WESTERN SYDNEY UNIVERSITY

Laboratory simulations of the City of Sydney's stormwater biofilter units to assess the impact of design, fill variation and substrate amendment on pollution removal efficiency

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Statement of authentication

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I certify that the work presented in this thesis in fulfilment of the requirements for the degree of Doctor of Philosophy is, to the best of my knowledge, original, except for those parts as acknowledged in the text by reference, and that the material has not been submitted, either in full or in part, for any degree enrolled at this or any other institution. I certify that I have complied in all other respects with the rules, requirements, procedures and policy relating to the award of this Degree at the Western Sydney University

[redacted]

James Macnamara

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Abstract

In 2013, Western Sydney University (WSU) formed a research partnership with the City of Sydney Council (City) to investigate the performance of street stormwater biofilters (raingardens) mainly in the Southern Sydney area. The City was in the process of constructing 21,000 square metres of bioretention systems as part of their Decentralised Water Master Plan for improving the quality of stormwater runoff to Port Jackson, the Cooks River and the historical Botany Bay. The City's program provided an excellent example for exploring urban stormwater biofiltration systems. The thesis reports on the completed laboratory component of the investigation, with the field component being ongoing. The laboratory component was intended to inform the design, potential performance and maintenance of field biofilters, and to establish a transferable simulation technology. In the laboratory biofilter simulations, synthetic stormwater was fed to 104 mm diameter soil columns with the same vertical cross-sections and fill material as the street units. Sufficient time was allowed for the development of biochemical processes, and removal results were compared with relevant local pollution reduction targets. A 104 mm column diameter minimised the edge effect associated with narrower columns, while containing the cost and spatial footprint of the equipment to facilitate technology transfer. This prohibited column planting as is possible in larger experiments, giving a potentially conservative result. Of particular interest to the City was the removal of Total Nitrogen (TN) and Total Phosphorus (TP), as indicators of eutrophication potential, with respective removal targets of 45% and 65% in terms of the City's Development Control Plan (DCP). In addition, the removal of the heavy metals zinc, copper, nickel, cadmium, lead and chromium as potential ecological toxicants, and the release of total suspended solids (TSS) from new media, were investigated. The median removal efficiency for TN and TP in both monophasic and biphasic biofilter designs was >65%, complying with local field unit specifications. While elevation of TN removal in biphasic designs was noted, suggesting the development of bacterial denitrification in the simulated saturation zone, this was not statistically significant at $p = 0.05$. Improved performance would, however, be likely in field units because of increased carbon levels from the planted area and stormwater contamination. The median removal efficiency for both designs for heavy metal toxicants was >75%, with median removals of >90% for lead and the potentially carcinogenic cadmium. The researchers have suggested that copper and zinc be added to the City's targets as an indicator of road-derived pollution. Results of simulations involving two different fills used by the City's field unit designs pointed to a need to provide quarries with fill specifications if the release of fine particulates as SS for a prolonged period was to be avoided. Experimentation was also extended to potential augmentation or “amendment” of biofilter fills with recycled substances presently not used in field units, but with the potential to improve performance and increase service life. Biochar, blast furnace slag, crushed concrete, gypsum and zeolite were applied at rates of between 0.38 to 30% w/w to the biofilter fill, with significant improvements in removal efficiencies being obtained for lead using gypsum, lead and cadmium using recycled crushed concrete, and lead, copper and zinc using biochar. Significant improvement was also noted for TSS with both gypsum and crushed concrete amendments. All amendment materials significantly increased fill hydraulic conductivity with the exception of biochar, which reduced hydraulic flow to unacceptable levels. The research highlights the knowledge gap in recycling and reuse of industrial products, particularly gypsum and crushed concrete, opening an avenue for diverting these waste materials from landfill and beneficially improving pollution removal performance of the biofilter designs. The study concluded that simplified, low-footprint soil column simulations of decentralised water treatment devices, such as street stormwater biofilters, can be successfully applied to improvements in design, performance and maintenance cycles, with potential for the same simulation equipment to be used for performance-testing of commercial fills, avoiding subsequent costly remediation operations for field units. Overall, the study contributed materially to biofilter design and operation for purifying street stormwater runoff to promote safe and sustainable water recycling and secure high-quality environmental flows, with implications for technology transfer and hence contribution to global water security.

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Chapter 1: Introduction

1.1. The nature of the research

Laboratory simulation of the street stormwater biofilter units as operated in Southern Sydney was carried out to assess the potential impact of design, fill variation and substrate amendment on pollution removal efficiency under warm temperate conditions, in order to guide future construction and operation of these field units and provide standard procedures for future laboratory research.

The simulation series consisted of four core experiments:

i. The development of the biofilter simulation column array emulate design standards used in the local units and aspects of soil column experiments carried out elsewhere (Yang et al., 2010, Hatt et al., 2007). In this experimental phase, general operational procedures were also tested and established.
ii. The assessment of pollution removal efficiency of biofilter design variations including monophasic and biphasic configurations, the latter including a saturation sump to enhance bacterial denitrification activity.
iii. The assessment of fill variation in terms of TSS release, hydrological and pollution removal performance. A study was undertaken to compare two proprietary fills, investigating the potential effect that alternative fill specifications had on biofilter performance.
iv. The assessment of TSS release, hydrological and pollution removal performance of biofilters based on substrate amendment with recycled materials including blast furnace slag (BFS), biochar, crushed concrete, gypsum and zeolite at amendment rates of between 0.38 and 30% w/w.

Accompanying the main experiments were several supportive and supplementary experiments, which included:

i. The development of a synthetic stormwater with characteristics designed to test biofilter pollution removal efficiency.
ii. Particle size distribution and chemical composition analysis to characterise fill properties and qualities.
iii. Hydraulic testing, including soil infiltration and subsurface flow rate experiments.
iv. Testing of fill amendments in full-column settings.

v. Biofilter simulation assessing the potential impact that sidewall preferential flow paths had on column hydrological performance.

The need for a number of core, supplementary and supportive experiments led to a complex study design as summarised in Figure 8, chapter 2.

The simulation experiments were carried out in building K29 of the Environmental Science laboratories of the Hawkesbury Campus of the Western Sydney University (WSU) in Richmond, New South Wales (NSW). Details of the column design, fill materials, synthetic stormwater composition and operational procedures are given in chapter 2. In order to produce simulation columns in which filtration and biochemical conditions would closely resemble the City's field stormwater biofilters, the researcher carried out fieldwork relating to these biofilters as follows:

i. A study of the designs and plans for the field biofilter units with discussion with representatives of the engineering and environmental divisions of the City, to understand the rationale behind the units' designs and functions.
ii. Field visits when these units were under construction to observe practicalities involved with their installation and any modifications carried out.
iii. Attendance of meetings with representatives from the City of Sydney Council to identify any variations which might be applied in the field units.
iv. Assistance with the construction of monitoring units for the field component of the biofilter research program to understand how sampling would be carried out in the field (not part of the present thesis) with a view to developing a compatible system for the capture of samples in the laboratory.
v. A study of requirements for the layering and properties of the fill material used in the field units so that this could be emulated as precisely as possible in the laboratory soil columns.

The close liaison with the City's environmental engineering personnel on the design of the simulation experiments ensured that the results would accommodate the City's needs within a broader, scientific framework.

The City of Sydney's program (in which this research was partnered with, and as discussed in detail in this chapter, section 2.4) was designed to improve the quality of stormwater runoff from the City's heavily urbanised catchment, which would directly improve the quality of water recharge to the Botany Sand Beds Aquifer in the South of the City, and the water quality of receiving waterways like the Cooks River, which runs from west to east through the southern part of the City and then enters the historical Botany Bay (City of Sydney, 2019). Environmental degradation of the Bay from polluted urban stormwater has been linked to the decline of several important marine species and has seen the halt in oyster harvesting in the area, which has had important economic and agricultural impacts (Department of Primary Industries, 2019).

In order to explore the pollution removal efficiencies of biofilter systems and the potential impact biofiltration may have upon downstream environmental quality, Western Sydney University formed a research partnership with the City of Sydney Council in 2013, part of which included the carrying out of the simulation experiments as reported in this thesis. The partnership was funded by an equal contribution from Western Sydney University and the City of Sydney Council in terms of the WSU Partnership Grants scheme. This grant enabled the construction of the infrastructure for the simulation experiments, payment for certain casual work carried out as part of the research and the carrying out of core analysis at the University and at a NATA accredited external laboratory (ALS Environmental).

An important product of the laboratory simulation research was a publication of a paper titled *Pollution removal performance of laboratory simulations of Sydney's street stormwater biofilters* (Macnamara and Derry, 2017) where removal efficiencies in compliance with the City's removal targets for total nitrogen (TN), total phosphorus (TP) and metals were reported. Results in the paper augured well for the ongoing construction of field units of all street biofilter designs used by the City.

The paper and other key preliminary results have been presented to the City of Sydney Council as part of their ongoing stormwater biofilter program and will be used in ongoing presentations and publications in this field. Augmentation experiments using recycled materials, some of which are from the burgeoning Sydney building construction industry, also showed great promise in the study, and these will also be published in relevant recycling journals.

1.2. Importance of the research

The research was primarily motivated by the growing challenge of potable water scarcity. The United Nations (UN) identifies that globally there will be a 40% deficiency in freshwater resources by 2030, meaning that there will not be sufficient water available to meet the social and environmental needs of the growing world population. The UN under its Sustainable

Development Goals, has defined Action 6, as ensuring access to water and sanitation for all and has designated 2018-2028 as the Water Action Decade (UN, 2015).

This research contributes to addressing this international goal by increasing understanding on methods for purifying street stormwater runoff to promote safe and sustainable water recycling, and the maintaining of high-quality environmental flows on a local level, and though its application will contribute to addressing this global water crisis.

From an Australian context, water sustainability as a research target is paramount for social, economic and environmental continuity, especially during prolonged periods of drought with burgeoning population increase as experienced in parts of south-eastern Australia, and in particular the Sydney Basin. Given this, drought and water demand in this region needs discussion at this point in order to understand the environmental and social conditions which motivate water sustainability in Australia.

1.2.1. Australia as a dry country

Australia is considered to be the driest inhabited continent and experiences some of the world's most extreme climatic fluctuations (Wahlquist, 2008). The climate in south-eastern Australia oscillates through multidecadal 'storm' and 'drought' periods (Helman and Tomlinson, 2018), which are influenced by the prevailing tropospheric conditions of the Asia–Australia Dipole (AAD) and the El Niño Southern Oscillation (ENSO) (Wang et al., 2016).

Climate change is likely to have a long-term influence on climatic conditions in south-eastern Australia, with increasing temperatures, more frequent heatwaves, and decreasing rainfall, which leads to intensified drought conditions (CSIRO, 2018). The Australian government defines drought as "a prolonged, abnormally dry period when the amount of available water is insufficient to meet our normal use" (BOM, 2019).

Frequent and prolonged drought conditions exert undue pressure upon social, economic, environmental and agricultural stability; with less water availability for industrial and agricultural needs, leading to crop and herd deaths, financial hardship for farmers, and reduced storage volumes of potable water and limited recharge capacity of dams following rain events (BOM, 2019). In Sydney, to manage drought-related water scarcity risks, there have been a series of drought response measures developed, including water use restrictions, desalination plant reactivation, and development of further desalination and water reservoir capacity (Metropolitan Water, 2017).

