofilters has not been specifically tested. As such, further research is needed to understand how Skye sand filter media influences plant growth and nutrient removal in biofilters.

Iron-rich soils are typically associated with limited nutrient availability (Handreck, 1997; Lambers et al., 2008; White and Hammond, 2008; Wild, 1950). The ability of plants to respond to such conditions is fundamentally important to environmental adaptation. Root development responses to nutrient limited conditions can have a profound effect on root system architecture and nutrient acquisition (Lambers et al., 2008; López-Bucio et al., 2003; Schmidt and Schikora 2001). Such responses include: elongation of primary roots; formation of lateral roots, to increase the exploratory capacity of the root system; and the formation of root hairs, which increase the total surface area of primary and lateral roots and allow roots to exploit a considerably larger cylinder of soil (López-Bucio et al., 2003).

Previous studies investigating plant traits that enhance nutrient removal in biofilters have found that plant biomass and root traits, such as root length, surface area and fineness, are strongly correlated with nutrient removal, particularly dissolved N and P species (Payne et al., 2014b; Read et al., 2010, 2008). As such, nutrient limited conditions may present advantageous conditions for the development of plant traits which correlate with enhanced nutrient removal. This may explain in part why the use of Skye sand filter media has been shown to be beneficial for nutrient removal.

Building upon existing studies of the influence of plant traits on nutrient removal (Payne et al., 2014b; Read et al., 2010), the present study aims to investigate how using Skye sand as a filter medium affects the growth and morphology of plants in biofilters and the implications for nutrient removal performance. Investigating plant responses to Skye sand in conjunction with a saturated zone is a key focus of this study and an essential part of the research needed to develop a better understanding of how co-optimisation of N and P removal in biofilters can be achieved.

2. Materials and methods

2.1. Experimental design

Three biofilter column configurations were designed to compare nutrient removal performance and plant growth characteristics of loamy sand and Skye sand biofilters with a saturated zone and Skye sand biofilters with and without a saturated zone (Table 1). A saturated zone inclusive biofilter with loamy sand filter media was not included because nutrient removal performance and plant growth characteristics of this configuration have been thoroughly investigated by a number of preceding studies, using the same experimental apparatus and testing facility (Bratieres et al., 2008; Payne et al., 2014b). Five replicate columns were constructed for each configuration. The columns were made of PVC (600 mm x 150 mm diameter) with a 200 mm acrylic collar attached to create a ponding zone. The configurations without a saturated zone drained freely from the base, while a riser pipe was attached to the outlet of the saturated zone inclusive systems to maintain a 300 mm pool of water in the lower half of the column. The biofilters contained four layers of media (from top to bottom): (1) loamy sand or Skye sand filter media (300 mm); (2) coarse, washed sand transition layer (200 mm); (3) pea gravel drainage layer (70 mm); (4) gravel drainage layer (30 mm). A cross section of the columns is shown in Fig. 1a.

The biofilter columns were each planted with a single *C. appressa* plant. *C. appressa* is an Australian tall sedge that is relatively drought tolerant and has been found to provide effective nutrient removal in biofilters (Bratieres et al., 2009; Read et al., 2008). Prior to transplanting into the columns, the plants were established for 12 weeks in small pots containing either loamy sand or Skye sand, depending on their destination biofilters. The pots were housed in a greenhouse maintained at 25 °C and watered twice weekly with tap water. The biofilter columns were constructed in July and placed in an open-air shade house (Fig. 1b). After an initial flush with tap water to settle the filter media, stormwater dosing commenced in early August.

Because of the uncertainty and inconsistency associated with the use of real stormwater, a semi-synthetic stormwater was prepared using methods described by previous biofilter column studies (e.g. Bratieres et al., 2008; Hatt et al., 2007). This approach utilises natural sediment collected from a stormwater retention pond and laboratory-grade chemicals to produce a semi-synthetic stormwater of a quality consistent with typical stormwater pollutant concentrations (Duncan, 1999; Taylor et al., 2005). The frequency and volume of dosings were designed to simulate typical Melbourne rainfall patterns. During 'wet' periods (August-November and April-July) the columns were dosed twice weekly with stormwater. Throughout the intervening 'dry' months (December-March) the dosing schedule varied, with up to 18 antecedent dry days occurring between events. Dosing volumes remained constant at 3.7L per event, which is equivalent to the rainfall received by a biofilter sized to 2.5% of its catchment area in Melbourne (540 mm effective annual rainfall, Bureau of Meteorology, 2013). Water quality was monitored by collecting bulk effluent samples from each column every five weeks for twelve months and analysing for total phosphorus (TP), total nitrogen (TN), ammonium (NH_4^+), nitrate/nitrite (NO_x), dissolved organic nitrogen (DON), particulate organic nitrogen (PON) and filterable reactive phosphorus (FRP) using standard methods and quality controls (APHA/AWWA/WPCF, 2001).

2.2. Column deconstruction and plant harvesting

In order to quantify the effect of biofilter design on plant growth and morphology, the plants were harvested from the vegetated columns (15 plants; 5 replicates per configuration) at the end of the experimental period. A longitudinal quarter segment of each column casing (the PVC pipe) was removed to allow visual examination of the filter media layers and plant roots (Fig. 2). Filter media samples were collected before the plants were removed from the columns by carefully washing away the filter media. After washing, the clean plants were stored for a few days (maximum of 14) in 10L buckets filled with tap water until growth and morphological analysis commenced.

2.3. Plant growth and morphological analysis

Plant morphology was characterised using several techniques (Table 2). The longest root and shoot length of each plant was measured, along with the bulk root length (the length to which approximately 95% of roots grew to) and bulk shoot length (length of ~95% of shoots). Each plant was then separated into roots, shoots (i.e. leaves), and stems. Roots were cut into 2–4 cm segments and placed in 10L buckets filled with water. This allowed the roots to separate and mix well. Approximately 10 g wet weight

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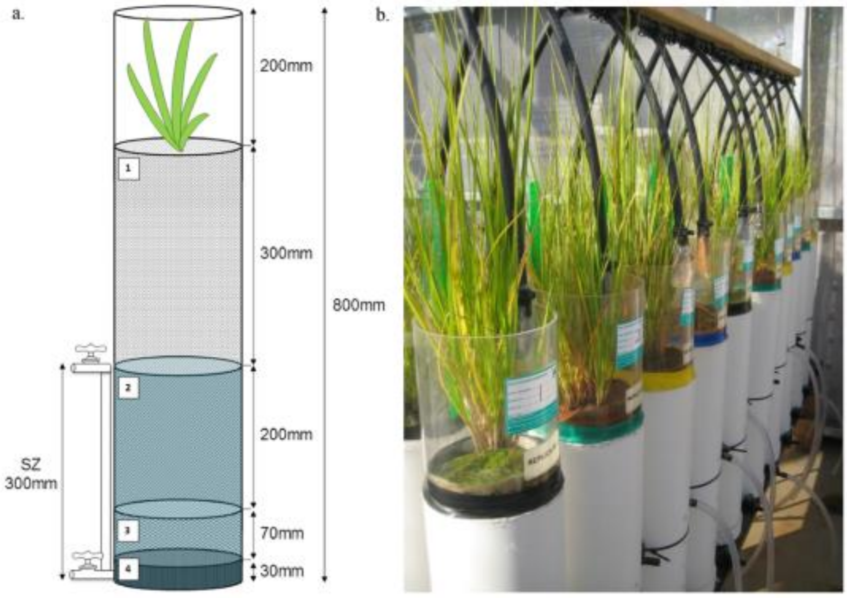

Fig. 1. a. Schematic diagram of the biofilter columns (with SZ riser outlet attached) and b. set-up of biofilter columns in the open-air shade house.

Table 2
Plant growth and morphological characteristics measurement methodology. dw = dry weight.

Characteristic	Method of measurement/calculation	Units
longest root	Manual measurement	mm
longest shoot	Manual measurement	mm
bulk root length (95%)	The length to which 95% of the roots grow to is visually estimated then manually measured	mm
bulk shoot length (95%)	The length to which 95% of the roots grow to is visually estimated then manually measured	mm
number of shoots	Counted manually after disassembling the plants	-
root sub-sample mass (dw)	Scanned roots were dried to a constant weight in a 60 °C oven	g
shoot sub-sample mass (dw)	Scanned shoots were dried to a constant weight in a 60 °C oven	g
total root mass (dw)	Unscanned roots were dried to a constant weight in a 60 °C oven. Unscanned root mass and root sub-sample mass were added determine the total root mass.	g
total shoot and stem mass (dw)	Unscanned shoots and stems were dried to a constant weight in a 60 °C oven. Unscanned shoot mass and shoot sub-sample mass were added determine the total shoot and stem mass.	g
total plant mass (dw)	Sum of total root mass and total shoot and stem mass	g
average root diameter	Calculated by WinRHIZO	mm
root length	Calculated by WinRHIZO. Represents total length of all roots	cm
root surface area	Calculated by WinRHIZO. Represents total root surface area	cm^2
root volume	Calculated by WinRHIZO. Represents total volume of roots	cm^3
shoot length	Calculated by WinRHIZO. Represents total length of all shoots	cm
shoot surface area	Calculated by WinRHIZO. Represents total shoot surface area	cm^2
root length per gram	root length/root sub-sample mass (dw)	cm/g dw
root surface area per gram	root surface area/root sub-sample mass (dw)	cm^2/g dw
root volume per gram	root volume/root sub-sample mass (dw)	cm^3/g dw
shoot length per gram	shoot length/shoot sub-sample mass (dw)	cm/g dw
shoot surface area per gram	shoot surface area/shoot sub-sample mass (dw)	cm^2/g dw
total root length	root length per gram*total root mass	cm
total root surface area	root surface area per gram*total root mass	cm^2
total root volume	root volume per gram*total root mass	cm^3
total shoot length	shoot length per gram*total shoot and stem mass	cm
total shoot surface area	shoot surface area per gram*total shoot and stem mass	cm^2
root length, surface area and volume distributed across root diameter classes	Calculated by WinRHIZO. Root diameter class boundaries: $0 < n < 0.04$, $0.04 < n < 0.08$, $0.08 < n < 0.16$, $0.16 < n < 0.2$, $0.2 < n < 0.25$, $0.25 < n < 0.3$, $0.3 < n < 0.35$, $0.35 < n < 0.4$, $0.04 < n < 0.45$, $0.45 < n < 0.5$, $0.5 < n < 0.6$, $0.6 < n < 0.8$, $0.8 < n < 1.0$, $1.0 < n < 2.0$, $n > 2.0$	mm

of roots were sub-sampled from each plant and spread out over a transparent acrylic tray containing a few millimetres of water to help maintain separation between the roots. The sub-sample size was based on the results of a bootstrapping and sensitivity analysis performed by Payne (2013), who conducted a similar study. The samples were scanned (EPSON Flatbed scanner Expression

Fig. 2. Partial removal of the biofilter column casing allowed visual inspection of the filter media and root architecture.

Fig. 3. Dense root growth at the column base was more extensive in the saturated zone-inclusive biofilters.

10000XL 1.8 V3.49) at a resolution of 800 dpi and analysed using the WinRHIZO software package (v. 2009©, Regent Instruments Canada Inc.). After scanning, the roots were oven-dried at 60 °C to constant weight. Shoots were analysed using a similar approach to the root analysis. First, the healthy shoots from each plant (i.e. shoots not dead or showing signs of die-off) were counted. From these, a sub-sample of 20 shoots was randomly collected and cut into three segments of approximately equal length. The shoots were pressed onto an adhesive sheet to ensure that the whole area of the shoot was visible to the scanner. The shoots were scanned and analysed and then oven-dried at 60 °C to constant weight. The unscanned roots, shoots and stems of each individual plant were also dried to determine total plant biomass, above-ground biomass and root mass.

2.4. Data analysis

The plant morphological data did not all fit the assumptions of normality and homogeneous variability required for parametric tests, even when log-transformed. As such, statistical significance was measured using non-parametric tests. A 2-Independent sample Mann Whitney test (significance accepted at $p < 0.05$) was performed to test for significance between the design configurations (i.e. loamy sand (S) vs. Skye sand (S) and Skye sand (S) vs. Skye sand (NS)). Based on the Bonferroni post-hoc method these values should be multiplied by 2 when testing for significance, however, the reliability of such adjustment methods has been challenged (Perneger, 1998, 1999). In light of this, unadjusted 'p' values are presented to minimise the chance of overlooking a true relationship.