At the time of writing this thesis, much of south-eastern Australia, and the entirety of the state of NSW was experiencing prolonged drought conditions, characterised by record high temperatures and lower than seasonal average rainfalls, making recycling and improved use of all water resource imperative (Figure 1 and Figure 2).

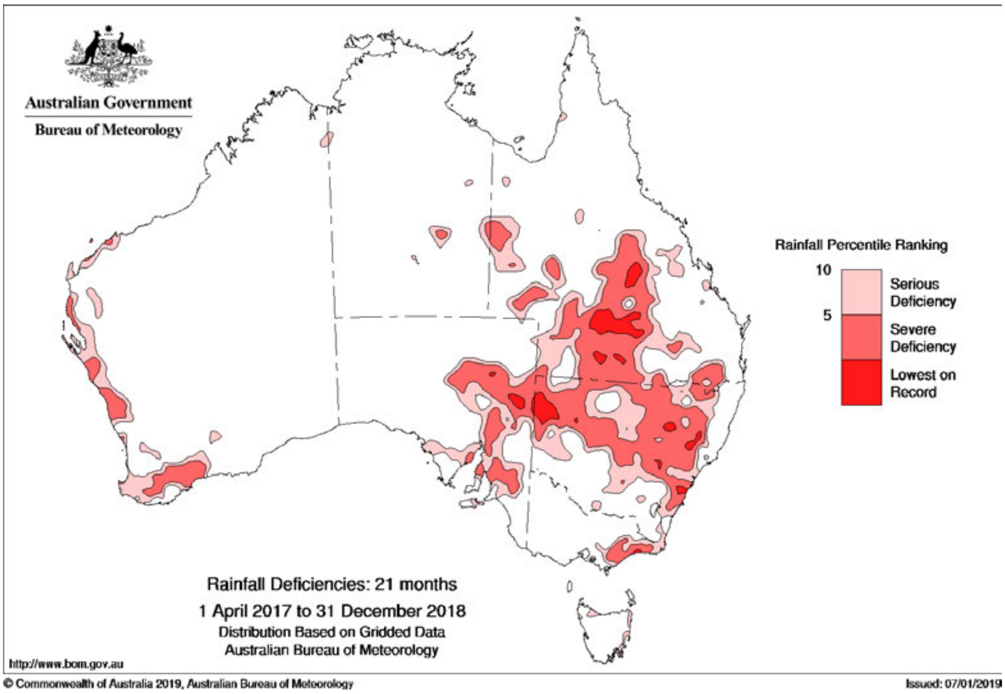


Figure 1: Rainfall deficiencies for the 21 months between 1 April 2017 and December 2018 (BOM, 2019)

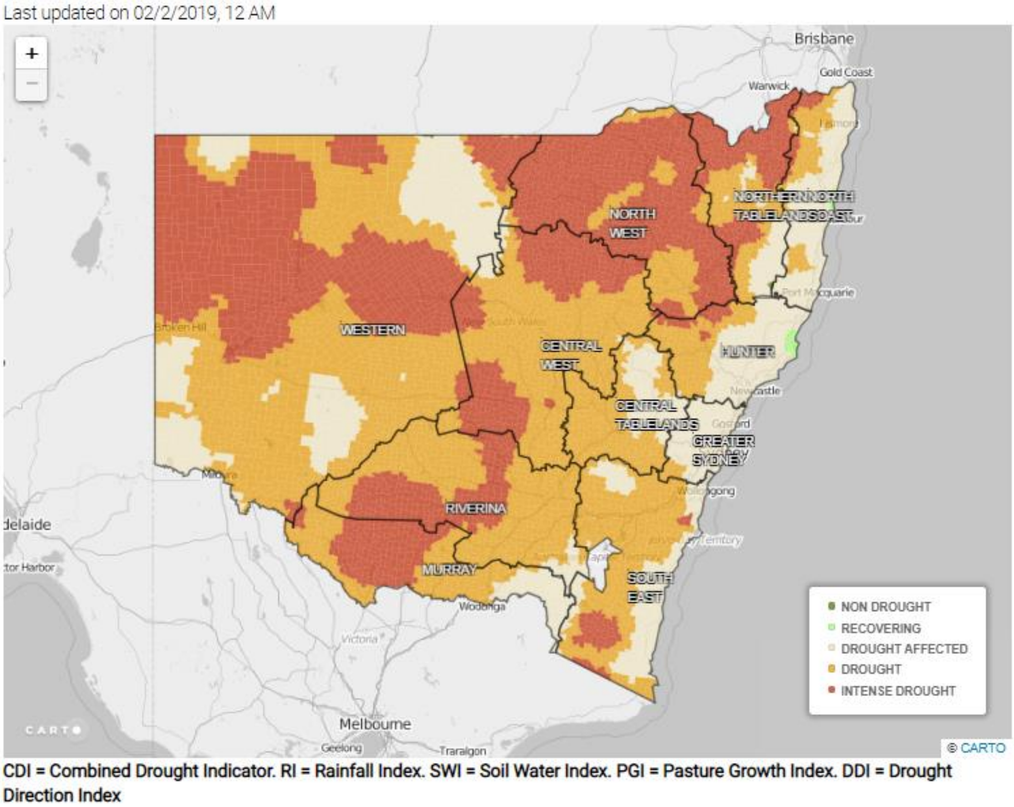


Figure 2: Extent of drought conditions across NSW (Department of Primary Industries 2019)

1.2.2. Water demand and stormwater recycling

There are two anthropogenic impacts that are putting pressure upon water supplies; population growth and urbanisation. The Australian population is predicted to expand from the 25 million presently to between 37.4 and 49.2 million people by 2066 (ABS, 2018). Urbanisation means that greater portions of the population will reside in urban centres, with an estimated 68% of the global population will live in cities by 2050 (United Nations, 2018).

Sydney is experiencing continual population growth; having increased by over 40% from an estimated population of 3.6 to 5.1 million people in the last 20 years. Further expansion is predicted with Sydney's population to swell by 60% to 7.7 million people by 2050, which will represent over 70% of the total state population of NSW (Apostolou, 2014).

Sydney Water Corporation forecasts three possible future water demand scenarios (Figure 3):

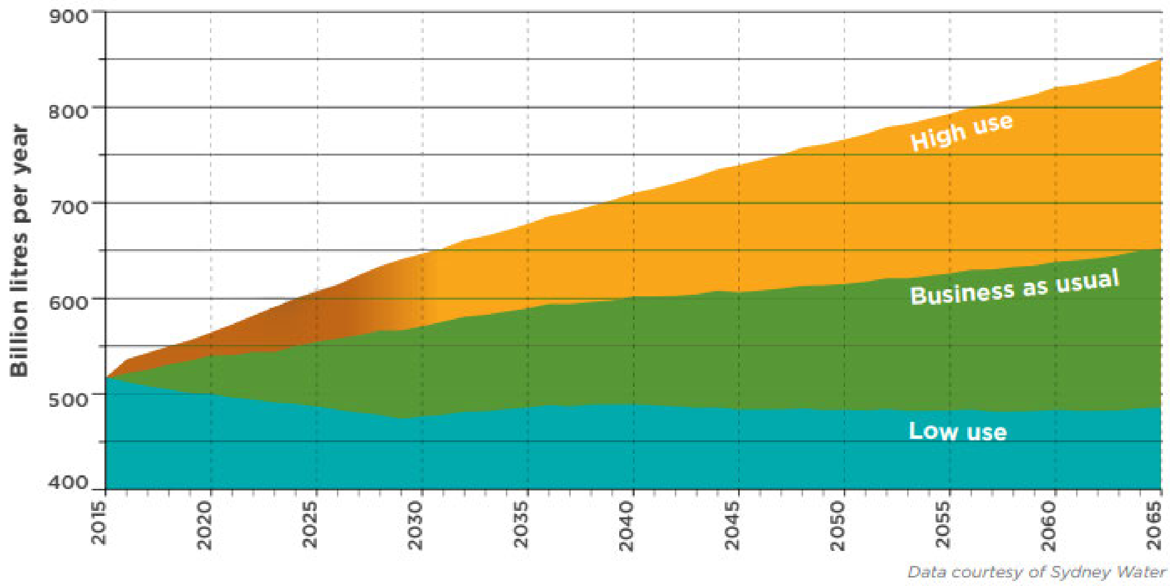


Figure 3: Forecast water demand (based on mid-population growth projection) derived from the Sydney Metropolitan Water Plan (2017)

i. The "business as usual" scenario assumes future water use will be at the same rate of consumption as presently used, that of a daily usage of approximately 324 L per person (2017-2018 statistics), so water demand increases purely by population growth (Sydney Water, 2018).

ii. The "high use" scenario assumes a greater rate of water consumption than the current rate, which is the most likely future given current trends, where urbanisation with high population numbers and densities creates increased water demands (Metropolitan Water, 2017). Future water demand may exceed water supply capacity, particularly during drought periods.

iii. The "low use" scenario assumes a lower rate of water consumption than the current rate of use. A low use scenario is still achievable but will require investment in water conservation and recycling initiatives, such as the ones described in this thesis. Water recycling schemes already save approximately 63 gigalitres (GL) per year in the Sydney metropolitan since 2010, although this only represents less than 10% of the 660 gigalitres of water currently used annually (Metropolitan Water, 2017). Therefore, there are still many opportunities for enhanced water savings to secure this low water demand future, with the outcome of this research will help the City to recycle and use stormwater more efficiently, which will increase water security, particularly during periods of drought.

The City of Sydney's current water demand is 33.7 GL of water per year; however, it allows most of its 26.1 GL of stormwater to run off into the sea (City of Sydney, 2012, GHD, 2012). The City of Sydney has been investigating the potential for treated stormwater recycling using the Botany Sand Beds Aquifer as a vast underground storage reservoir.

The 141 km^2 Botany Sand Beds Aquifer underlies the south-eastern part of Sydney, stretching between Centennial Park to Botany Bay (Figure 4). The aquifer currently supplies approximately 6000 ML water annually, with the aquifer being estimated to be able to sustainably supply up to 22500 ML of water per year (McAuley, 2017).

The primary problem with the use of the Botany Bay aquifer as a water source is groundwater contamination. Previous poor environmental management and waste disposal practices from industrial activities since 1942 in the Botany Industrial Park (within Zone 1 on Figure 4 between East Botany and Banksmeadow) has resulted in substantial chemical contamination of overlying soil and groundwater (EPA, 2017). The NSW Environment Protection Authority (EPA) has charged the commercial company Orica (previously Imperial Chemical Industries) with being the cause of mercury and chlorinated hydrocarbon contamination. Orica is legally responsible under EPA licence to address and remediate these contamination legacies through soil excavation, remediation and groundwater pumping and transfer of extracted water to treatment plants for removal of the hydrocarbon contamination (EPA 2017). Until remediation is completed, a substantial portion of the water in the aquifer will remain unavailable for intended uses, with water extraction being heavily restricted in the yellow and red zones of the aquifer (Figure 4).