To investigate relationships between plant characteristics and nutrient removal in biofilters, effluent nutrient concentrations from the last water quality monitoring event conducted (i.e. that closest in time to the plant harvest) were correlated with the plant growth and morphology data. This event was conducted in July 2012 during a 'wet' dosing period. Relationships between water quality and plant growth characteristics were investigated across all biofilter configurations simultaneously using a bivariate correlation analysis and quantified by the Pearson correlation coefficient and two-tailed significance tests. To determine if plant characteristics become more or less important during dry spells the water quality results for April (which followed an 18 day dry period) were also correlated with the plant growth characteristics using a bivariate analysis. Although this water quality data was collected four months prior to harvesting it was assumed that plant growth characteristics between these periods would be relative.

3. Results and discussion

3.1. In-situ observations

Visual observation of the plants when the PVC column segments were removed indicated that the roots of *C. appressa* grown in the biofilters containing a saturated zone grew deeper than those with no saturated zone. In the saturated zone-inclusive biofilters, roots typically grew to the base of the columns where they formed a dense mat tightly woven into the shade cloth swatches located between the gravel drainage layer and the outflow pipe (Fig. 3). The formation of a dense mat of root hairs such this has been recognised as a strategy to improve P acquisition in nutrient-poor soils (Shane et al., 2005). In contrast only a small amount of fine roots (<2 mm) were observed in the base of the non-saturated columns. Payne et al. (2014b) also observed shallow root growth in non-saturated biofilter columns planted with *C. appressa*. In heterogeneous soils, roots tend to proliferate in zones with a high availability of nutrients rather than depleted zones, thus maximising the efficiency of each unit of root production (Lambers et al., 2008). Therefore, given that the saturated zone stores nutrient-rich stormwater between events it is not surprising that plants in the saturated zone-inclusive biofilters established deeper root systems.

3.2. Plant growth and morphological analysis

3.2.1. Manual measurements

Neither filter media type nor the presence of a saturated zone had a significant effect on the longest root (Fig. 4a) or bulk root length (Fig. 4b) ($p > 0.05$), however, these measurements were notably more variable in the loamy sand configuration. Longest shoot length was significantly affected by filter media type ($p < 0.01$) although not by the presence of a saturated zone (Fig. 4c).

3.2.2. Biomass analysis

Biofilter media is deliberately nutrient poor so that plants rely on stormwater to meet their nutritional requirements, therefore, nutrient availability to plants is at least partially dependent on the ability of filter media to capture and retain nutrients. Plant biomass allocation was not significantly affected by filter media ($p > 0.05$) (Fig. 5), indicating that plants can successfully acquire nutrients from Skye sand, which therefore can reliably support plant growth.

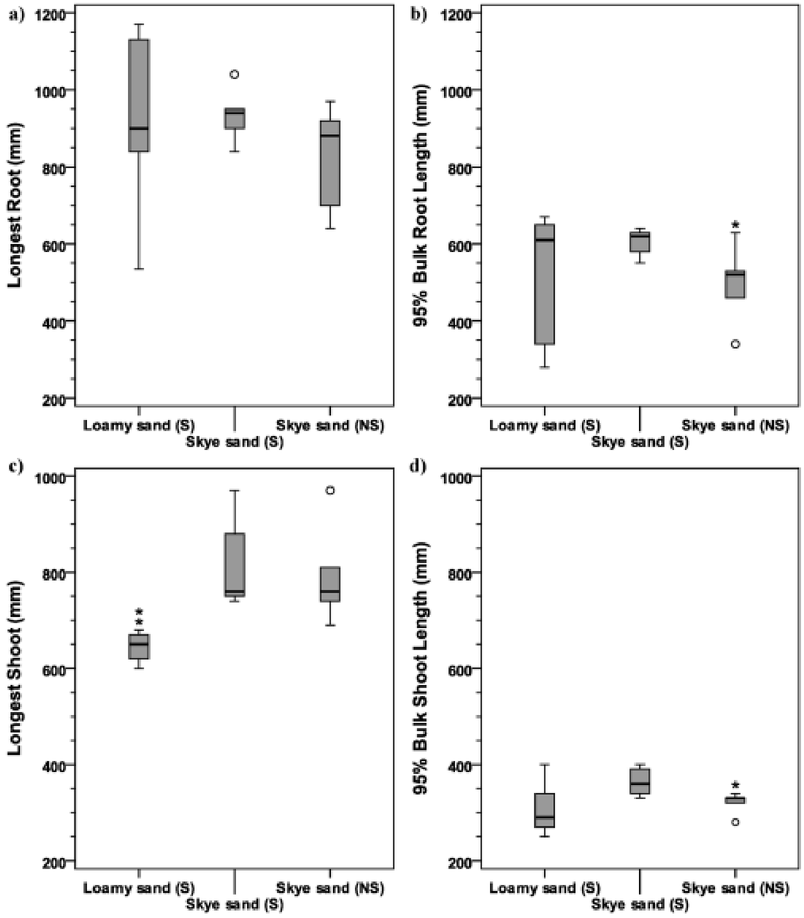

Fig. 4. Effects of filter media and saturated zone on root and shoot characteristics (manually measured) (n = 5). S, saturated zone; NS, no saturated zone. "**" and "*" represent a statistically significant difference ($p < 0.01$ and $p < 0.05$ respectively) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

However, further testing of Skye sand with plant species other than *C. appressa* is warranted.

Inclusion of a saturated zone resulted in plants with a significantly higher total and above-ground biomass ($p < 0.01$) and total number of shoots ($p < 0.05$) (Fig. 5b, d). This implies that prolonged detention promotes increased nutrient acquisition, which is consistent with the findings of other studies (Lambers et al., 2008; Taylor et al., 2005). However, the presence of a saturated zone did not significantly affect total root mass ($p > 0.05$) (Fig. 5a), suggesting perhaps that water stress and poor nutrient diffusion during dry months prompted plants in non-saturated zone inclusive systems to prioritise root growth. Under P-limited conditions plants often increase their root mass, by inhibiting shoot growth in favour of root growth, to increase the absorptive surface area of the root system and improve phosphate acquisition efficiency (López-Bucio et al., 2003; Lynch 1995; Lynch and Brown, 2008).

3.2.3. *Root morphology*

Inclusion of a saturated zone had a significant effect on root traits when scaled for the whole plant ($p < 0.05$) (Fig. 6b, d, f) however, specific root length (i.e. root length per unit root dry mass), specific root surface area and specific root volume were not significantly influenced by inclusion of a saturated zone ($p > 0.05$) (Fig. 6a, c, e). In contrast, filter media type significantly affected root length ($p < 0.05$), surface area ($p < 0.01$) and volume ($p < 0.05$) per unit weight but not when scaled for the whole plant, except in the case of total root length (Fig. 6b). The average specific root length, which is typically used to describe root etiolation ("fineness"), was far greater in the saturated and non-saturated Skye sand configurations (21,200 cm/g and 22,700 cm/g respectively) than the loamy sand (14,000 cm/g). These results imply that *C. appressa* adapts its root architecture in response to growing in Skye sand filter media, most notably by increasing the available absorptive root surface

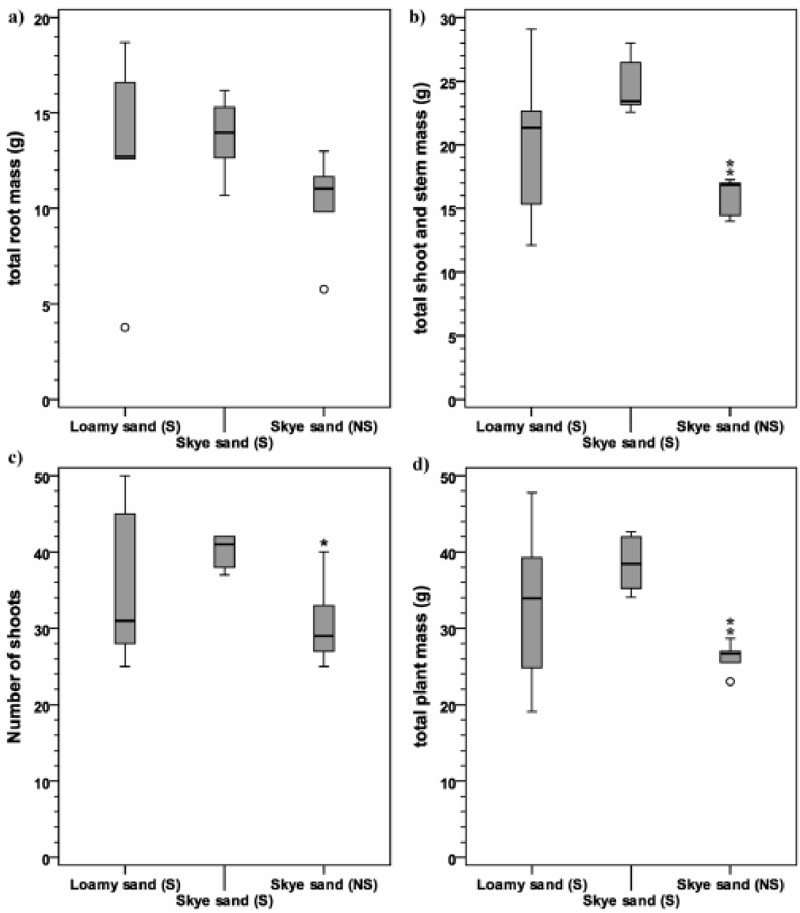

Fig. 5. Effects of filter media and saturated zone on plant biomass allocation (n = 5). S, saturated zone; NS, no saturated zone. '**' and '*' represent a statistically significant effect ($p < 0.01$ and $p < 0.05$ respectively) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

area. This is not surprising, given that Skye sand has a strong affinity for phosphorus sorption and in P-limited environments plants typically favour the development of fine roots, which require less energy to construct and forage through soils (Lambers et al., 2008). However, root etiolation increases exploration at the expense of mechanical strength and also creates vulnerabilities such as high turnover rates, desiccation intolerance, and susceptibility to herbivores (Eissenstat et al., 2000).

3.2.4. Root diameter class characteristics

Neither filter media nor inclusion of a saturated zone had a significant effect on average root diameter ($p > 0.05$), which across the three configurations ranged from 0.13 to 0.19 mm. The root diameter class analysis revealed that, in all biofilter configurations, approximately 80% of total root length and 40% of total surface area was associated with very fine roots <0.16 mm diameter. Accordingly, the root structure of the plants analysed would be considered very fine, with a high proportion of root hairs. In a low-P environment, root hairs may be responsible for as much as 90% of phosphate uptake (Gahoonia and Nielsen, 1998). This is largely related to the high absorptive surface area of root hairs which can account for up to 70% of total root surface area (López-Bucio et al., 2003). The diameter of roots typically involved in ion uptake ranges from 0.15 to 1 mm (Lambers et al., 2008). The percentage of total root surface area associated with roots in this diameter range was between 52 and 60% across all biofilter configurations. This may explain in part why *C. appressa* has consistently been found to provide excellent nutrient removal performance in biofilters (Bratieres et al., 2008; Payne et al., 2014b; Read et al., 2008).