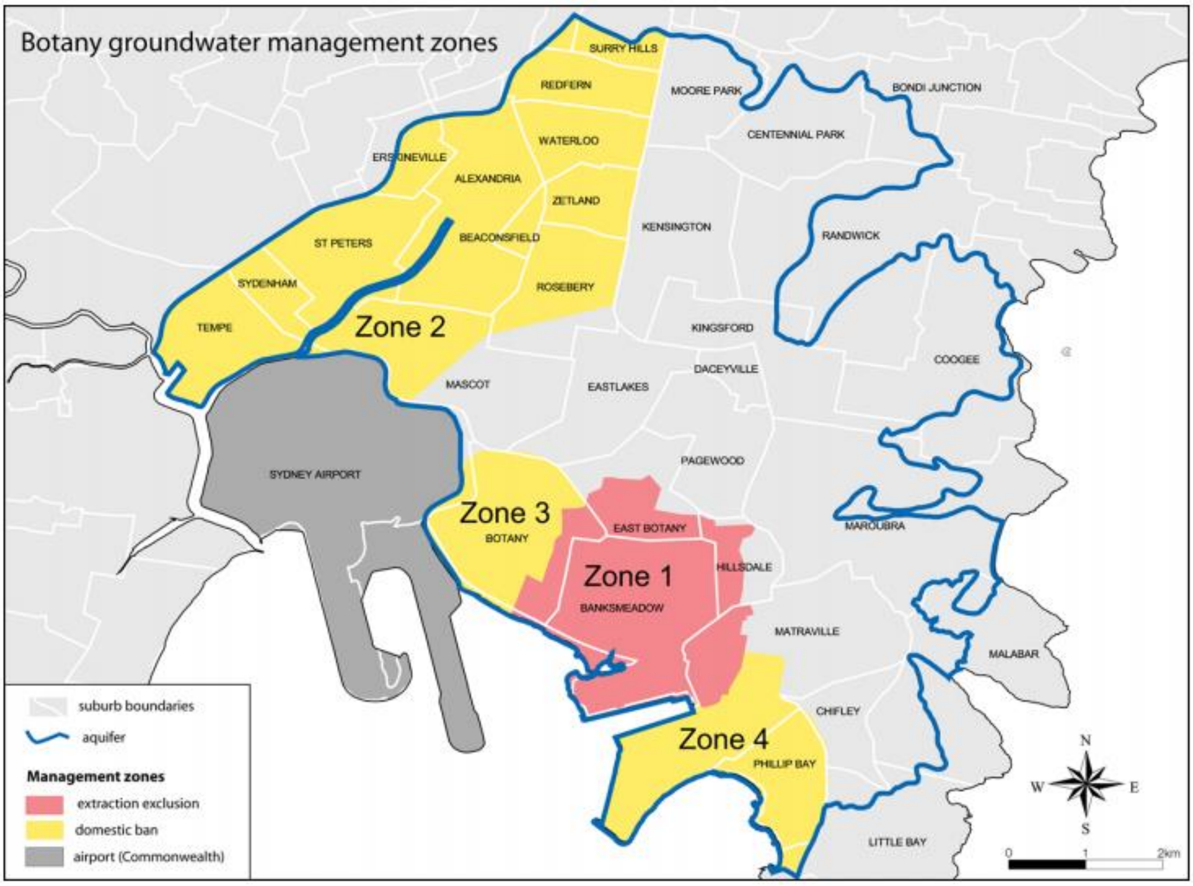


Figure 4: Map of the Botany Sand Beds Aquifer catchment extent, depicting suburb boundaries and polluted groundwater extraction exclusion management zones (McAuley, 2017)

Given these initiatives, this research will contribute to a hypothesised plan by the City for the use of the aquifer as a massive storage for recycled stormwater, and the research will contribute towards the control of receiving water quality from the stormwater biofilters.

1.2.3. Imperative for optimising the urban stormwater resource

Urbanisation has irreversibly altered the hydrology of urban catchments; resulting in the degradation of downstream aquatic systems through scouring and eutrophication (Wright et al., 2011, McGrane, 2016). The increase in impervious surfaces has decreased groundwater recharge by infiltration and has intensified the volume and velocity of stormwater runoff being produced (Jacobson, 2011, Sartipi and Sartipi, 2019), while the design of urban drainage systems has created an efficient vector for stormwater pollutants to enter natural aquatic systems (Hatt et al., 2004). Intensification of human activities in urban areas has led to a greater concentration of stormwater pollutants being available in stormwater flows, including sediments, heavy metals, nutrients, petrochemicals and pathogenic microorganisms (Gobel et al., 2007).

Since the early 1990s in Australia, there have been several urban design principles developed that aim to minimise the adverse hydrological consequences of urbanisation and this thesis research aims to support these. In Australia, Water Sensitive Urban Design (WSUD) principles have been developed, which aim to conserve and improve urban water quality by minimising runoff, buffering peak flows and reducing water pollution through reducing urban imperviousness and facilitating decentralisation of water treatment. Under a WSUD approach, urban stormwater is seen as a resource, made available through stormwater harvesting and reuse, and returned to natural waterways or used to recharge perched water or aquifers following suitable decentralised treatment (Fletcher et al., 2015, Lloyd et al., 2002).

1.2.4. Stormwater improvement by local councils

In Australia, local government is largely responsible for the management of stormwater (Commonwealth of Australia, 2015). In the past, stormwater has been considered to be wastewater, and something to be removed from urban centres as quickly as possible, leading to the development of extensive drainage networks. With the advent of WSUD principles many councils have begun to view stormwater differently, and have been actively trying to incorporate this water resource back into the urban system.

1.2.5. City of Sydney's stormwater biofilter program

Sydney is a relatively green city containing many parks and bushland remnants; however, many areas of Sydney are dominated by hard impervious surfaces, like roads, roofs, pavement and compacted soils, representing over 40% of total catchment surface area in some suburbs (Jacobson, 2010, GHD, 2012). The City's engineered stormwater pipe and canal network allow for the efficient capture, concentration and channelling of stormwater from these impervious catchments into receiving natural waterways. This stormwater network effectively bypasses the terrestrial phase of the water cycle resulting in the loss of a valuable urban water resource, reduced perched water and aquifer recharge, and increased natural waterway scouring and flood events.

Pollutants, particularly nutrients and heavy metals, accumulate on hard surfaces during dry periods and are washed off in stormwater runoff events producing heavily polluted flows. The collected pollutants in the stormwater runoff exert a negative influence on the quality and health of receiving aquatic ecosystems like the Cooks River, Botany Bay, Parramatta River and Port Jackson, which includes Sydney Harbour (Spooner et al., 2003, Birch et al., 2010, Nath et al., 2014).

The City of Sydney under its Sustainable Sydney 2030 vision and their Decentralised Water Master Plan (DWMP), has progressively been working towards a water sensitive city status by actively incorporating WSUD into their urban parks and streets in order to reuse and treat stormwater to protect the iconic Botany Bay and Sydney Harbour catchments and the Botany Sand Bed Aquifer (Healey et al., 2012). A key strategy for achieving stormwater control and meeting pollutant reduction targets (Table 1) relates to the construction of street stormwater biofilter systems in this heavily urbanised metropolitan region, particularly in southern Sydney incorporating the Cooks River, Botany Bay and Sydney Harbour sub-catchments (Derry et al., 2013, City of Sydney, 2012). The City's plans detail the design, implementation and construction of 21,000 square meters of decentralised street biofilter units to intercept and treat stormwater before discharge to receiving waters or the aquifer, and presently over 150 stormwater biofilters have been constructed (City of Sydney, 2019). The unlined stormwater biofilters could make a substantial contribution to managed aquifer recharge of the Botany Sand Bed Aquifer, and thus allow for approximately 5% of Sydney's annual water demand to be sustainably sourced from the aquifer (UTS 2015).

While assessment of the efficiency of the field units is a long-term research proposition, the simulation experiments reported in this thesis were designed to give an early indication of specific pollution removal efficiencies, to guide design direction and to explore opportunities for filter amendment with recycled materials.

Table 1: Sydney's stormwater improvement targets

Water quality parameter	Development control plan (DCP) removal target	Botany Bay water quality improvement plan (BBWQIP) removal target
Total Nitrogen (TN)	45%	45%
Total Phosphorus (TP)	65%	60%
Total Suspended Solids (TSS)	85%	80%
Gross Pollutants	90% (>5 mm)	90% (>5 mm)

1.3. Stormwater biofilters

1.3.1. Basic biofilter characteristics

There are several best management practices (BMPs) available for the treatment of urban stormwater as an important resource, including the construction of wetlands, green roofs, sedimentation basins, grassed swales and stormwater biofilter systems (Yu et al., 2013, Hoss et al., 2016). Stormwater biofilters, also referred to as raingardens, are green infrastructure commonly used for the mitigation of stormwater peak flows and improvement of water quality in the United States, the United Kingdom, Australia and China (Winston et al., 2016, Zhang et al., 2018, Berretta et al., 2018, Winfrey et al., 2018).

A stormwater biofilter is an engineered soil and vegetation based system that is constructed to intercept and filter stormwater flows from urban impervious catchments (Figure 5, Figure 6 and Figure 7). In the Sydney metropolitan area, stormwater biofilters are typically situated at the edge of roads and extend into the pavement area, in order to intercept the surface stormwater from these areas. They are generally sized to be approximately 2-5% of the relevant stormwater catchment area (Figure 7) and are vegetated with endemic wetland plants whose roots directly absorb nutrients and provide attachment points for bacteria and fungi, which aid in the sorption and biodegradation of stormwater pollutants (Figure 5). Biofilters consist of a stratified substrate arrangement of four layers: mulch, filter, transitional and drainage (Figure 6). These layers are designed to carry out the system's hydrological and pollutant retention properties while being supportive of the biofilter's vegetation growth.

Figure 5: Field stormwater biofilter system, operated by the City of Sydney (photo courtesy of Chris Derry)

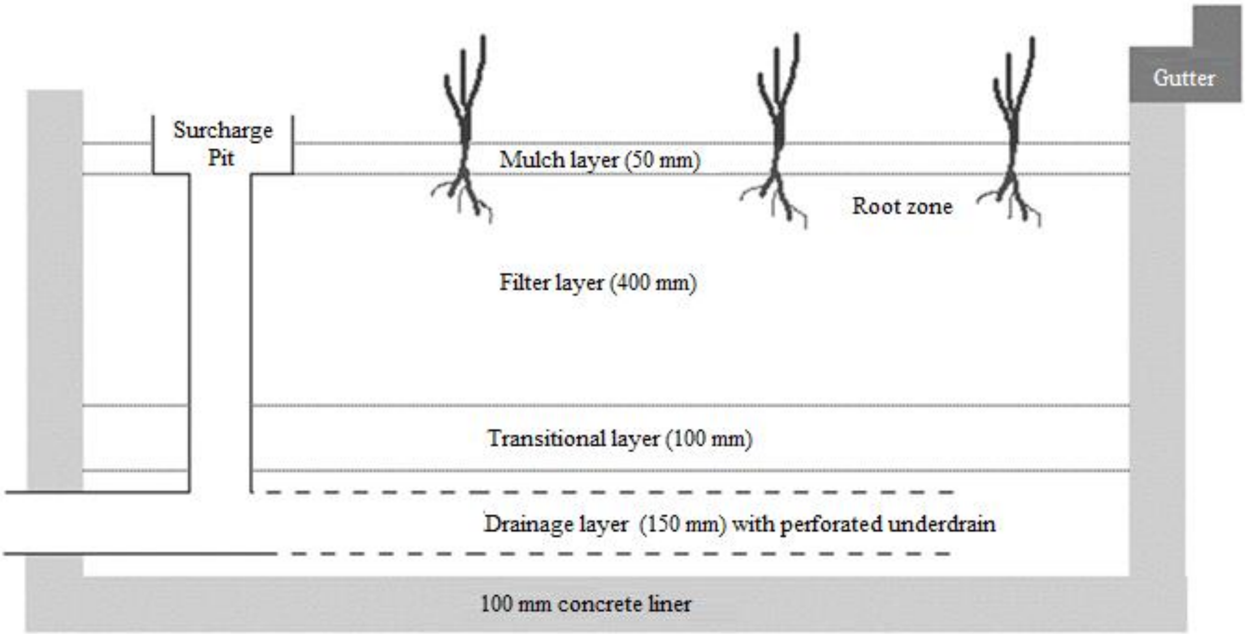


Figure 6: Conceptual design of a typical lined stormwater biofilter, as per the City of Sydney Council designs (Macnamara and Derry, 2017)

Figure 7: Biofilter at Kingsgrove, NSW and its catchment to illustrate typical size relationship (Cooks River Alliance, 2016)

1.3.2. Biofilter design variations

Biofilters are based on the following three broad design categories (Derry et al., 2013):

i. An **Unlined** biofilter design is primarily intended to achieve aquifer recharge. The treated stormwater can percolate directly into the aquifer from the unlined unit or is otherwise removed to the traditional stormwater network via a porous agricultural underdrain. An unlined design cannot be used where surrounding structures, such as road and building foundations, power cabling and telecommunications equipment and conduits, will be detrimentally affected by the ingress of water.

ii. A **lined** biofilter design in which the entire biofilter system is encased in an impervious outer chamber, usually made of reinforced concrete, and in which an underdrain captures the infiltrated water for discharge into the existing stormwater drainage network. The encasement is required because of the poor loadbearing nature of some soils, or where subsidence, owing to the soil's physical characteristics or a high-water table exists, could detrimentally affect adjacent roads and buildings.

iii. A **lined biofilter design with saturation zone** which includes an impervious (usually reinforced concrete) biofilter sump where stormwater is retained after passage through the upper layers in order to generate anoxic conditions under which denitrification takes place in the presence of adequate dissolved carbon. Anoxic conditions are maintained in the sump by progressive biochemical removal of oxygen as water trickles through the filter medium above. An inverted syphon arrangement in the drainage line from the sump to the biofilter outlet physically retains water in the saturation zone.

Two broad biofilter categories, "monophasic" and "biphasic", are identified in the literature (Yang et al. 2010). Designs 1 and 2, are monophasic, allowing free movement of stormwater through the biofilter, whereas design 3, with the inclusion of the saturation zone, is biphasic. Monophasic biofilter systems have been reported as being more effective removers of cationic pollutants such as heavy metals and ammonia, whereas biphasic units can remove the nutrient nitrate more effectively (Wang et al., 2018a).

In biphasic units, denitrification (biochemical conversion of dissolved nitrate to free atmospheric nitrogen gas) takes place in the anaerobic saturation zone under the action of nitrifying bacteria of the genera *Nitrosomonas*, *Nitrosococcus*, *Nitrobacter* and *Nitrococcus*, when sufficient dissolved carbon is present (Blecken et al., 2009b, Zhang et al., 2011, Dietz and Clausen, 2006). In biphasic biofilters, pollutants in the stormwater are exposed to a range of environmental conditions, from partially saturated to saturated, aerobic to anaerobic and anionic to cationic, providing an array of biochemical conditions for the retention or bioremediation of organic and inorganic pollutants (Yang et al., 2010).

In addition to the design variations as described above, biofilter design may also differ with regards to fill type, fill depth and vegetation characteristics, all of which can affect the hydrological and pollution removal performance of the system (Read et al., 2010, Brown and Hunt, 2011, Shrestha et al., 2018). These core biofilter characteristics formed the subject matter of several “supportive experiments,” as discussed in chapter 2.

1.3.3. Link between the City of Sydney’s street biofilter program and the simulation research

Research into the hydraulic and chemical pollution removal performance of the City of Sydney’s street biofilter systems is a long-term project which motivated the need for indicative laboratory simulation experiments to provide early feedback on the design and siting of future field biofilter units. Information could also be provided on the potential for amendment of the biofilter fill through the inclusion of recycled building materials, avoiding the cost and inconvenience of removing recycled materials found to be unsuccessful were amendment trials were to be directly carried out in the field (Davis, 2011, Derry et al., 2013).

This thesis investigated the performance of stormwater biofilters through controlled laboratory simulation, using 104 mm polyvinyl chloride (PVC) soil columns with fill material and layer thicknesses modelled on those found in the the City of Sydney’s field units. The laboratory simulations allowed for an improved understanding of the functioning of the biofilter soil column by allowing the investigation of areas which could not be otherwise explored in the field owing to cost limitations and the undesirability of experimenting with already functioning units. In addition, confounding field variables relating to climate and road work could be avoided.

The laboratory biofilter simulations permitted the manipulation of biofilter parameters, such as design and fill variations (including substrate amendment), allowing for multiple experimental permutations not possible in the field. The concentration of chemical substances in the incoming water and hydraulic loading rate could also be controlled. The quantity of pollutants run through the column simulations was minimal compared to that which would have to be added to and run through an entire field unit so environmental contamination could be minimised.

The laboratory simulation linked with the field biofilter program in three areas:

i. Understanding of the potential effectiveness of the City's biofilter program, contributing to the City's reduction targets as set in the DCP and water master plan (Table 1).
ii. Providing information for the potential effectiveness of stormwater aquifer recharge.
iii. Informing the design of future field biofilters, by identifying weaknesses and strengths associated with design types, fill specifications and fill amendment variations.

1.4. Literature review

In Australia, there are two broad issues with stormwater; 1) it is under-utilised as a resource and 2) polluted stormwater runoff contributes to the degradation of downstream waterways (Commonwealth of Australia, 2015). Stormwater biofilters address both concerns, as they can readily be retrofitted into urban drainage systems, and depending on design, the treated stormwater can be directed to a storage tank where it can be used for many non-potable uses (Feng et al., 2022). Alternatively, it can be used for aquifer recharge or returned into the traditional drainage network. By capturing and treating the stormwater, the literature suggests that effective pollutant removals are possible for field biofilter systems such as the ones designed by Sydney Council. This can ultimately result in significantly reduced pollutant loads, particularly total suspended solids, heavy metals and nutrients in the stormwater received by downstream waterways (Hatt et al., 2009, Elyza Muha et al., 2016).

Although studies have suggested high removals of upwards of a possible 90% removal efficiency for some metals, TSS and phosphorus (Kabir et al., 2014, Blecken et al., 2010), there a several limitations in the studies; including extensive range of results in and between studies, which stems from great variations in biofilter and experimental designs.

Biofilter experimental design varies in terms of:

- Field or laboratory column scale conditions the research is conducted under
- Type of stormwater – i.e. synthetic, semi-synthetic or natural sources which the raingardens are dosed with
- Concentration of pollutants in the stormwater

- Biofilter design – monophasic or biphasic with saturation zone
- Inclusion and availability of carbon source to aid nitrification especially in systems with saturation zone, and
- hydrological considerations such as fill infiltration rate, hydraulic head depth, dosing volumes and rates.

Generally, raingarden research suffers from a lack of standardisation, making interpretation of results between studies with these differing design parameters problematic.

These variables can create a great deal of disparity in pollutant removal performance in and between studies; for instance, the removal of nitrogenous compounds is highly variable. Ammonium (NH_4^+) tends to be effectively removed due to cation exchange with the filter media (Zhou et al., 2016, Hsieh et al., 2007b). Whereas, nitrate and nitrite (NO_3^{2-} and NO_2^-) is highly variable showing removals as high as possible 80%, but tends to be much lower at around 30-50% (Tang and Li, 2016). Many studies also show leaching where concentration of these anionic nitrogenous compounds is greater in biofilter's outflow than they were in the stormwater inflow (Blecken et al., 2010, Bratieres et al., 2008, Davis et al., 2006).

Inefficient and inconsistent nitrogen removal (particularly for nitrates-nitrites) was the primary reason for saturated sump development and inclusion into the biofilter design (biphasic design). Although this is considered a standard design and strongly recommended in the literature (Zinger et al., 2013), nitrogen removal can still be quite variable, having possible removal efficiencies for nitrates of 30% to 70% (Tang and Li, 2016, Yang et al., 2010, Nabiul Afrooz and Boehm, 2017).

Local pollution control guidelines only consider nitrogen as total nitrogen (City of Sydney, 2012), which stems from a reliance on the Model for Urban Stormwater Improvement Conceptualisation (MUSIC) were TN is a key parameter for simulating the effectiveness of WSUD infrastructure on catchment water quality (Freewater et al., 2014, Singh and Kandasamy, 2010). However, given the above noted variability in removal of nitrogen between its oxidative states, a single measure of nitrogen removal over-simplifies the nitrogen indices, potentially creating a misleading representation of nitrogen removal performance. It is thus considered important to explore nitrogen in all its oxidative states, and therefore the removal of nitrogen was studied in this thesis as TN, NH_4 (as TKN) and NOx.

Past biofilter research has highlighted the potential range of pollutant removal that the biofilter system is capable of, with focus on removal of nitrogen and phosphorus macronutrients from the stormwater (Blecken et al., 2010). To a lesser extent, heavy metal removal has also been explored, although this tends to focus on a select few metals, such as copper, lead and zinc (Li and Davis, 2008, Muthanna et al., 2007). This thesis covers a wider range of metal pollutants than typically studied, exploring additional metals like hexavalent chromium and the metalloid arsenic, which are present in urban stormwater and are known to be toxic to human and aquatic life (Cederkvist et al., 2013, Rahman and Singh, 2019).

In this thesis, a series of laboratory experiments was established, in which design variations could be controlled, allowing for the pollutant removal performance of a wide array of pollutants to be explored on a single standardised laboratory column system, across design and media fill variations. This research extends the base understanding established in the literature of what biofilters are capable of and explores methods for enhancing raingarden pollutant retention capacity (chapters 6 and 7), which is important if the technology is going to continue to provide effective pollutant removal.

Past amendment research has shown some promise for amendment to enhance the filter pollutant removal performance, exploring materials such as zeolite, fly ash, biochar, steel wool, amberlite, chitosan and crab shell (Vijayaraghavan et al., 2010, Erickson et al., 2007, Boehm et al., 2020, Hermawan et al., 2021). However, this past research tends to be limited to small scale batch column experiments, trialling tiny quantities of amendment materials. For instance, Vijayaraghavan (2010) only explored 0.2 g per 100 ml in batch experiments, or a small 2.4 cm diameter by 35 cm column, and Hermawen et al. (2021) explored zeolite and fly ash at a limited rate of 2% w/w. Past studies indicate that amendment can promote removal, but it does not explore amendment over a gradient of concentrations which is needed to ascertain optimal amendment rates for enhanced pollutant removal.

The research in chapters 6 and 7, explores the augmentation of biofilter fill with novel recycled industrial materials over a concentration gradient of upwards of 30% w/w, which far exceeds the limited rates previously explored in the literature. The current study also employs a large (104 mm) and more comprehensive column scale approach, which is not as influenced by column edge effects as would have been in the smaller-scale literature column experiments. A laboratory column simulation system lends well to this amendment research as it allowed for multiple permutations of biofilter designs and fill compositions to be trialled in a resource efficient manner.