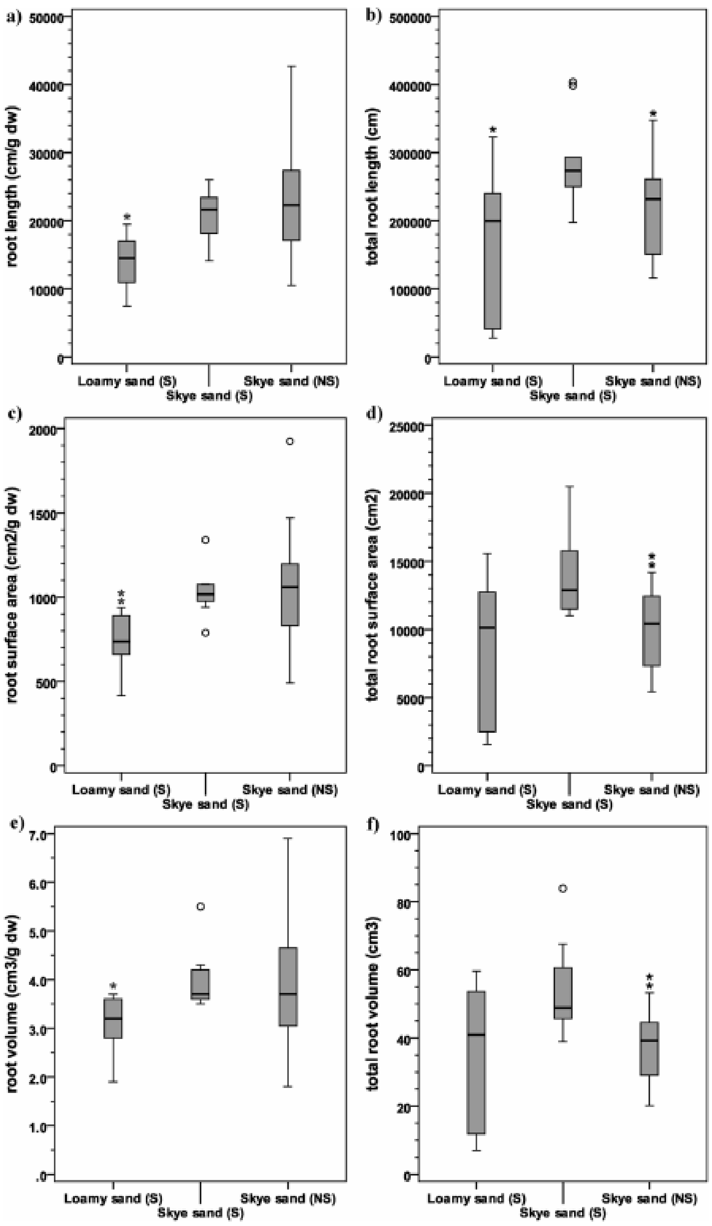

Fig. 6. Effect of filter media and saturated zone on root characteristics per unit root dry mass (a, c, e) and for the entire plant (b, d, f) (measured using WinRHIZO). S, saturated zone; NS, no saturated zone. "**" and "*" represent a statistically significant difference ($p < 0.01$ and $p < 0.05$ respectively) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

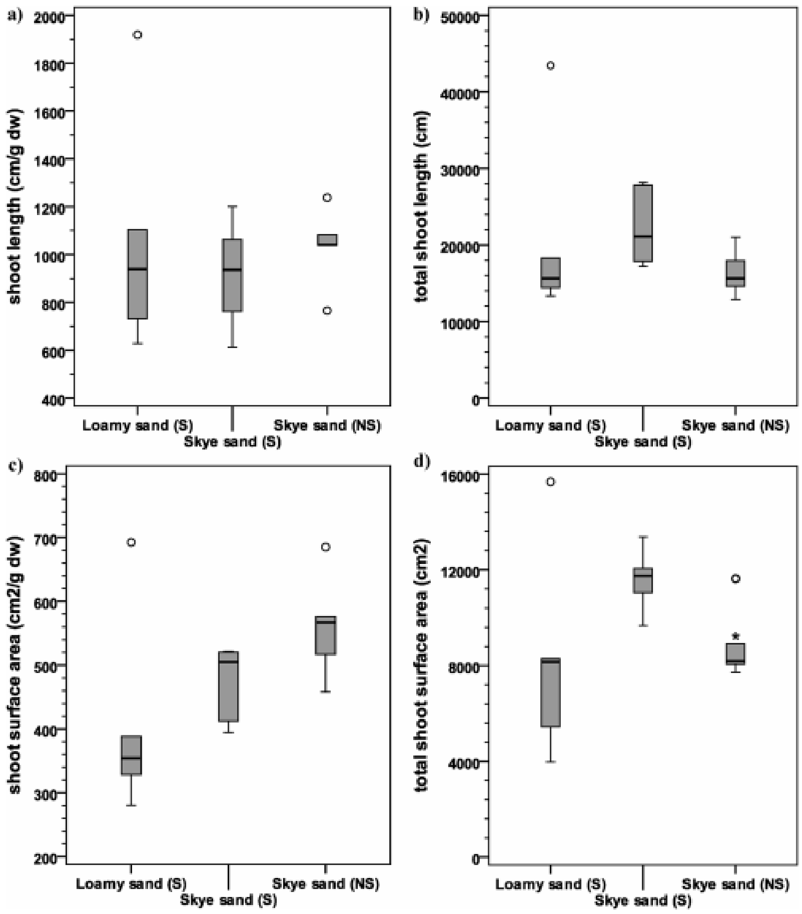

Fig. 7. Effect of filter media and saturated zone on shoot characteristics per gram of roots (i.e. specific shoot characteristics) (left) and for the entire plant (right) (analysed using WinRHIZO). S, saturated zone; NS, no saturated zone. "*" represents a statistically significant difference ($p < 0.05$) compared with Skye sand (S). Data shown are the interquartile range (IQR, box), median (solid horizontal line), 1.5IQR above or below the IQR (whiskers) and outliers (open circles).

3.2.5. Shoot morphology

Shoot length represents the sum of the length of all shoots scanned. Neither filter media nor the presence of a saturated zone had a significant influence on specific shoot length (i.e. shoot length per unit shoot dry mass) or total shoot length ($p > 0.05$) (Fig. 7a, b). Inclusion of a saturated zone significantly increased total shoot surface area in the Skye sand configuration (Fig. 7d) but not specific surface area (Fig. 7c), suggesting that this relationship is being driven by the significant difference in above-ground biomass between the Skye sand configurations (Fig. 5b).

3.3. Correlation between nutrient removal and plant characteristics

Significant correlations between plant biomass characteristics (total plant mass, total shoot and stem mass and total root mass) and nutrient removal (i.e. total nitrogen (TN), nitrate + nitrite (NO_x), dissolved organic nitrogen (DON,) particulate organic nitrogen (PON) and filterable reactive phosphate (FRP)) were observed under both wet and dry conditions (Table 3). When scaled for the entire plant, root traits (total root length, total root surface area and total root volume) also correlated significantly with nutrient removal under wet and dry conditions; this was driven largely by correlations with total root mass. This is demonstrated by the significant correlations between ammonium (NH_4^+) and NO_x concentrations and total root characteristics during the dry and wet periods, respectively (Table 3).

Total phosphorus (TP) concentrations correlated significantly with total shoot and stem mass during the dry period (Table 3). Suggesting that, following dry spells, soil desiccation and formation of preferential flow paths may compromise filter media function, increasing the reliance on adhesion to above ground biomass to

Table 3
Significant (p < 0.05) ("*") and highly significant (p < 0.01) ("**") correlations between plant growth characteristics and nutrient treatment during 'dry' and 'wet' weather periods. Pearson's correlation coefficient values (r) are shown in parentheses.

Characteristic	Water Quality Monitoring Period	
	Dry	Wet
total root mass (g)	NH_4^+ (−0.60)*	TN (−0.75)** NO_x (−0.78)** DON (−0.53)* FRP (−0.57)*
total shoot & stem mass (g)	TP (−0.54)* TN (−0.72)** NO_x (−0.67)** DON (−0.63)* FRP (−0.57)*	TN (−0.73)** NO_x (−0.70)** DON (−0.72)** PON (−0.56)* FRP (−0.68)**
total plant mass (g)	TN (−0.68)** NO_x (−0.66)** DON (−0.56)* FRP (−0.56)*	TN (−0.82)** NO_x (−0.81)** DON (−0.71)** PON (−0.59)* FRP (−0.70)**
total root length (cm)	NH_4^+ (−0.63)* FRP (−0.62)*	TN (−0.63)* NO_x (−0.65)*
total root surface area (cm^2)	NH_4^+ (−0.60)* DON (−0.55)* FRP (−0.66)*	TN (−0.69)** NO_x (−0.70)** DON (−0.55)* FRP (−0.58)*
total root volume (cm^3)	NH_4^+ (−0.56)* TN (−0.58)* DON (−0.59)* FRP (−0.67)*	TN (−0.72)** NO_x (−0.73)** DON (−0.60)* FRP (−0.62)*
average root diameter (mm)		TP (−0.83)** PON (−0.54)*
specific root length (cm/g)	NH_4^+ (−0.60)* PON (−0.54)*	
specific root surface area (cm^2/g)	NH_4^+ (−0.60)*	
specific root volume (cm^3/g)	NH_4^+ (−0.56)* FRP (−0.63)*	
specific shoot surface area (cm^2/g)	PON (−0.54)*	

filter or adhere P-bound sediment. Specific shoot surface area also correlated with PON concentrations during the dry period, further emphasising the role of above-ground biomass in particulate adhesion.

Under dry conditions, no significant correlations were identified between NO_x concentrations and total root characteristics (Table 3), suggesting that during dry periods, when oxygen concentrations become depleted, the division of NO_x removal between plant-uptake and denitrification may shift towards the latter. However, this is unlikely to be the case in the non-saturated 'freely draining' systems in which dry conditions are likely to increase nitrification while limiting conditions for denitrification (Parkin, 1987). Total nitrogen maintained a strong correlation with total root volume under dry conditions driven by correlations between total root volume and NH_4^+ and DON removal (Table 3).

During the wet period, no significant correlations were identified between specific root characteristics (specific root length, specific root surface area, specific root volume) and nutrient removal (Table 3), implying that under wet conditions plant biomass is a more significant driver of nutrient removal than specific root traits. Under dry conditions, all root characteristics, both dependent and independent of total root mass, correlated significantly with NH_4^+ removal. This is perhaps because NH_4^+ removal is governed mainly by rapid adsorption to the filter media and nitrification by soil microbes, which are highly active under wet conditions (Lambers et al., 2008; Mortland and Wolcott, 1965). Accordingly, plant-uptake becomes more critical for NH_4^+ removal during dry periods, when microbial processing slows down and filter media desiccation reduces the effectiveness of adsorption.

Filterable reactive phosphorus and PON were significantly negatively correlated with specific root traits under dry conditions (Table 3). However, biofilter effluent concentrations of FRP and PON were consistently low regardless of design (standard deviation <0.001) (Table 4). Therefore, although statistically significant, these correlations are of little practical importance. This could also be said for the negative correlations between TP and PON concentrations and average root diameter observed under wet conditions, which are also somewhat counter-intuitive because mechanical straining of particulates is typically enhanced by a fine root structure.

The correlations identified between nutrient concentrations and plant characteristics highlight the importance of high plant biomass, in particular root mass, and fine root architecture in facilitating nutrient removal under both wet and dry conditions. These findings corroborate the results of previous studies investigating plant traits that enhance pollutant removal in biofilters. For instance, in a study across 20 plant species, Payne et al. (2014b) found that plants with a high root surface area and root mass performed best in terms of N removal. Read et al. (2010), in a study of 20 plant species, also identified significant correlations between N and P concentrations and total plant mass, total root mass, total root length and the percentage of fine roots (<0.25 mm diameter). Read et al. (2010) found that these characteristics had a strong negative correlation with TP concentrations. This correlation was not observed in the present study because only one species was tested and TP was consistently removed in all biofilter configurations.

3.4. Interactions between design, plant growth and nutrient removal

Analysis of root morphology determined that plants grown in Skye sand filter media had a significantly higher total root length, specific root length, specific root surface area and specific root volume than those grown in loamy sand. Synthesising these findings with the correlations observed between nutrient removal and plant traits infers that using Skye sand filter media would be advantageous for nutrient removal, most notably NH_4^+ during dry periods and NO_x during wet.

Inclusion of a saturated zone significantly increased plant biomass and total root traits. Given that these characteristics correlated significantly with enhanced removal of N and P species during both wet and dry periods, including a saturated zone would be considered advantageous for nutrient removal in stormwater biofilters under all operating conditions. Including a saturated zone also provides additional benefits for biofilters such as protection of roots against the vulnerabilities of increased etiolation and prolonged dry periods.

4. Conclusions

Plants play an essential role in the removal of nutrients from stormwater in biofilters. However, the extent to which plants can assimilate N and P is largely dependent on root structure, stormwater detention time and the ability of plants to acquire nutrients from filter media. The capacity of filter media to provide primary nutrient retention is also a factor. Skye sand filter media had a significant effect on the root morphology of *C. appressa*, increasing total root length, specific root length and root fineness compared with the loamy sand configuration and this increased root etiolation correlated with better nutrient removal. The increased opportunity for nutrient uptake facilitated by prolonged detention was demonstrated by the significantly higher biomass and extensive root system growth in the saturated zone inclusive biofilters. Inclusion of a saturated zone would be recommended in conjunction with Skye sand filter media to protect plants against the vulnerabilities

Table 4
Mean outflow pollutant concentrations (mg/L, n = 5) and removal rates, measured in April (dry period) and July (wet period). Standard deviations are shown in parentheses.

Configuration		Loamy Sand (S)				Skye Sand (S)				Skye Sand (NS)			
Monitoring Period		Dry		Wet		Dry		Wet		Dry		Wet	
TP	Conc. (mg/L)	0.03	(0.004)	0.01	(0.0)	0.03	(0.005)	0.02	(0.008)	0.08	(0.03)	0.03	(0.007)
	Removal (%)	92	(1.1)	98	(0.0)	93	(1.4)	95.6	(1.8)	77	(8.7)	93	(1.5)
TN	Conc. (mg/L)	0.46	(0.1)	0.29	(0.35)	0.16	(0.04)	0.08	(0.04)	0.88	(0.05)	0.68	(0.08)
	Removal (%)	77	(5.1)	88	(13)	92	(2.0)	96.5	(1.4)	56	(2.4)	72	(3.0)
NH_4^+	Conc. (mg/L)	0.017	(0.026)	0.002	(0.001)	0.004	(0.002)	0.001	(0.000)	0.003	(0.002)	0.002	(0.002)
	Removal (%)	95	(7.8)	99	(0.1)	99	(0.7)	99.7	(0.1)	99	(0.6)	99	(0.4)
NO_X	Conc. (mg/L)	0.12	(0.06)	0.16	(0.32)	0.05	(0.02)	0.01	(0.02)	0.54	(0.03)	0.41	(0.05)
	Removal (%)	86	(7.9)	83	(31)	94	(2.9)	98.4	(1.6)	35	(3.7)	55	(4.9)
DON	Conc. (mg/L)	0.24	(0.03)	0.10	(0.03)	0.07	(0.01)	0.04	(0.004)	0.32	(0.01)	0.22	(0.02)
	Removal (%)	56	(6.1)	80	(5.5)	87	(2.3)	92	(0.8)	41	(2.3)	59	(3.1)
PON	Conc. (mg/L)	0.005	(0.0)	0.03	(0.005)	0.005	(0.0)	0.03	(0.02)	0.005	(0.0)	0.05	(0.02)
	Removal (%)	71	(3.4)	94	(0.8)	89	(1.3)	95	(3.6)	94	(2.5)	92	(2.9)
FRP	Conc. (mg/L)	0.002	(0.0)	0.001	(0.0)	0.001	(0.0)	0.001	(0.0)	0.003	(0.0)	0.002	(0.0)
	Removal (%)	99	(0.2)	96	(0.2)	99	(0.2)	99	(0.0)	99	(0.2)	99	(0.2)

of increased etiolation and prolonged dry periods. Future research should be undertaken to validate the use of Skye sand biofilter media by testing its nutrient removal performance in combination with a broader variety of plant species.

Acknowledgements

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A5.2 Plant harvesting photos

Figure A5.1. Plant harvesting activities: column deconstruction, filter media sampling, washing out of plants, separation of roots, shoots and stems, scanning of roots and stems.

A5.3 In-situ plant growth August 2011-2012

Figure A5.2. In-situ plant growth monitoring during the 12 month column study. Columns with the black bands represent the loamy sand (S) columns, yellow the Skye sand (S) and green the Skye sand (NS) columns.

A5.4 Harvested plant photos

Figure A5.3. Photographs of the plants harvested from the loamy sand (S) biofilter columns: replicates 1-5 (top left to right) and a higher resolution composite image of the 1st replicate.

Figure A5.4. Photographs of the plants harvested from the Skye sand (S) biofilter columns: replicates 1-5 (top left to right) and a higher resolution composite image of the 4th replicate.

Figure A5.5. Photographs of the plants harvested from the Skye sand (NS) biofilter columns: replicates 1-5 (top left to right) and a higher resolution composite image of the 5th replicate.

Chapter 6 Appendix

A6.1 Conference Paper: Water Sensitive Urban Design Conference 2013

Long-Term Phosphorus Accumulation in Stormwater Biofiltration Systems at the Field Scale

B. J. Glaister[1], P. L. M. Cook[2], T. D. Fletcher[3] and B. E. Hatt[1]

[1]*CRC for Water Sensitive Cities, Water for Liveability Centre, Department of Civil Engineering, Monash University, Victoria, 3800 (E-mail: Bonnie.Glaister@monash.edu; Belinda.Hatt@monash.edu)*

[2]*CRC for Water Sensitive Cities, Water Studies Centre, School of Chemistry, Monash University, Victoria, 3800 (E-mail: Perran.Cook@ monash.edu)*

[3]*Waterway Ecosystem Research Group, Department of Resource Management and Geography, Melbourne School of Land and Environment, the University of Melbourne, Victoria, 3121 (E-mail: tim.fletcher@unimelb.edu.au)*

ABSTRACT

Previous research has demonstrated that biofilters are an effective technology for the removal of phosphorus (P) from stormwater. However, biofiltration is a relatively new technology and most field-scale systems are still fairly young, therefore little is understood about the long-term ability of biofilters to act as a sink for P. Studies from a board range of disciplines indicate that iron (Fe) and P interactions are an important mechanism for P sequestration in soils. To investigate long-term P retention dynamics and associations between Fe and P in biofilters we collected filter media cores from six biofilters in both Melbourne and Brisbane. The filter media was subjected to a four-step sequential extraction scheme designed to measure P associated with the following phases: I) Bioavailable P; II) P-adsorbed to iron oxyhydroxides; III) P associated with amorphous iron oxyhydroxides; and IV) Organic P. The results suggest that P accumulation varies spatially (areally and with depth) in biofilters. P concentrations were highest in the top 10cm of the filter media and near stormwater inlets. In all biofilters tested, surface layer P was mostly associated with the amorphous Fe and organic phase, which is largely related to the build-up of trapped sediment. P concentrated in the Fe-adsorbed phase increased at lower depths suggesting that Fe-P sorption interactions may play an important role in long-term P retention. This result emphasises the importance of maintaining good hydraulic performance in biofilters, since Fe-adsorbed P may be sensitive to changes in redox potential, leading to release under reducing conditions. These findings may influence how we design biofilters and plan system maintenance to ensure effective long-term P removal.

INTRODUCTION

Widespread implementation of stormwater biofilters has occurred across Australia over the last decade. This is expected to continue since biofiltration has been shown to be one of the most effective WSUD technologies (Davis et al. 2009). Biofilters treat stormwater by filtering through a vegetated porous media, typically loamy sand. As the stormwater percolates through the media, pollutants are removed through a range of physical, chemical and biological processes (Henderson et al. 2007). Removal of phosphorus (P), a major stormwater pollutant of concern, is governed by multiple processes. The bulk of total phosphorus (TP) is particulate-associated, which is removed predominately by physical straining and sedimentation. Removal of dissolved forms of phosphorus, including phosphate, which constitute approximately 44% of TP (Pitt et al. 2005), is facilitated primarily by geochemical processes (adsorption and/or precipitation) (Kadlec and Knight 1996). As stormwater flows through the media “rapid-reversible” P-sorption occurs predominately through electrostatic ion-exchange with outer sphere hydroxyl complexes. Over time slower more irreversible sorption reactions (chemical bonding with inner-sphere complexes) and precipitation of cation-P complexes out of solution can occur (Lucas and Greenway 2008). Biological interactions also play an important role in P removal. Plants increase the availability of sorption sites in the filter media through root growth and oxidation of ferrous iron and provide a removal pathway via direct uptake of PO_4-P by plants and rhizosphere microorganisms (Bolan 1991, Lucas and Greenway 2008, Read et al. 2010). Transition between these biogeochemical pools is dynamic and changes as biofiltration systems establish. Transfer of P into ‘fixed’ geochemical or organic forms releases rapid sorption sites for further uptake and reduces the risk of P mobilisation from reversible sites which are sensitive to changes in the hydro-chemical environment (Boström et al. 1988, Jansson 1987).

Results from field based and laboratory scale biofilter experiments demonstrate very good removal of P from stormwater - when configured correctly (e.g. Davis 2007, Hatt 2009, Henderson et al. 2007, Lucas and Greenway 2008). However, these studies use a “black box” approach to estimate P-removal and therefore do not provide a quantitative measure of P retained in the filter media. Given that biofiltration is a relatively new technology and most field-scale systems are still fairly young, the availability of empirical data about P retention in biofilters remains limited, thus little is understood about the long-term ability of biofilters to act as a sink for P. Consequently, study of long-term P-sorption in bioretention media has mostly been limited to laboratory based experiments (column studies and batch tests) which are not wholly representative of field scale environments (e.g. Erickson et al. 2007, Hsieh et al. 2007). A recent study by Komlos and Traver (2012) investigated long-term P-retention in field scale bioretention system after 9 years of operation using an acid-extraction procedure. This study determined that filter media in the top 10cm of the infiltration bed was saturated with PO_4-P but saturation at deeper depths would not occur for >20 years. This research provided new insight into long-term removal of P in biofilters, however, the extraction method used in this study did not distinguish between the different pools in which P is retained in filter media. This is an important area of research given that P retained in reversible forms (e.g. bound to Fe(III)) may become labile under reducing conditions, which can occur in poorly performing systems or where a saturated zone is included. Furthermore, partitioning of retained P is needed to better understand P-removal and cycling processes in biofilters and accurately estimate the P-removal longevity of systems. The present study aims to address these knowledge gaps by quantifying long-term P accumulation in biofilters and characterising the phases in which P is retained.

METHODOLOGY

Field site descriptions

Three biofilters from Melbourne (Cremorne St., Clifton Hill and Banyan Reserve) and Brisbane (Wakerley, Hoyland St. and Saturn Crescent) were selected for analysis. These biofilters vary in age, size, filter media configuration, vegetation and catchment characteristics (Table 1). All biofilters are located in residential catchments, except for Cremorne Street, which is located within an industrial/commercial area. See Appendix A for detailed site descriptions and filter media core sampling locations.

Table 1. Summary characteristics of the biofilters tested (Ratio refers to biofilter surface area as a proportion of the total catchment area).

Biofilter	Location	Year Constructed	Area (m^2)	Ratio (%)	Filter media depth (mm)	Sediment Pre-treatment
Hoyland St.	Brisbane	2001	720	4%	700	Nil
Cremorne St.	Melbourne	2003/4	11	3.4%	400	Nil
Saturn Cres.	Brisbane	2006	20	2%	400	Nil
Wakerley	Brisbane	2006/7	2865	0.3%	800-1000	Pond
Clifton Hill	Melbourne	2007	200	0.3%	500	Trap
Banyan	Melbourne	2008	3750	1.6%	400	Pond/Marshes

Sample collection and preparation

Filter media cores were manually extracted using 400mm PVC pipes (25mm diameter). The depth of the core void was measured following extraction so that in-situ compaction could be accounted for. The cores were frozen (-2C) until the media could be partitioned and extracted. Filter media from the following depth intervals: 0-10mm; 10-20mm; 20-40mm; 40-80mm; 80-120mm; 150-200mm and; 300-350mm were homogenised before two 0.5g samples were collected. One sample was used to measure the dry weight of the media, by recording the weight of the sample after 24 hours of drying (105°C). The other sample was analysed using the four step sequential extraction scheme outlined in Table 2.