A wide range of soil column diameters have been used in laboratory experiments elsewhere, offering problems of standardisation and performance, such as the introduction of excess edge effects where the columns are too narrow, or the issue of increased dispersivity and maintenance where diameters are much larger (Blecken et al., 2009a, Lewis and Sjöstrom, 2010, Nordström and Herbert, 2017, Cameron et al., 1990).

Column methodology, as described in chapter 2, whereby 104 mm column was established, which attempted to strike a balance between the extremes in column size reported in the literature, in order to create a system to allow for technology transfer to local council, who place a strong imperative on resource efficiency, in terms of construction materials and substrate, and disposal of contaminated substrate once experiments are completed. The literature defends this design, as it highlights that smaller columns offer remarkably similar pollution removal results to those of their larger counterparts, for instance a 50 mm column (Yang et al., 2010) achieved similar 50-90% phosphorus removal result to that of 400 mm columns (Bratieres et al., 2008).

Laboratory biofilter columns systems are either vegetated or unvegetated. The literature highlights that wetland plants can improve pollution removal (Henderson et al., 2007) and maintain hydraulic performance of the system. Vegetated columns have been shown to significantly increase nitrogen and phosphorus retention in comparison to unvegetated columns (Lucas and Greenway, 2008), with raingarden plants improving retention performance by directly absorbing the nutrients, filtering inorganic and organic particulates and creating an oxidized rhizosphere (Zhang et al., 2011).

Plant growth, particularly root length, depth and total mass, have been demonstrated to be key to plants' pollutant removal ability (Read et al., 2010). The Australian native, *Carex appressa,* is often heralded for its high pollutant removal properties, and is frequently recommended for used in raingarden systems (Read et al., 2010, Winfrey et al., 2018, BCC, 2017). Fully grown, *Carex* is 1 m wide and upwards of 1.2 m tall, taking a few years to reach full maturity. In column research, the effectiveness of *Carex* mediated pollutant removal was not assessed until about 28 weeks of plant growth, well after the roots and plant had sufficiently established (Read et al., 2010). Also, in long-term column studies, the column itself can influence root development and distribution, leading to root-to-media ratios that are not representative of field conditions (Dagenais et al., 2018).

Despite the demonstrated affect that plants may have on pollution removal performance of the biofilter system, smaller unvegetated columns have been shown to have comparable removal performance to that of larger vegetated columns. For instance, there was a 60-80% NO_3 removal for a 50 mm biphasic unvegetated column (Yang et al., 2010), which has comparable performance to that of a 400 mm vegetated column with saturated zone (about 80% removal) (Glaister et al., 2014). Plant do not appear to substantially impact metal removal, with there being remarkedly similar metal removal performance with a possible 80% removal between large 250 mm vegetated columns (Vijayaraghavan and Praveen, 2016) and smaller 100 mm unvegetated columns (Lim et al., 2015).

Until plant root mass has sufficiently developed, it is likely that the plants may have limited influence on biofilter performance. To date no studies have identified the earliest point when plants may significantly influence biofilter pollutant removal performance, which would be a valuable avenue of research, especially in quantifying performance of newly planted and establishing biofilter systems.

When the focus of the study is on the soil component of the biofilter system, past research often omits plants from column experiments, to avoid the variable impact of plants may have in the soil columns (Hsieh and Davis, 2005, Paus et al., 2014, Yang et al., 2010). Following this precedence, raingarden plants were omitted from the column experimental design. Given the potential of plants in the field systems, the results obtained from the column experiments should be considered as a conservative approximation of field biofilter performance.

1.5. Research aim and objectives

The aim of this research was to carry out laboratory simulation experiments using the City of Sydney's street stormwater biofilter units as a model in order to assess the impact of design, fill variation and substrate amendment on the efficiency of removal of selected stormwater pollutants, with reference to local pollutant control guidelines as pollutant removal targets.

Within this framework, there were five main objectives:

i. To develop simple, compact and cost-effective laboratory scale biofilter column simulations to model street biofilter systems.
ii. To assess the impact of monophasic and biphasic biofilter design on pollutant removal performance of the biofilter system.
iii. To assess the impact of fill specifications on biofilter TSS release, hydrological and pollutant removal performance.

iv. To trial the augmentation (amendment) of the biofilter fill with recycled industrial waste products; biochar, blast furnace slag, crushed concrete, gypsum and zeolite, to promote enhanced pollution removal performance by the biofilter system while providing recycling opportunities for selected common industrial materials.
v. To develop a cost- and space-efficient technology for potential transfer to institutions such as quarries and government departments wishing to test the performance of biofilter fill material.

1.6. Project scope

The thesis research developed a basic laboratory model to simulate field biofilter’s pollutant removal performance, using the City of Sydney’s biofilter design as a basis in this process. Although some field research was conducted to calibrate the laboratory model, field verification was outside the scope of this laboratory project and was part of a project still in progress under another research team. There is potential for a future linkage of the laboratory and field research projects, to cross verify the two research streams, possibly during the later publication stage.

Following study of simulation results for the wide range of column diameters used elsewhere, an intermediate diameter of 104 mm was selected as standard throughout the experiments, as narrower units have an increased risk of an “edge effect” occurring, as discussed elsewhere in the thesis.

The selection of a 104 mm diameter soil column and the relatively short nature of the experiments after which the experimental fill media was changed and discarded, prevented the vegetation of the simulation system’s surface with a spectrum of plant species typical to field units, but the use of fills sourced by supplying quarries from natural, largely aquatic sites, and the use of a well composed synthetic stormwater, would ensure the transfer and survival of many microscopic species important in the treatment of water in field soil columns. While the absence of macrophyte species could be seen as an experimental weakness, results for similar diameter unvegetated columns have shown similar results to those obtained with larger diameter vegetated columns, as discussed elsewhere in the thesis, and the use of such columns is therefore defensible.

The column experiments were designed to examine biofilter pollutant removal performance of different fill characteristics and configurations during the initial biofilter establishment phase, as biotic features were excluded from the column design, long-term fate, total soil absorption capacity and regeneration were not explored in this thesis.

The amendment materials were studied individually across a concentration gradient to ascertain the effect of each amendment material on biofilter system performance. Combinations of amendments were not studied in this project, as this would have blown-out the number of existing complex and time-consuming amendment experiments from the 60 to 151,200, but this suggests the opening of a new area for future research projects.

The column systems were dosed with carefully composed synthetic stormwater, which mimics stormwater conditions prevalent in the heavily urbanised Sydney City. TN and TP parameters, with addition of a suite of heavy metal parameters, which are known contaminates of urban stormwater were studied, given their local relevance and the metal parameters potential ecotoxic and negative human health considerations. Pollutant reduction performance of the biofilters was assessed against local pollution control targets, of the City's DCP and BBWQIP targets for TN and TP (Table 1), and metals were compared against the ecological protection toxicant limits of the ANZG (2018) guideline (Table 7).

Chapter 2: Study design, biofilter simulation column development and common experimental procedures

2.1. Introduction

This chapter outlines the study design and the general laboratory method developed to assess the potential pollution removal performance of the field stormwater biofilters. The study design incorporated four core experimental components with supportive experimental components (Figure 8). While general methods common to all experiments are covered in this chapter, specific methods relevant to each simulation experiment are covered in chapters 3 to 6.

2.2. Study design

The performance of the biofilters were studied under warm (25-35°C) temperate conditions, whereas the literature tended to study biofilters under cool (<20°C) temperate conditions (Blecken et al., 2011, Khan et al., 2012, Muthanna et al., 2007, Søberg et al., 2014), with the methods developed in the literature being adapted for this study.

A series of experiments were developed to explore the performance of stormwater biofilters, with the schematic in Figure 8 shows how the experimental components fitted together in the overall study design.

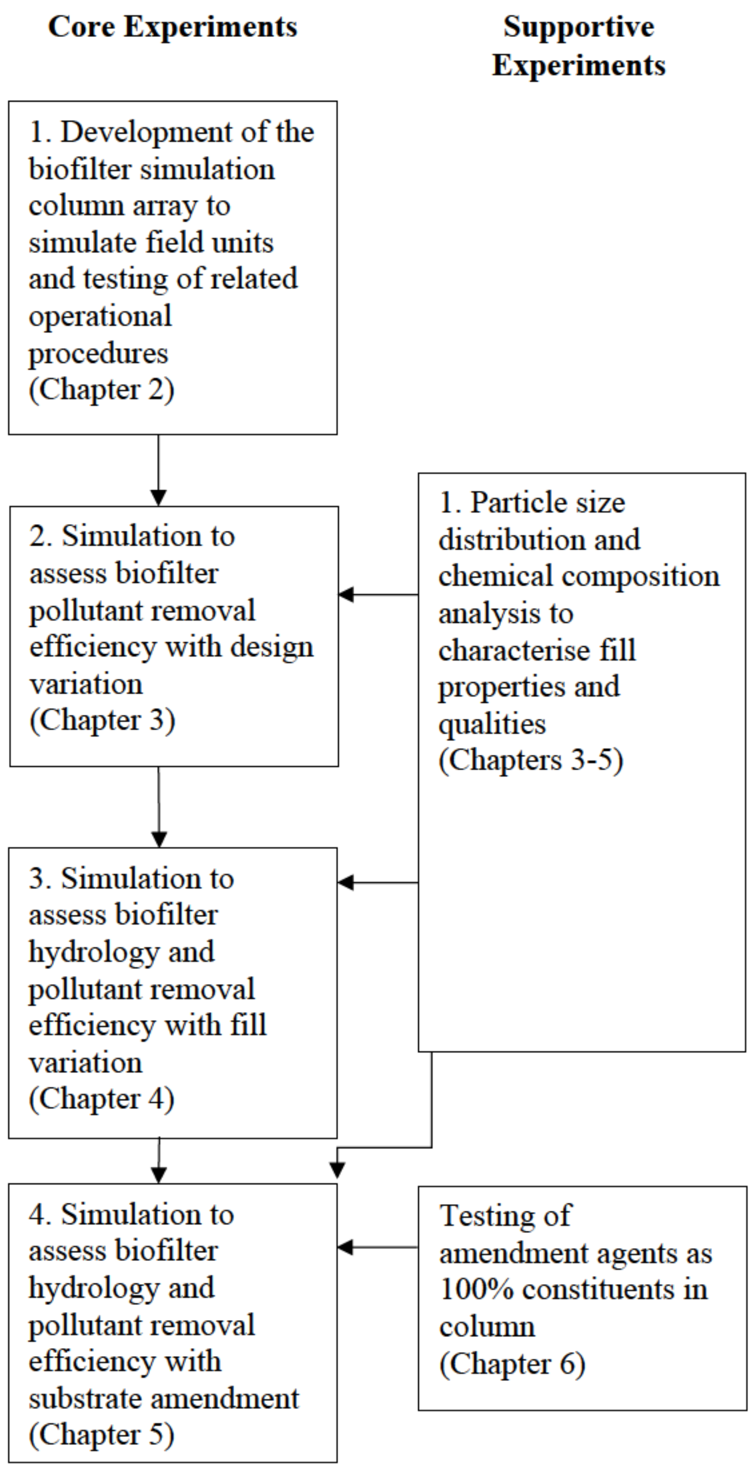


Figure 8: Different experimental components in the overall study design, with relevant chapter references

The four core experimental phases are as below:

i. **Column simulation design and development:** This involved the development of the biofilter simulation column array and related operational procedures, to emulate the standard designs and environmental conditions of the field biofilters units as operated by the City of Sydney. These column designs and operational procedures formed the basis for the experimental design for the subsequent three experimental phases.

ii. **Simulation experiment 1 – biofilter removal efficiency with design variation**: Here the effects of design variation (unsaturated monophasic and saturated biphasic biofilter designs) on potential pollution removal efficiency of the field designs were explored under controlled laboratory simulation conditions.

iii. **Simulation experiment 2 – biofilter removal efficiency with fill variation**: Here the impact of alternative fill variations on biofilter performance was explored. During field biofilter construction the City of Sydney introduced fill specifications to improve the quality of fill supplied. In the laboratory assessment of the impact of these specifications on biofilter performance was carried out on two biofilter fill sets, which have both been previously employed in the construction of field biofilters in southern Sydney.

iv. **Simulation experiment 3 – biofilter removal efficiency with substrate amendment**: Here the effects of substrate amendment with recycled industrial products of blast furnace slag (BFS), biochar, crushed concrete (CC), gypsum and zeolite on the potential pollution removal performance of the biofilter was explored. The biofilter simulation columns, as established in the previous three experimental phases, were augmented with the amended fills to assess if there was any enhancive effect upon biofilter's pollution removal performance.