Phosphorus sequential extraction scheme

The following four-step sequential extraction was adapted from existing methods (Jensen 1993, Kostka and Luther 1994, Ruttenberg 1992) to determine selected inorganic and organic pools of P in bioretention media. First, extraction with 0.5M magnesium chloride released loosely sorbed inorganic phosphate (Bioavailable-P). Next, extraction with an ascorbate solution released inorganic phosphate considered sorbed to poorly crystalline or loosely sorbed iron oxyhydroxides (Adsorbed-P). Third, extraction with 0.5M HCl released inorganic phosphate sorbed to or in mineral phase with any remaining amorphous Fe(III) oxides as well as newly formed acid volatile sulfides (AVS) (Mineral-P). The ascorbate and HCl extractions may also liberate P from Al and Mn oxides and carbonate minerals, although, based on the composition of the filter media these contributions are expected to be minimal compared with Fe associated P. Finally, ashing and 0.5M HCl acid extraction was used to release the residual organic phosphorus fraction (Organic-P). These extraction steps are described in Table 2. Each filter media sample was added to a 50mL Falcon™ tube, along with 10mL of the first extractant, and agitated on an orbital shaker table for the designated time period (i.e. Step I – 2 hours). The Falcon™ tubes were centrifuged at 4000rpm for 10 minutes, after which the supernatant was drawn off, filtered (0.45µm) and analysed for PO_4-P using Flow Injection Analysis (molybdenum blue method) (APHA/AWWA/WPCF 1998). The next extraction solution (i.e. Step II) was then added to the filter media sample in the same Falcon™ tube and the process repeated for the required time period. This process was repeated again for extraction Step III. Prior to the final 0.5M HCl extraction (Step IV) the sediment was ashed in a furnace at 450°C for 4hrs. The leftover filter media was then returned to the Falcon™ tube to undergo the last extraction step.

Table 2. Phosphorus sequential extraction scheme.

Step	Extractant	Time	Phases Extracted
I	0.5M $MgCl_2$	Shake for 2hrs	Dissolved Fe(II) Bioavailable P (loosely bound exchangeable P)
II	Ascorbate solution (pH 8) 4g Ascorbic Acid + 10g sodium citrate + 10g sodium bicarbonate in 200mL milliQ	Shake for 24 hrs	Poorly crystalline or loosely sorbed iron oxyhydroxides Adsorbed P (Fe-bound P)
III	0.5 M HCl Cold Extraction (pH <2)	Shake for 2 hrs	Fe primarily amorphous iron oxyhydroxides as well as newly formed acid-volatile sulphide Mineral P (sorbed to or in mineral phase with amorphous iron oxyhydroxides)
IV	Ash Sediment 450°C 0.5 M HCl (pH<2)	Ash for 4 hrs Shake for 2 hrs	Organic P (associated with the organic phase)

RESULTS AND DISCUSSION

Depth profiles showing the total PO_4-P extracted from the filter media are presented in Figure 1. These profiles indicate that spatial distribution of P varies both areally and with depth. The highest P concentration profiles generally correspond to cores surrounding the system inlets. This was particularly evident in Saturn Cres., Clifton Hill and Hoyland St. inlet profiles. Of the 3 inlets at Hoyland St. it is not surprising that concentrations at 'Inlet A' are highest given that this inlet conveys stormwater from the largest of the three contributing sub-catchments into the biofilter. The results indicate that P concentrations are typically highest in the top 10cm of the filter media. This corroborates findings from several other field and laboratory studies which indicate that TSS, TP and heavy metals accumulate in the top 10cm of a biofilter (Feng et al. 2012, Hatt et al. 2007, Komlos and Traver 2012). Despite variation in the design and age of the biofilters tested, the P profiles generally showed consistency in accumulation and phase distribution. The results did not show any clear signs of P-breakthrough, providing confidence that biofilters are being designed in a way which provides good P removal and can effectively retain P in the long-term. The Cremorne St. biofilter demonstrates quite different P accumulation behaviour compared to the other systems (Figure 1). P concentrations in these cores are increase with depth. The cause of this is unclear. Visual inspection of the cores suggested that the organic content of the filter media at lower depths might be higher. However, the P-phase profile for Cremorne St. (Figure 2) revealed that this P is predominately bound in the Fe-adsorbed phase. Further investigation is needed to determine the underlying cause of this behaviour.

Concentrations of PO_4-P are lowest in the cores from the Wakerley and Banyan biofilters. These systems were the largest tested and both include sediment pre-treatment zones. Pre-treatment of TSS would significantly reduce the concentration of TP entering the biofilter. Furthermore, distributing inflow over a large surface area would reduce concentrations across the system. The low PO_4-P concentrations retained in the Banyan system may be attributed to the engineered sand filter media used in place of the typical loamy sand bioretention media. This sand has been shown to have a poor P-removal capacity compared with loamy sand due to a lower ion exchange capacity and low clay fraction (Bratieres et al. 2009). Nonetheless, given that this system has experienced clogging due to insufficient protection from sediment during high-volume flows, we would expect PO_4-P concentrations in the filter media to be higher (see Appendix A for further details). This initially suggests that the filter media might not be functioning effectively in terms of removing PO_4-P. However, water quality monitoring at the site indicates that PO_4-P reduction is quite good. It is therefore suggested that P removal at Banyan Reserve is being driven by the prolific plant growth that is evident at this site.

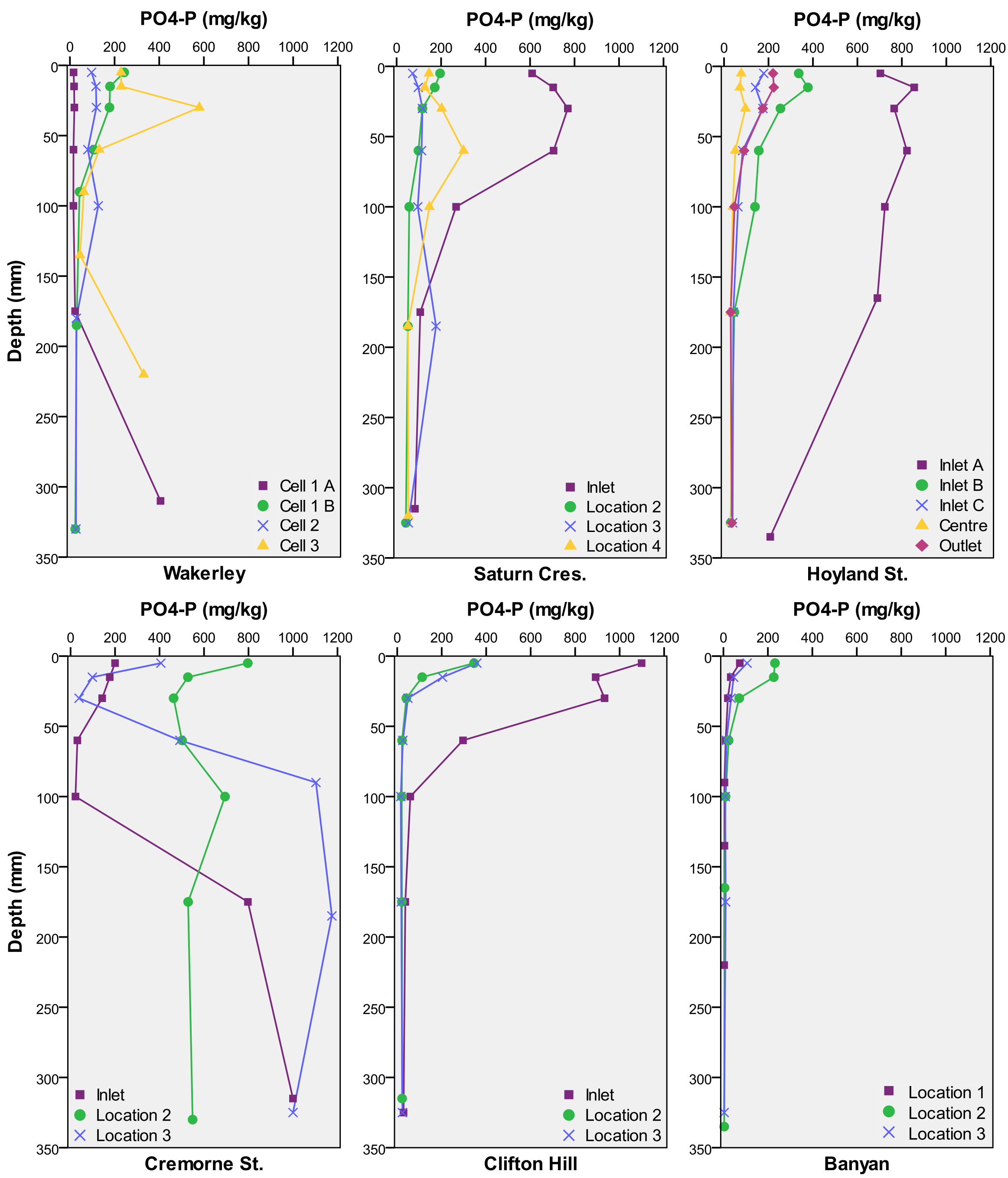

Figure 1. Total PO4-P (mg/kg) extracted from the filter media cores (depth represents mean interval depth). Refer to Appendix A for core sampling location details.

Very low PO_4-P concentrations were evident along the Wakerley biofiltration system 'Cell 1 A' core profile until 310mm where a spike in P concentrations occurred (Figure 2). This behaviour is characteristic of PO_4-P mobilisation in anaerobic sediments. The 'Cell 1 A' core was collected from an area where clogging and permanent ponding (~5cm) had developed. Comparatively, the 'Cell 1 B' core, which was collected nearby in an area without surface clogging, presented a typical P accumulation profile. This suggests that the clogging is driving the difference in these P profiles. Surface clogging changes the redox potential in the underlying filter media creating conditions under which dissimilatory Fe(III) reduction can occur. As a result P-adsorbed to Fe(III) is released back into the soil solution. The reduced Fe(II) and free PO_4-P then migrates down the profile until unsaturated conditions returned causing oxidation of Fe(II) and forming an Fe(III) rich layer within which PO_4-P is readily captured. This explains the spike observed in the ‘Cell 1 A’ PO_4-P profile. Surprisingly though, the P phase profile indicates that at this depth P is mostly associated with the organic phase, rather than the Fe-adsorbed or mineral bound phases, where we would expect it to be under these conditions (Figure 2). This could be explained by conversion of Fe-bound P into organic forms through microbial uptake, although further investigation would be required to confirm this. Nonetheless, the distinctive difference in the ‘Cell 1 A’ and ‘B’ profiles demonstrate the sensitivity of P retention to changes in redox potential and emphasises the importance of maintaining good hydraulic performance in biofilters.

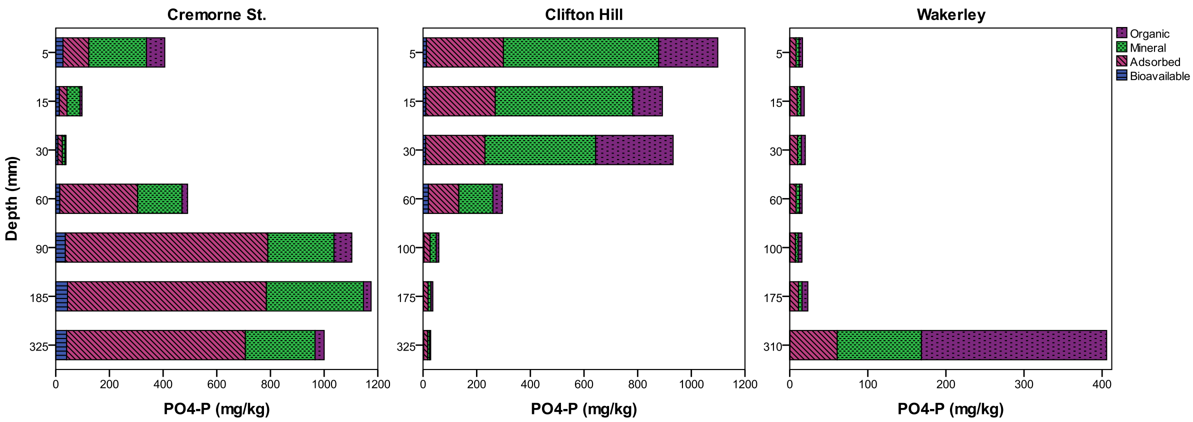

Figure 2. PO4-P concentration (mg/kg) profiles of P associated with the following phases: Bioavailable P, Fe-adsorbed P, Mineral-bound P and Organic P, in the Cremorne St. (Location 2), Clifton Hill (Inlet), and Wakerley (Cell 1 A) cores. Y-axis values represent the mean depth of the filter media segment. Note x-axis scale change for Wakerley.

The Clifton Hill profile shown in Figure 2 illustrates the typical P phase distribution observed for the cores analysed. In the top 10cm of the filter media, where concentrations are generally highest, P is concentrated mostly in the mineral and organic bound phases. This observation was generally consistent between the biofilters and is likely associated with sediment accumulation at these depths. Build-up of organic detritus on the surface, from plant die-off and incoming leaf litter, also contribute to the organic-P present at these depths. Designing systems to include sediment pre-treatment or gross pollutant traps to capture TSS and incoming organic detritus may reduce build-up of these in the filter media and improve biofilter P life-span.

An increase in the Fe-adsorbed P phase was observed with depth across all biofilters (Figure 3). This may correspond with decreasing sediment accumulation, meaning the concentration of rapid sorption from dissolved P in stormwater. Reduced acquisition of P from Fe-adsorption sites, by plants and other soil microbes at lower depths may also be a factor. The gradual reduction in the organic phase-P along the filter media profile is attributed to the decreasing density of plant roots and sediment accumulation. The individual biofilter P-phase profiles show that there is very small quantities of bioavailable-P present in the filter media (Figure 3, right). This result is not surprising given that bioavailable-P present is readily transferred into other phases. Particularly low bioavailable-P concentrations were found at the Brisbane sites (Wakerley, Saturn Cres., Hoyland St.), which may be due to the extended dry period which preceded the sampling (~30 days). The mean percentage of total P extracted by phase across all biofilters is illustrated in Figure 3 (right). The biofilters are listed on the x-axis in order of youngest to oldest. The decline in P associated with the Fe-adsorbed phase suggests that over time P transfers into mineral complexes or into an organic form via biological uptake. This suggests that P captured in the media slowly moves into more “fixed’ forms which enable long-term retention. As previously discussed, the cause of the large fraction of Fe-adsorbed P in the Cremorne St. biofilter is unclear at this time.

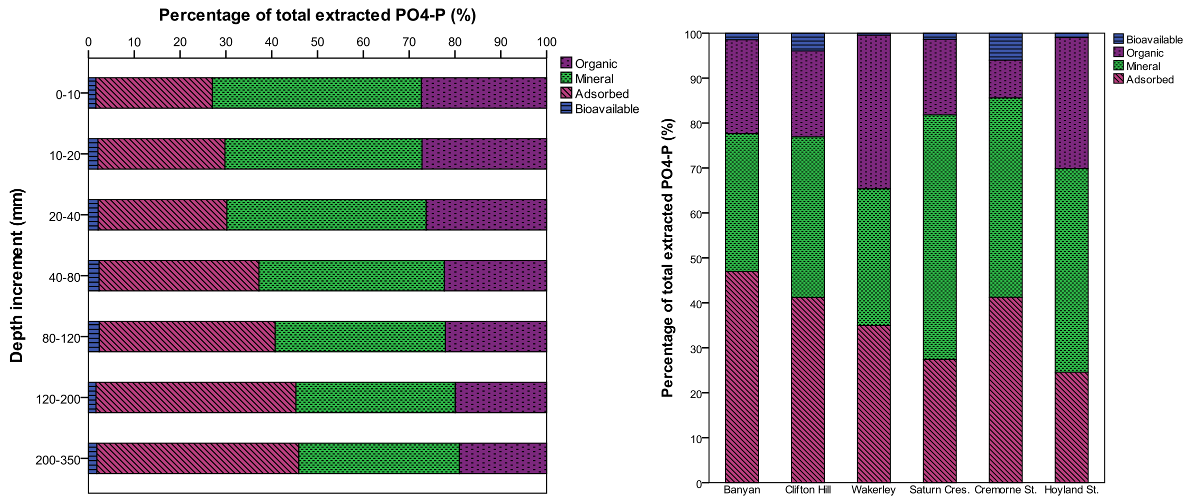

Figure 3. Mean percentage of total PO4-P extracted from each phase across all samples analysed as a function of depth (mm) (left) and on a per biofilter basis (right).

CONCLUSIONS

This study used a sequential extraction scheme to analyse P concentration and distribution in six biofilters of varying age, size and catchment characteristics. The results show that phosphorus removal varies spatially (areally and with depth) within biofilters. P accumulation is most concentrated in the top 0-10cm of the filter media and in areas surrounding the inlet. At the surface P is mostly associated with TSS and found in the mineral-bound and organic phases. At lower depths (>10cm) the concentration of iron-bound P increases coinciding with a decrease in mineral and organic bound P fractions. This also correlates with a decreasing density of plant growth and rhizosphere activity, which is responsible for transforming P into the organic phase. The large fraction of Fe-adsorbed P emphasises the importance of maintaining good hydraulic function in biofilters given that this P-pool has the potential to become mobile under oxygen depleted conditions. These results highlight the contribution that Fe-P interactions have in P-retention. Despite the distinctive variation in the design and age of the biofilters tested, the results generally showed consistency in PO_4-P accumulation and distribution between phases, with some exceptions. No clear signs of P-breakthrough were observed, offering positive reinforcement that the current biofilter design specifications are producing systems which function well in the long-term.

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A6.2 Field study site descriptions

Wakerley, Brisbane

The Wakerley biofiltration system (Figure A6.1) forms the second part of a two stage treatment train where runoff is temporarily suspended in a sediment basin before entering one of three biofilter cells. The layout of the cells is illustrated in Figure A6.1. With a total treatment area of 2865m2 the Wakerley bioretention basin is the largest in Queensland sized at 0.3% of the contributing 87ha residential catchment. The Wakerley filter media meets guideline specifications (FAWB, 2009b) and varies from 800mm deep in Cells 1 & 2 to 1000mm in Cell 3. Cell 3 also includes a saturated zone (900mm), designed to increase detention time and facilitate denitrification. The vegetation selection differs between the cells and includes a variety of groundcovers, grasses and sedges (e.g. *Cyperus ecaltatus, Juncus usitatus, Lomandra hystrix, Carex appressa*). Cells 1 and 2 also include a variety of trees (e.g. *Melaleuca linarifolia*). The locations where filter media cores were collected from the biofilter are indicated in Figure A6.1.

Figure A6.1. Site photo from the Wakerley bioretention system (top) and schematic diagram outlining the location of filter media cores extracted from the Wakerley biofilter cells (bottom) (not to scale).

Hoyland Street, Brisbane

The Hoyland Street bioretention system, constructed in 2001, is understood to be the second oldest biofilter in Australia (Figure A6.2). The system is designed to treat runoff from the surrounding catchment (1.8ha) before discharging into Bald Hills Creek. The surrounding catchment is made up of three sub-catchments, which drain separately into the Hoyland Street system via three individual inlets (see Figure A6.2). The main inlet (A) conveys runoff from the largest of the three sub-catchments (1.034ha). Inlet B flows from the smallest contributing sub-catchment (0.228ha) and inlet C conveys flow from the southern sub-catchment (0.297ha) (Davis, 2009). The catchment ratio of the bioretention basin is approximately 4% (Davis, 2009). A steep grassed embankment on the upstream side of the catchment also contributes some overland flow into the system. The filter media depth in the Hoyland Street system is approximately 700mm (Dalrymple, 2012). The system is densely vegetated with both trees (*Melaleuca Quinquenervia*) and grasses (*Lomandra Longifolia*), *Pittosporum revolutum* are also planted on the system batters (Davis, 2009). Figure A6.2 describes the Hoyland street biofilter and the locations from which filter media cores were sampled.

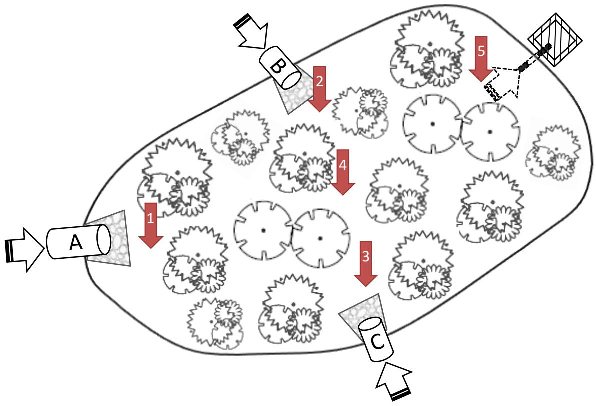

Figure A6.2. Site photo of the Hoyland St. biofilter (left) and a schematic diagram outlining the location of the filter media cores extracted from the system (not to scale) (right).

Saturn Crescent, Brisbane

The Saturn Crescent bio-pod in Brisbane's north-west is a relatively small system ($20m^2$) which services a $900m^2$ low density residential catchment (Figure A6.3). The filter media composition meets the FAWB soil filter media guideline specifications (FAWB, 2009b) and has a depth of approximately 400mm (Dalrymple, 2012). The vegetation consists of groundcover plants including blue flax lily (*Dianella caerulea*) and knobby club rush (*Ficinia nodosa*) (Dalrymple, 2012). The locations where filter media cores were collected from the biofilter are indicated in Figure A6.3.

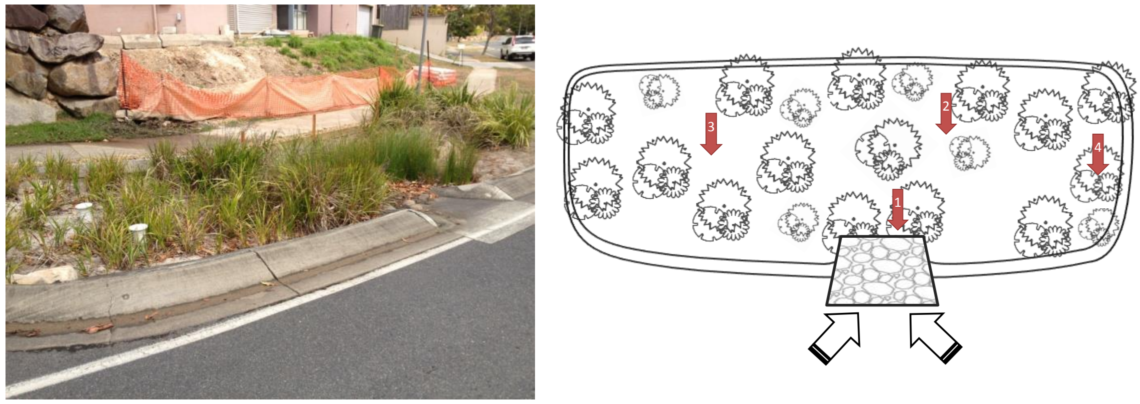

Figure A6.3. Site photo of the Saturn Crescent biofilter (left) and a schematic diagram outlining the location of the filter media cores extracted from the system (right) (not to scale).

Cremorne Street, Melbourne

The Cremorne St. bioretention system located in Melbourne's inner east was the first example of incorporating WSUD into an extremely confined and built up predominately commercial/industrial inner urban area (Melbourne Water, 2004). The system consists of 29 bioretention cells which have been built in traffic outstands along the street. The cells contain sandy loam filter media (200-600mm) and vegetation (e.g. *Carex appressa, Isolepis nodosa, Lepidosperma, Lomandra and Lophostemon*). The biofilter cell sampled (Figure A6.4, left) comprises and area of 13m², representing 16.3% of the total contributing catchment (80m²); which is also serviced by several other biofilter cells. Figure A6.4 (right) illustrates the location where the filter media cores collected from the biofilter cell.