In addition to the four core experimental phases, there were several supportive sub-experimental phases (Figure 8), which employed modified experimental designs to those of the main experiments. These "supportive experiments" were carried out to contextualise the results of the core experiments.

2.3. Biofilter simulation column design

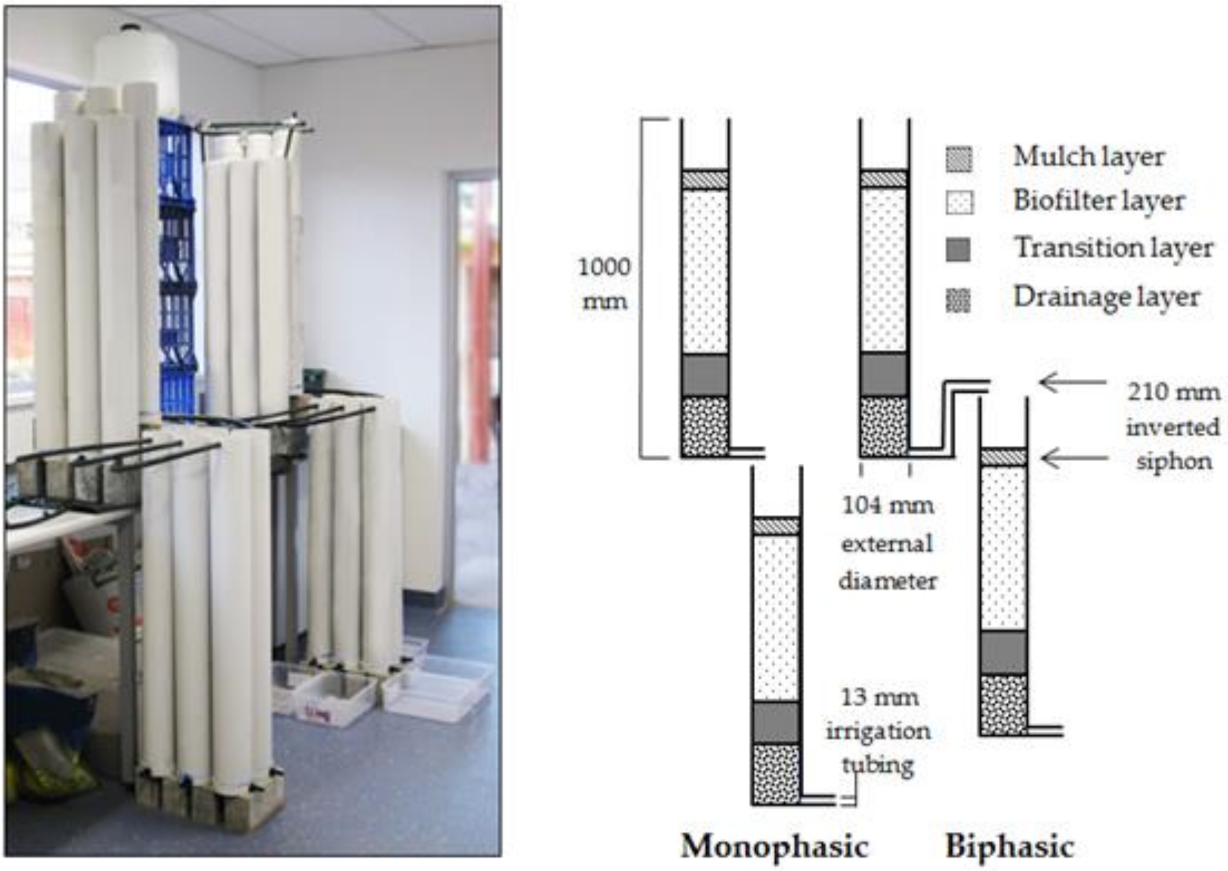


Figure 9: Laboratory column design: (a) view of general layout; (b) sectional schematic showing arrangement and layering

The laboratory biofilter column simulations were designed to emulate the vertical section of the City’s street biofilters in terms of fill, fill depth, and biofilter design (monophasic and biphasic). The biofilter simulation consisted of a series of soil columns using off-the-shelf 104 mm diameter PVC tubing, which is nominally 100 mm construction tubing in Australia (Figure 9). The base of each column was sealed with a PVC endcap and fitted with a drainage connector to allow for sample collection. The internal column surfaces were roughened by lightly sanding with 100-grade carborundum paper to retard short-circuiting through edge flow, as per the literature recommendations (Bergstrom, 1990, Chandrasena et al., 2014, Lewis and Sjöstrom, 2010).

In baseline experiments, the biofilter simulation columns were established in tandem (Figure 9), as the City's street biofilters tended to be designed with two units linked by pipework under a central pedestrian access way leading to a safe road crossing point. These tandem columns were in keeping with laboratory designs described in Yang et al. (2010). Later experiments relating to fill and hydraulic properties, and recycled substrate augmentation used a single-column matching laboratory designs reported elsewhere (Blecken et al., 2009a, Fowdar et al., 2017, Hsieh and Davis, 2005). Statistical analysis indicated that for the majority of the pollutants studied there was no statistical difference in the removal efficiency between the tandem and single-column designs (Table 31 in appendix).

2.3.1. Selection of column design

There are no standard column designs, with the literature reporting many variations in diameter and construction material, as shown in Table 2 below (Lewis and Sjöstrom, 2010).

Table 2: Diameter specifications of laboratory column units employed in previous studies

Column diameter (mm)	Construction material	Reference
24	Glass	(Vijayaraghavan et al., 2010)
50	PVC	(Yang et al., 2010)
100	PVC	(Fowdar et al., 2017)
100	Black Acrylic Plastic	(Cheng et al., 2018b)
100	PVC	(Hatt et al., 2008)
150	PVC	(Tang and Li, 2016)
310	Plastic – unspecified	(Sun and Davis, 2007)
375	PVC	(Bratieres et al., 2008)
465	Unspecified	(Good et al., 2012)
500	Stainless Steel	(Bester and Schafer, 2009)

A 104 mm diameter column was selected for the experiment as narrower columns have an increased risk of “edge effect” occurring. Edge effect is the formation of preferential flow paths at the interface between the retaining column wall and the soil column itself, leading to short-circuiting of the fill matrix and hydrological pollutant results that would not otherwise be representative of filed conditions being simulated (Blecken et al., 2009a, Lewis and Sjöstrom, 2010, Nordström and Herbert, 2017, Cameron et al., 1990).

In comparison, larger columns tend to show signs of increasing dispersivity, which is the establishment of preferential channels through a wide filter medium. Wider columns would have also escalated cost and experimental footprint, reducing the transferability of the technology under development.

PVC was selected over other column materials as it is a rigid, inert material internationally available with a wide range of standardised fittings, enabling the continuation of research into the future with the potential for transfer of the simulation and fill-testing technology to other regions.

2.3.2. Biofilter simulation column fill

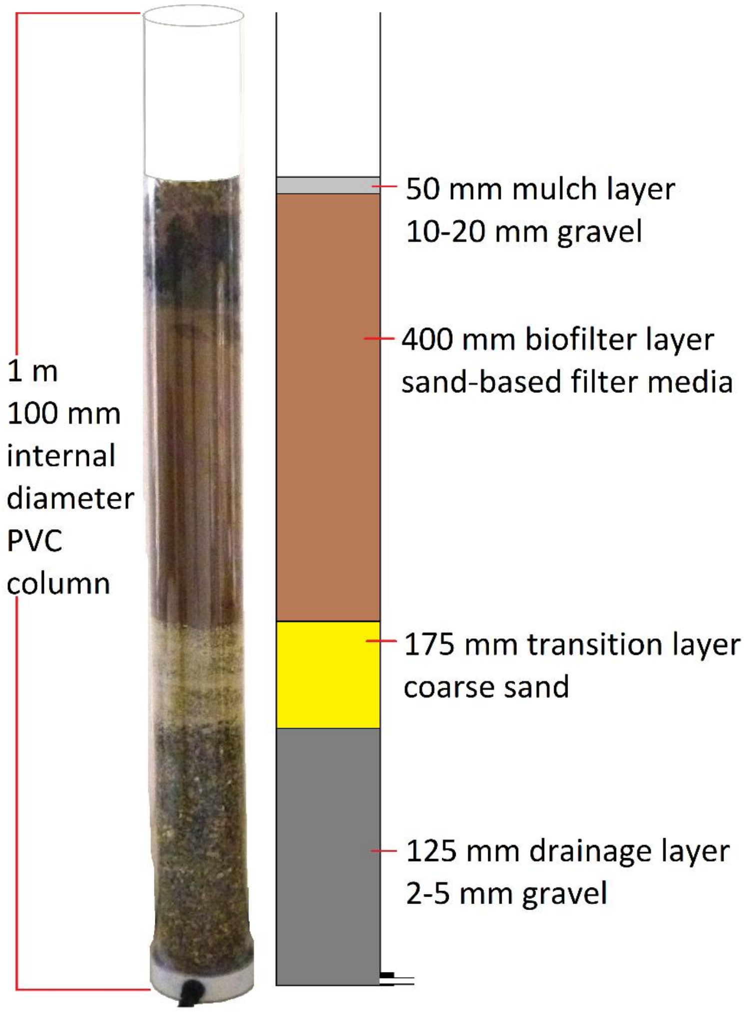


Figure 10: Fill depths of simulation biofilter column units, based on design specifications of the City of Sydney's field unit

All biofilter column units were filled to match the layered structure as depicted in Figure 10, with the median dimensions shown being derived from designs of the City's biofilter units, as validated with soil cores taken in already constructed field units. Fill depth was kept constant through all simulation experiments; however, the substrate used in the column units varied across the experimental phases. The biofilter fill is described in detail in chapters 4 and 5, as many studies have been criticised for not providing sufficient characterisation of the filter media properties (Barrett et al., 2013).

A dry packing method whereby 250 mL increments of the biofilter fill were added into the column and then mechanically compressed by applying a 100 g weight to the soil surface, which was equivalent to approximately 100 psi compactive force (Gilbert et al., 2012). A dry packing method was considered to decrease the potential occurrence of edge effects by increasing soil bulk density by excluding air spaces within the fill media. Additionally, the soil media experiences expansion when wet, which increases the soil bulk density further by swelling to fill air spaces along columns walls, further mitigating against column edge effects (Bergstrom, 1990). Compaction also reduced fill hydraulic conductivity, resulting in a fill column that complied to hydrological specifications (Figure 112 in appendix).

2.3.3. Vegetation considerations

Plants were omitted from the column simulation design, as per the precedence established in the literature for column experiments with primary focus of the soil component (Hsieh and Davis, 2005, Paus et al., 2014, Yang et al., 2010). Also, it was not feasible to be fully representative of the variety of plants typically used in the City's street stormwater biofilters and their field distribution within the small experimental column diameter It is recognised, however, that wetland plants and their related root zone are an integral part of the operation of field biofilters, with plants enhancing pollution removal through biochemical activity in the rhizosphere; therefore the study design should be expected to result in a conservative estimate of the biofilters pollution removal performance (Milandri et al., 2012, Read et al., 2010, Minett et al., 2013).

Furthermore, plant stem and root movement influence the macroporous soil structure of the biofilter fill, which is key to maintaining drainage pathways from the surface into the field soil horizon (Virahsawmy et al., 2014). Reduction in hydraulic performance, which would otherwise be maintained by the biofilter vegetation, was avoided in the columns by using a 50 mm gravel-mulch that distributed the applied hydraulic load more evenly and prevented scouring of the surface biofilter layer (Tang and Li, 2016).

2.3.4. Synthetic stormwater

Stormwater is essentially a cocktail of different chemical species, with the presence and concentration of pollutants being dependent upon the catchment characteristics from which the stormwater drains (Gobel et al., 2007). As the City's street biofilter systems are constructed within urban catchments comprised of roads, roofs, paved surfaces, and grassed parklands, the stormwater in the simulation experiments was designed to match the type and concentration of pollutants found in preliminary sampling of the City's urban catchments.

Synthetic stormwater was produced by dissolving stoichiometric amounts of high-solubility salts containing relevant pollutant ions in deionised water, followed by iterations of analysis and adjustment until a stable product complying with the desired concentrations was achieved (Table 3). The synthetic stormwater product had a pH of 7.4 ± 0.1. A synthetic approach was employed in the creation of the stormwater as it is the most common production method reported in the literature, and it allows for stormwater to be readily produced in the quantities and quality needed for laboratory simulation (Davis et al., 2006, Henderson et al., 2007).

Table 3: Chemical composition of synthetic stormwater used in the dosing of the biofilter simulation column units

Source chemical	Ion	Concentration (mg/L)
Ammonium nitrate NH_4NO_3	NH_4^+	2.300
	NO_3^{2-}	16.370
Trisodium phosphate Na_3PO_4	PO_4^{3-}	10.000
Zinc chloride $ZnCl_2$	Zn^{2+}	0.690
Copper sulphate $CuSO_4$	Cu^{2+}	0.140
Nickel nitrate $Ni(NO_3)_2$	Ni^{2+}	0.070
Cadmium chloride $CdCl_2$	Cd^{2+}	0.013
Lead nitrate $Pb(NO_3)_2$	Pb^{2+}	0.300
Potassium chromate K_2CrO_4	Cr^{6+}	0.050
Arsenic Trioxide As_2O_3	As^{3+}	0.03

The synthetic stormwater was designed to include nitrogen, as nitrate, nitrite and ammonia, to be representative of a range of nitrogen redox states and phosphorus, as indicators of eutrophication potential, as the City was particularly interested in the removal of these pollutants under its Development Control Plan (DCP). In addition, the removal of the heavy metals zinc, copper, nickel, cadmium, lead and chromium and the metalloid arsenic were included based on their association with road runoff and their potential as ecological toxicants. The synthetic stormwater was created as a single solution that included all the target pollutant species (Table 3), as it was essential to examine the competitive adsorption of the pollutants by the biofilter simulation system (Nguyen et al., 2018).

There has been a wide range of pollutant concentrations used in biofilter column research, with these stormwater pollutant concentrations being based on specific experimental and catchment conditions relevant to each study. As there is no standard concentration for the preparation of synthetic stormwater for biofilter studies, the concentration of each pollutant in the synthetic stormwater (Table 3) was based on a combination of stormwater pollutant values that have been reported for laboratory simulations elsewhere and averaged with the median value for six grab samples for first flush events at several field biofilter sites across southern Sydney (Henderson et al., 2007, Yang et al., 2010, Read et al., 2008, Wan et al., 2017, Davis et al., 2006, Sun and Davis, 2007, Gobel et al., 2007). On this basis, the synthetic stormwater formulated would vary for each stormwater biofilter catchment and some standardisation of the synthetic stormwater may ultimately be needed (Davis et al., 2003).

Suspended solids (SS) were not included in the synthetic stormwater because of the potential for adsorption of the positively charged ammonium and metal ions at an unknown rate onto these particles during storage, and potential clogging of the biofilter fill from the TSS particles which could adversely affect the filters hydraulic and pollution removal performance. For these reasons, the study followed the direction of several published studies in omitting TSS from their versions of synthetic stormwater (Yang et al., 2010, Wan et al., 2017, Davis et al., 2006, Sun and Davis, 2007).

2.3.5. General column experimental method for pollution removal performance assessment

An experimental soil-column method was developed with the following steps:

2.3.5.1. Pre-experimental purging

Pre-experimental purging refers to the process of passing distilled water through the columns before use to remove any extraneous chemical species. It was performed prior to experimental pollutant dosing as per standard methods described in the literature (Hatt et al., 2008, Good et al., 2012), and was included to simulate the maturing/establishing of biofilters in terms of fill physical, chemical and hydrological properties. Pre-experimental purging had three main functions in establishing the biofilter units:

i. settlement of the biofilter fills,
ii. flushing fine particulates and soluble ions from biofilter fills, and
iii. minimising the prevalence of column edge effect during experimental dosing.

To limit background column “noise”, naturally occurring soluble ions were purged from the soil column using repeated deionized-water flushes of 3.4 L until the three-day median for electrical conductivity (EC), a proxy for ion content, fell to below 5% of that of the synthetic stormwater. Pre-experimental purging typically took eight consecutive days before column fill EC became compliant with the established EC goal. Total flush volume of approximately 30 L was applied to each column, which would be equivalent to about 1 to 2 months of operations of field unit, under typical Australian design and climatic conditions.

Consecutive purge events effectively reduced the fine particulate concentration in the biofilter substrate matrix, reducing the elevated turbidity levels in the water draining from the column units to acceptable levels (below 100 NTU), which allowed for chemical analysis to proceed by the end of the purge phase. The results of these purge events on the discharge of total suspended solids are investigated and discussed in chapters 3 to 5.

2.3.5.2. Dosing

A gravity-fed drip irrigation system was established to dose the simulation columns. Each column had an irrigation line with a single POPE vari-flow® drip irrigation fitting that delivered 3.4 L of synthetic stormwater at a rate of approximately 1.1 L/hr. This allowed for the steady infiltration of the synthetic stormwater into the biofilter column, as per the fills unsaturated hydraulic conductivity rate for the soil column, as determined by a decagon mini-disk portable tension infiltrometer. Dosing was maintained for three hours based on good hydraulic practice and the median rainfall duration in Sydney for the years 2010 to 2013 (Yang et al., 2010, Birch et al., 2005, Bureau of Meteorology, 2015).

The delivery volume to the column units was derived from four key proximations:

i. Biofilter area – This was assumed to be the surface area of the column biofilter (2700 mm^2).

ii. Catchment area – This was the area that would feed into the column biofilter simulation, calculated based on Australian sizing specification that biofilters should be 2-5% of its catchment (Berretta et al., 2018).
iii. Rainfall volume – This was estimated based on the average daily rainfall (20.9 mm) for a runoff generating event (>5 mm) at Observatory Hill, Sydney for years 2010 to 2013 (Bureau of Meteorology, 2015)
iv. Runoff volume – Runoff was assumed to be generated from a heavily urbanised catchment where 90% of the precipitate volume is converted to runoff, emulating the high imperviousness present in some areas of the City.

As per Equation 1 and Equation 2, this gave a total dosing volume of approximately 3.4 L per column.

Equation 1

$$(Area\ of\ Raingarden + Area\ of\ Catchment) \times Rainfall \times Runoff\ Coefficient$$

Equation 2:

$$\left(\pi 52^2 + \left(\frac{\pi 52^2}{5} \times 100\right)\right) \times 20.9 \times 0.9 \approx 3.4L$$

2.3.5.3. Post-dosing

Following dosing, the columns were drained to an inert sampling container for a median interval of 16 hours or until all the drainage ceased, yielding a median 2.3 L sample. Three dosing replicate events were applied for each of the column simulations, with second dosing event occurring five days after the first had occurred, and the final repeat was completed after a further five days had elapsed, in compliance with established hydrological principles for columns (Rusciano and Obropta, 2007, Davis et al., 2001, Vanderlinden and Giráldez, 2011).

An extended conditioning or establishment period for the columns as applied by some researchers was considered unnecessary given that the filter material was commercially sourced from riverine quarries where hardy microbial species that are likely to be present in wetland ecosystems would be represented. Given the organic component of the fill, it was likely that there would be good retention and rapid regrowth of the beneficial soil microbes (Pelissari et al., 2017).

2.3.5.4. Sample removal

Representative 60 mL aliquots of the treated stormwater were collected from the sample container at the base of each column unit after the completion of the 19-hour dosing event. The water quality in the collection trays was assumed to be representative of the quality of the stormwater discharged from the biofilter at any given time during column discharge, as studies have shown that the quality of stormwater discharged from the biofilter (at least for metals) does not vary with discharge time (Davis et al., 2003). Samples were bottled for transport and analysis as per standard collection procedures (American Public Health Association et al., 2005).

2.3.5.5. Laboratory analysis, data capture and statistical analysis

The treated stormwater samples were analysed for pH, conductivity, turbidity, dissolved oxygen content, water temperature and salinity by a portable HORIBA U-10 Field Water Quality Checker, as per the meters manufacturer's operational instructions.

The turbidity of the treated stormwater discharged from the column biofilters was analysed as a proxy for suspended solids (SS). The turbidity results were later converted to TSS values by applying the conversion curve and associated formula developed from the modelling of the City's street biofilters in southern Sydney (Derry et al., 2013). The conversion was only feasible given the well-established relationship between turbidity and TSS (Hannouche et al., 2011, Al-Yaseri et al., 2013), and the applied conversion curve was developed for the City's biofilter system that the laboratory biofilter columns simulated.

Chemical analysis of samples was carried out by Australian Laboratory Services (ALS) Environmental laboratories, in terms of a City of Sydney Council policy requirement that all their environmental samples be carried out by laboratories maintaining NATA accreditation, in case of later litigation. Analysis performed on each sample included Total Nitrogen (TN) (APHA 4500 Norg/NO_3 method), Total Phosphorus (TP) (APHA 4500 P-F method), and metals cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), zinc (Zn) and metalloid arsenic (As) (inductively-coupled plasma mass spectrometry).