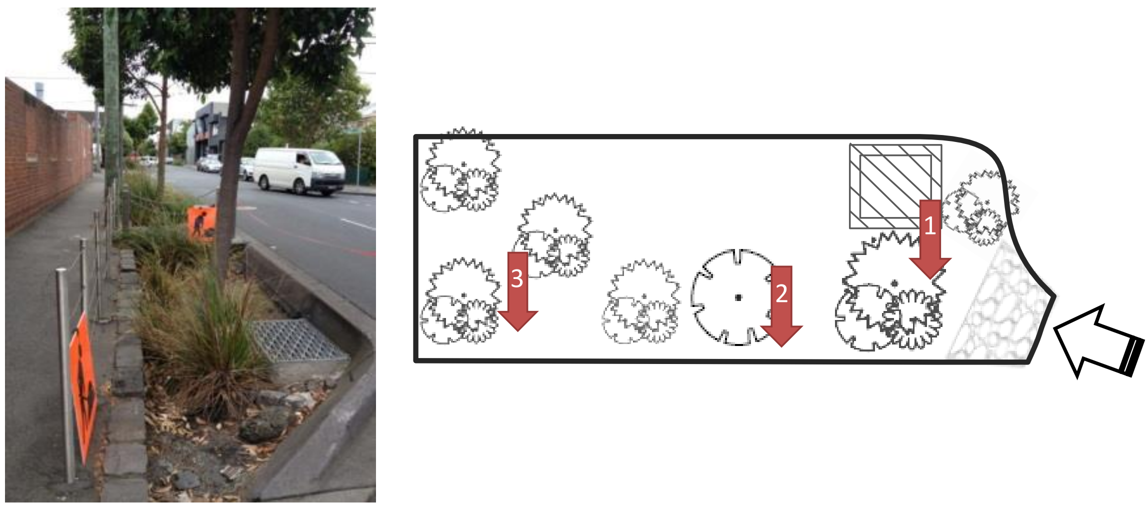

Figure A6.4. Site photo of the Cremorne St. biofilter (outstand Z2) (left) and a schematic diagram outlining the location of the filter media cores extracted from the system (not to scale) (right).

Clifton Hill, Melbourne

The Clifton Hill biofiltration system (Figure A6.5, right) is one component of a stormwater treatment train which treats residential runoff from a 7.3ha catchment prior to release to Merri Creek. The system directs stormwater into a sediment trap then through separate inlet pipes into to two parallel biofilters, each 100 m² in area, in total representing 0.3% of the catchment area (Hatt et al., 2012b). The biofilters are sealed with a 1mm HDPE liner and comprise a 400 mm deep filter media layer underlying 100 mm of topsoil planted with *Calocephalus lacteus*, *Poa labillardieri (sapling)*, *Centella cordifolia*, *Ficinia nodosa*, and *Lycopus Australia* (Hatt et al., 2012b). Treated water is collected through a 100 mm slotted pipe in the drainage layer then conveyed, along with untreated overflow which is collected through grated pits when ponding exceeds 175mm, is directed into a small wetland prior to discharge into Merri Creek (Hatt et al., 2012b). Figure A6.5 describes the treatment train and the locations where filter media cores were sampled.

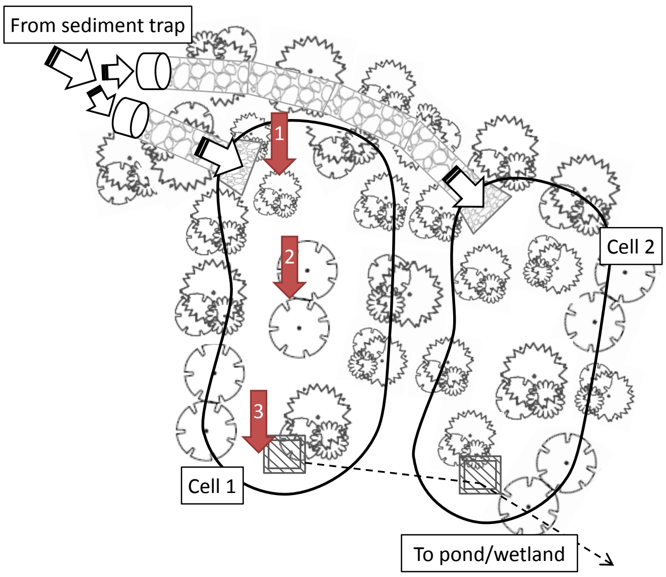

Figure A6.5. Site photo of the Clifton Hill biofilter (top) and a schematic diagram outlining the location of the filter media cores extracted from the system (not to scale) (bottom).

Banyan Reserve, Melbourne

The Banyan Reserve bioretention system located in Melbourne's south-east is the final stage in a stormwater treatment train designed to improve water quality within the Boggy Creek Catchment and provide local wildlife habitat (Figure A6.6). The bioretention system was constructed in an existing stormwater retention pond, and was the first example in Melbourne of a retrofit of this type. The biofilter was also one of the first constructed to include a saturated zone to enhance denitrification.

Stormwater flows are directed into the system via a gross pollutant trap and pre-treatment zone, consisting of an open water sedimentation pond and a vegetated wetland area (deep and shallow marsh), finally stormwater enters the biofilter zone which has an area of 3750 m^2 (thus making up only 0.32% of the impervious catchment compared to a typical design of 2%) (Hatt et al., 2012a). During high flow events (>ARI) the pre-treatment zone is bypassed and stormwater is conveyed via an overland flow channel directly into the biofilter. The biofilter media (engineered sand) has a depth of 400mm and overlies a transition layer (100mm washed sand) which includes hardwood chips for denitrification (Hatt et al., 2012a).

The undersized nature of this system, as well as insufficient protection from high flows and sediment, has led to extensive clogging of the biofilter to the extent that the system is almost permanently ponded; except for after extended antecedent dry weather periods. Consequently, the biofilter now functions more like a wetland, with retention times well beyond that considered for biofiltration. When ponding exceeds a depth of 1000mm untreated water overflows into grated pits located at various points within the biofilter as well as at the outlet (these conditions were present at the time of core extraction). Originally the biofilter was planted with twelve native Australian species including *Carex appressa*, *Ficinia nodosa*, *Juncus amabilis* and *Melaleuca ericifolia* (Hatt et al., 2012a). However, the permanent ponding has caused prolific growth of aquatic plants, many of which were not planted at the time of establishment.

Figure A6.6 describes the treatment train and the locations where filter media cores were sampled.

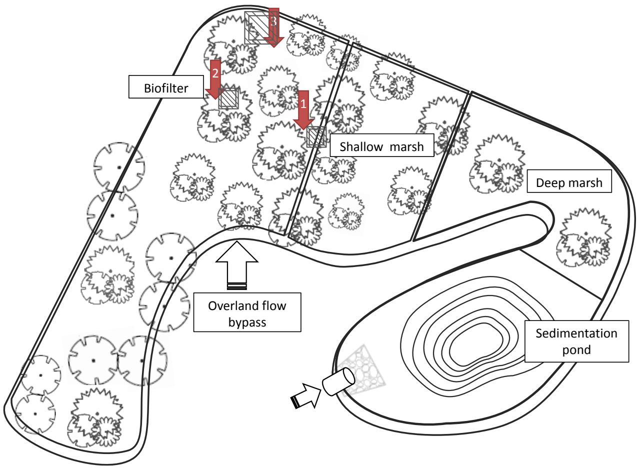

Figure A6.6. Site photos from the Banyan Reserve bioretention system (top) and a schematic diagram outlining the location of the filter media cores extracted from the system (not to scale) (bottom).

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A6.3 Cross-sectional images of the biofilter columns

The following images of the biofilter columns were taken prior to collection of filter media for P analysis. The filter media layers can be clearly visualised as can the extent of plant growth.

Figure A6.7. Loamy sand (LS-V-S) biofilter columns replicates 1-5 (left to right).

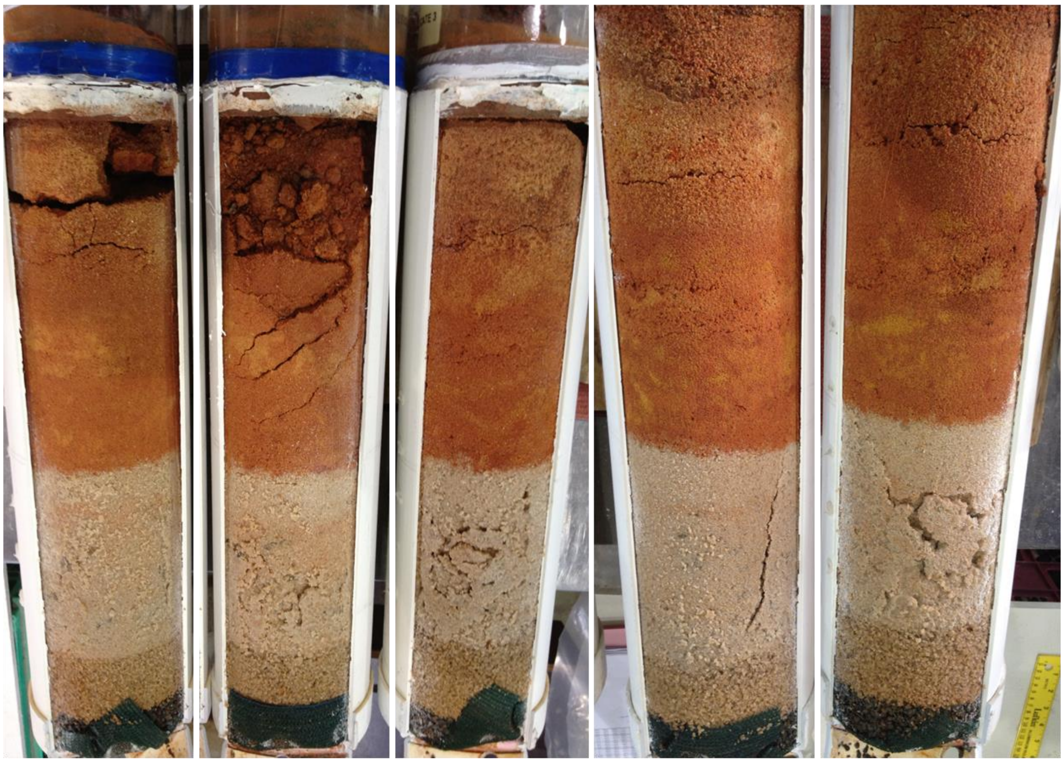

Figure A6.8. Skye sand (SS-NV-S) biofilter columns replicates 1-5 (left to right).

Figure A6.9. Skye sand (SS-V-S) biofilter columns replicates 1-5 (left to right).

Figure 6.10. Skye sand (SS-V-NS) biofilter columns replicates 1-5 (left to right).

A6.4 Cross-sectional images of the filter media cores

Wakerley, Brisbane

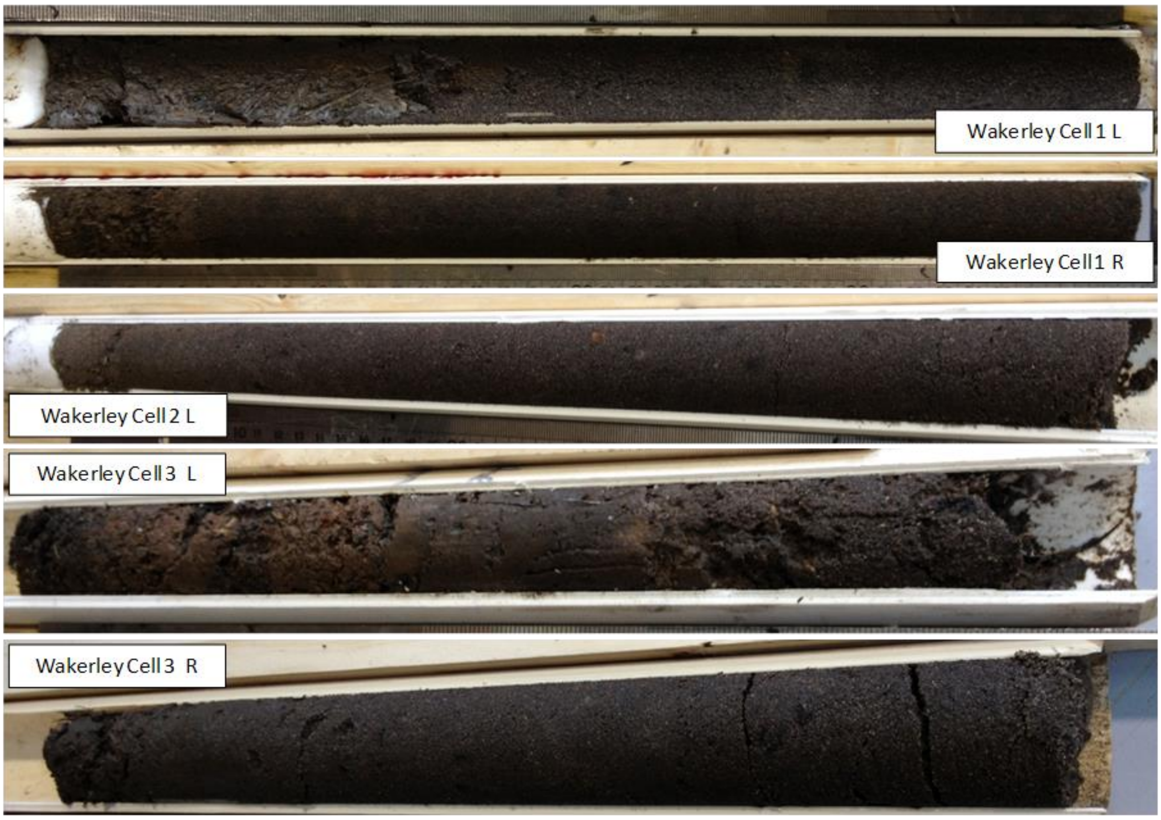

Figure A6.11. Filter media cores from the three cells of the Wakerley bioretention system.

Hoyland Street, Brisbane

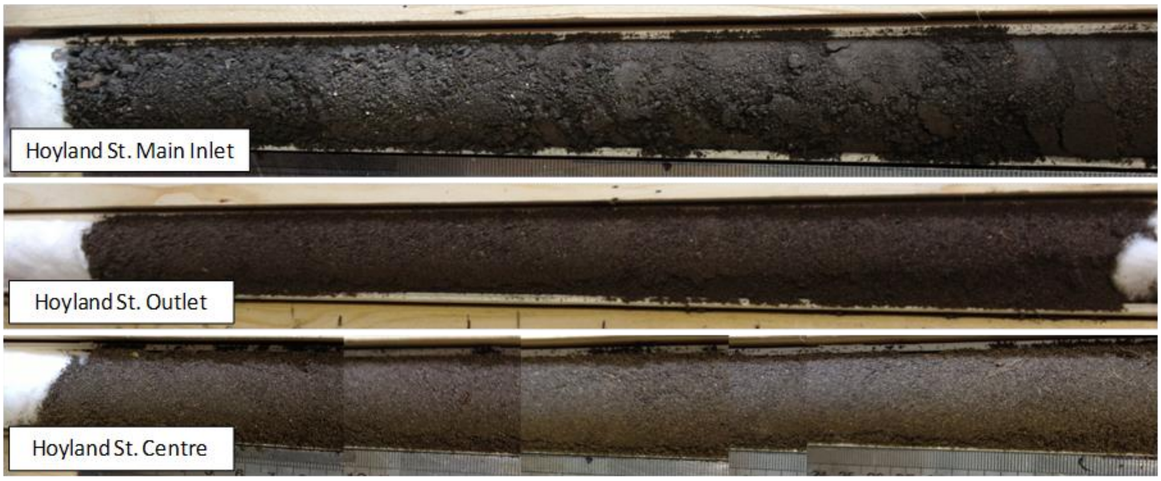

Figure A6.12. Filter media cores from the Hoyland Street biofiltration system.

Saturn Crescent, Brisbane

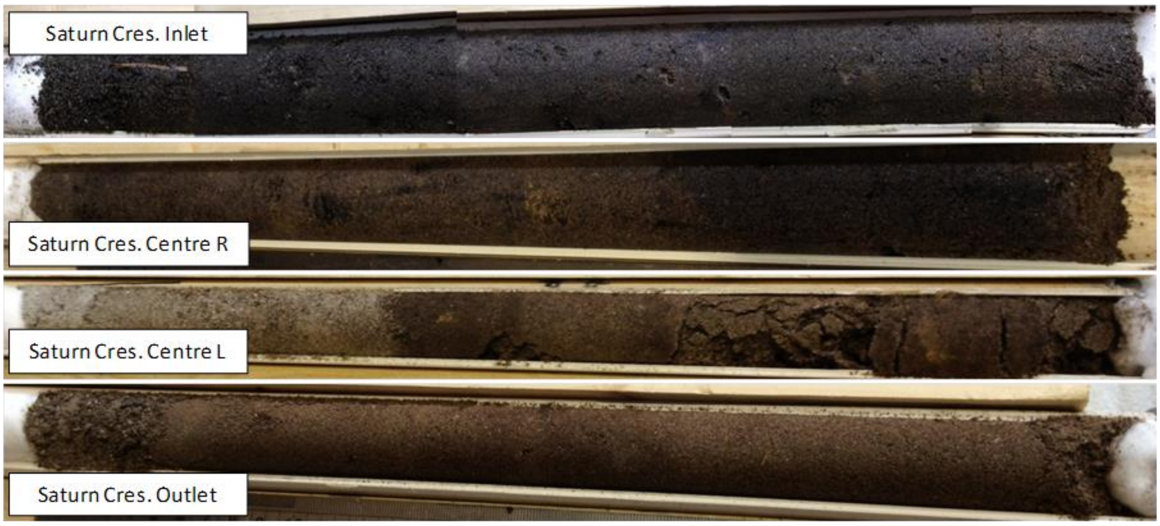

Figure A6.13. Filter media cores collected from the Saturn Crescent biopod-biofilter.

Cremorne Street, Melbourne

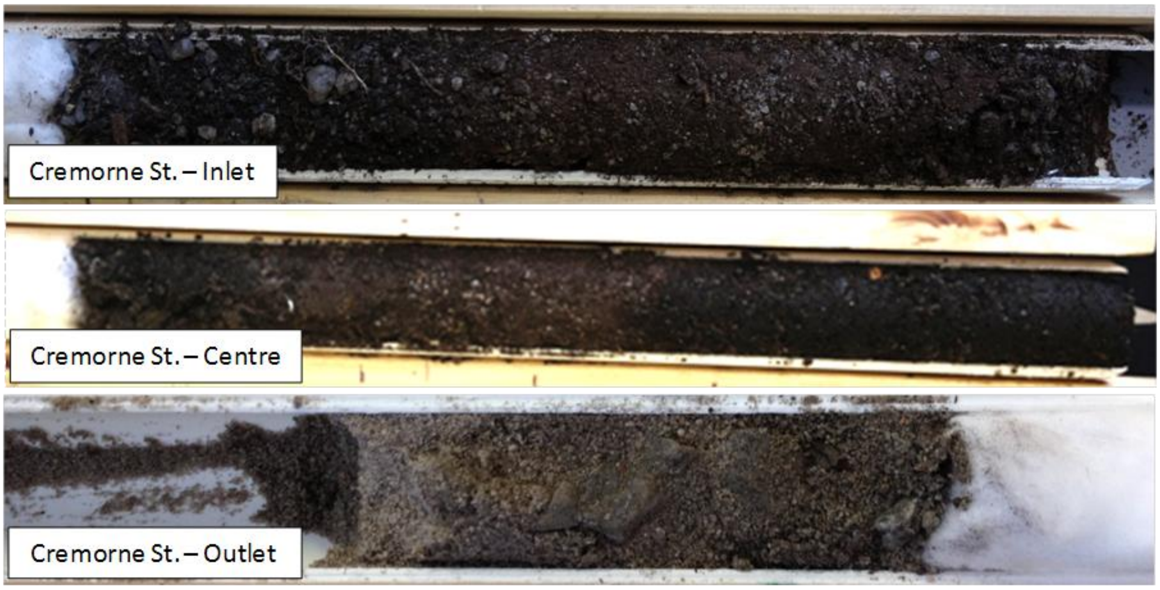

Figure A6.14. Filter media cores and partial cores (top and bottom) collected from the Cremorne Street biofiltration system.

Clifton Hill, Melbourne

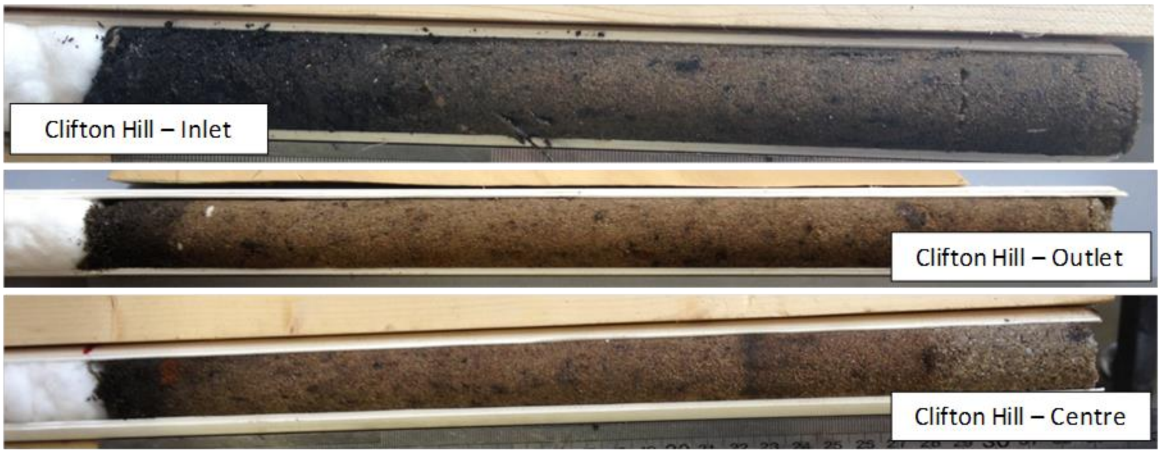

Figure A6.15. Filter media cores from the Clifton Hill biofiltration system.

Banyan Reserve, Melbourne

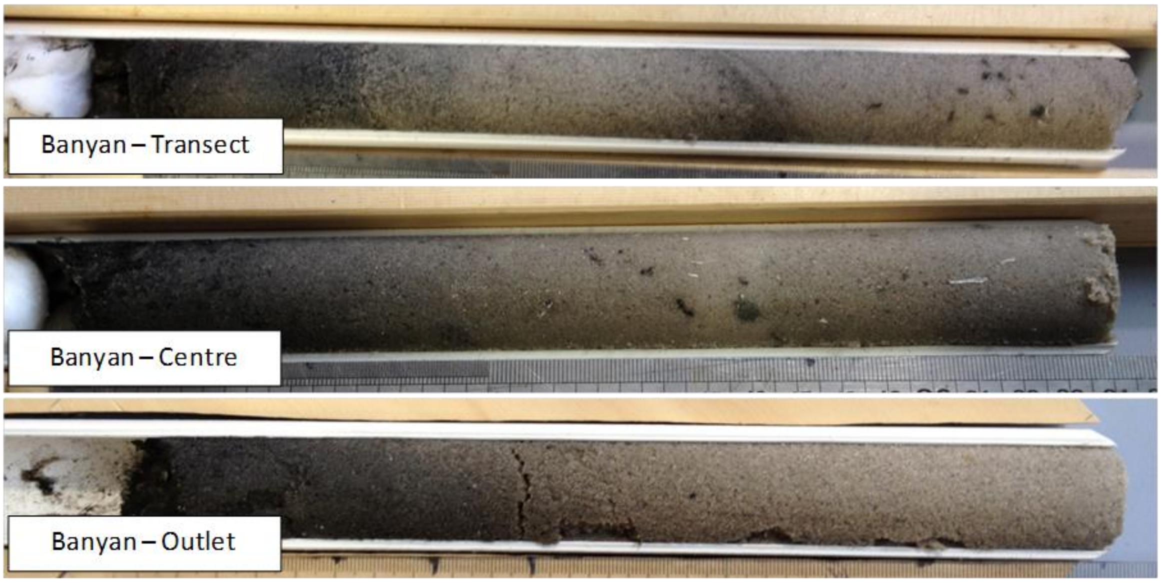

Figure A6.16. Filter media cores from the Banyan Reserve bioretention system.

THE END