The returned data was stored and manipulated in Microsoft Excel® spreadsheets, with data extracted for statistical analysis using the R® open source software environment for PC. After stripping statistical outliers, the data sets for each pollutant parameter were assessed for normality by the Shapiro-Wilks test at the assumed significance limit ($p = 0.05$), with the results indicating that a normal distribution of data was not able to be assumed for all experimental data groups. To provide consistency, even when the assumptions of normality were not met, a non-parametric test Kruskal-Wallis Hypothesis test was employed to determine the significance of differences between treatment groups, again at the assumed significance limit of $p = 0.05$.

For visual examination of data spread, box-and-whisker plots were constructed using the R® software, and XY scatter graphs were produced in Excel® and used as visual representations of the linear relationships between the biofilters pollution removal and hydrological performance with substrate design variations. The strength of the linear relationships presented was examined through computing Pearson r correlations.

2.3.6. Comparison with guideline values

The experimental results were compared against local water quality guidelines. The nutrient parameters removal efficiency was assessed against the key pollutant reduction targets set out in Table 1. The City did not have any specific reduction targets for metal and metalloids for which biofilter removal performance could be related to, so removal performance was compared against the default guideline values outlined in the Australian New Zealand Guideline for Fresh and Marine Water Quality (ANZG, 2018).

The ANZG (2018) guidelines provide a generic starting point for the consistent management of water quality; it establishes discharge limits for chemical toxicants in order to maintain a water quality suitable for human uses and to protect the aquatic life that inhabits Australian water bodies (Table 4).

Table 4: ANZG (2018) default guideline values for ecological protection of aquatic ecosystems

Water Quality Parameter	Ecological Protection Level	
	95% (mg/L)	**90% (mg/L)**
Ammonia	0.9	1.43
Arsenic	0.024	0.094
Cadmium	0.0002	0.0004
Chromium	0.001	0.006
Copper	0.0014	0.0018
Lead	0.0034	0.0056
Nickel	0.011	0.013
Zinc	0.008	0.015

The guideline sets default toxicant discharge limits which have been scientifically approximated so that if this level of chemical contamination is discharged into or is present in a water body, then a certain percentage (ecological protection targets of 80, 90, 95 and 99%) of the known biological life should be able to be maintained. The ecological protection levels are selected based on the current or desired ecosystem condition of the studied water body, with three condition levels being recognised (Table 5).

Table 5: Condition of the aquatic ecosystem and the ecological protection level for the discharge of chemical toxicants that would be standardly applied

Aquatic ecosystem condition	Applied ecological protection level
High conservation or ecological value systems	99%
Slightly to moderately disturbed systems	90 or 95%
Highly disturbed systems.	80 or 90%

Given that the treated stormwater from the simulated field biofilters would enter urban creeks and eventually into Botany Bay or Sydney Harbour, and these ecosystems are moderately to highly disturbed by past and present anthropogenic activity, a default guideline target of 90% ecological protection was selected as a minimum discharge target. The biofilter pollution removal performance was also compared against the higher protection level (95%) for toxicant discharge, as a comparison with the most stringent discharge limits for the specified aquatic ecosystem is desirable to promote the greatest environmental protection.

According to Warne et al. (2018), the default guideline values for cadmium, chromium, lead, nickel and zinc that are reported in the ANZG (2018) guidelines (Table 4) need to be corrected for site specific hardness as per equations in Table 6 below.

Table 6: Hardness correction algorithms as per Warne et al. (2018) for the conversion of chronic toxicity guideline values for cadmium, chromium (III), lead, nickel and zinc at site specific water hardness to a standardised hardness of 30 mg $CaCO_3$/L

Metal	Hardness Algorithm
Cadmium	$toxicity\ value^{a} \times (H/30)^{0.89}$
Chromium (III)	$toxicity\ value^{a} \times (H/30)^{0.82}$
Nickel and zinc	$toxicity\ value^{a} \times (H/30)^{0.85}$
Lead	$toxicity\ value^{a} \times (H/30)^{1.27}$

[a] toxicity value reported in Table 4, hardness (mg/L $CaCO_3$) at which the toxicity vales was determined

Total hardness was measured and analysed by ALS according to the international standard method (APHA 2340 B). A minimal number of hardness tests were conducted for use with - the conversion of the ANZG (2018) guideline values.

The treated stormwater discharged from the biofilter columns was quite hard, with the unamended (control) biofilter having a total hardness (as $CaCO_3$) of 187 mg/L, with fill amendment increasing hardness to up to 1820 mg/L for the 30% w/w gypsum amended biofilter treatment. Substrate amendment likely increased the hardness through the partial dissolution of the fill amendments and liberation of Ca^{2+} ions, which was a common mechanism, especially with gypsum amendment as gypsum is predominately composed of $CaSO_4.2H_2O$.

When the two hardness values were added into the correction equations there was a large disparity between the hardness dependent guideline values calculated, as guideline values increased with hardness concentration (Figure 11). This meant that the higher the hardness in the stormwater, the lower the perceived ecotoxicity for the metals, and thus the lower the default metal guideline threshold could be set.

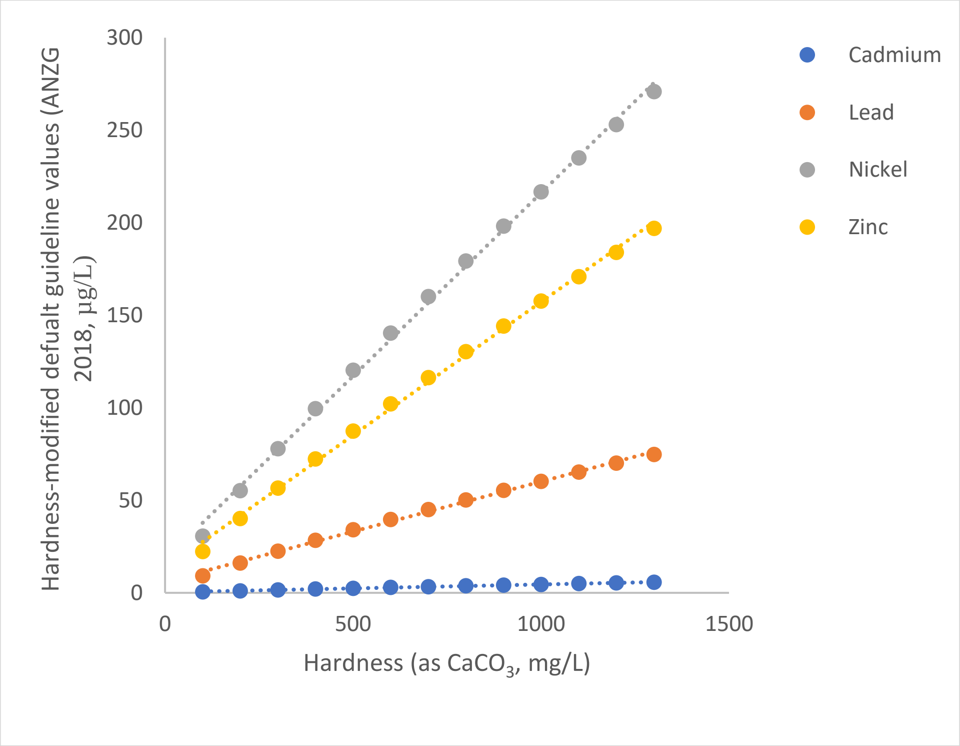


Figure 11: Effects of increasing hardness on modification of the default ANZG (2018) guideline values

The hardness values for the control biofilter units (187 mg/L) was selected for application in the hardness correction algorithms (Table 6), as this was precautionary, yielding the most stringent of the hardness-modified guideline values (Table 7) for comparison with the biofilter metal removal results.

Table 7: Biofilter specific hardness-modified default ANZG (2018) guideline values

Water Quality Parameter	Ecological Protection Level	
	95% (mg/L)	90% (mg/L)
Ammonia	0.9	1.43
Arsenic	0.024	0.094
Cadmium	0.001	0.002
Chromium	0.001	0.006
Copper	0.001	0.002
Lead	0.015	0.025
Nickel	0.052	0.062
Zinc	0.038	0.071

2.4. Further methods

In the next chapter, the first of the core experiments is discussed based on the general methods outlined in this chapter. While the description of general methodology will not be repeated, where methods have been modified, or further methods introduced to complete the simulation experiment, these approaches will be described.

Chapter 3: Simulation 1 – Biofilter efficiency with design variation

3.1. Introduction

This chapter investigated the performance of the City of Sydney's street stormwater biofilters through laboratory column simulations, as described in chapter 2. Two standard field biofilter configurations, monophasic and biphasic, were used to assess the influence that design variations have upon the pollutant removal efficiency of the biofilter system. Removal performance was assessed against local pollution control targets, of the City's DCP and BBWQIP pollution reduction targets for TN and TP (Table 1), and metals were compared against the ecological protection toxicant limits of the ANZG (2018) guideline (Table 7). Research findings from this chapter have been published in the peer-review journal Water (Switzerland) (Macnamara and Derry, 2017).

3.2. Specific experimental method

The column simulation experiment followed the general methods outlined in chapter 2; in terms of column design and operational conditions, while methodological differences unique for this phase related primarily to column configuration.

3.2.1. Column configuration

The column experiment followed the tandem column design, as depicted in Figure 9. Two of the City's biofilter designs were simulated; that of a lined monophasic and lined with saturation zone (biphasic) biofilters. The biphasic stimulation was achieved by arranging the second column inlet 210 mm above the first column outlet with a 13 mm diameter link, simulating the inverted siphon arrangement to maintain the saturation zone in field designs (Figure 9).

The simulation column units were filled to have the layered substrate structure as per Figure 10, using fill set 1, which is characterised in chapter 4.

3.3. Results and discussion

Median removal efficiency for each of the synthetic stormwater pollutant parameters for the two biofilter designs is shown in Table 8, with the spread of data shown by box-and-whisker plots (Figure 12 to Figure 17). In the plots, the box limits containing the median (horizontal bar) represent the interquartile range Q1–Q3, and the whiskers the full range. Discussion of results follows each graph, based on $p < 0.05$ as the assumed limit of statistical significance, and compliance to relevant pollutant control targets.

Table 8: Pollutant concentrations and removal efficiency by monophasic and biphasic simulations

Pollutant parameter	Source compounds in synthetic stormwater	Pollutant conc. in synthetic stormwater (mg/L)	Pollutant conc. (median) after biofiltration (mg/L)		Removal efficiency (median) for biofilter simulation (%)	
			Mono-Phasic	Bi-Phasic	Mono-Phasic	Bi-Phasic
Total Nitrogen	Ammonium, nickel and lead nitrates	16.19	2.58	1.78	84.1	89.0
Total Phosphorus	Trisodium phosphate	10.00	2.22	3.15	77.8	68.5
Zinc	Zinc chloride	0.690	0.098	0.103	85.8	85.1
Copper	Copper sulphate	0.140	0.044	0.042	68.6	70.0
Nickel	Nickel nitrate	0.070	0.006	0.008	91.4	88.6
Cadmium	Cadmium chloride	0.013	0.0004	0.0003	96.9	97.7
Lead	Lead nitrate	0.300	0.024	0.025	92.0	91.8
Chromium	Potassium chromate	0.050	0.006	0.004	88.0	92.0
Arsenic	Arsenic oxide	0.030	0.004	0.003	90.0	86.7

3.3.1. Nutrient removal: Total Nitrogen and Total Phosphorus

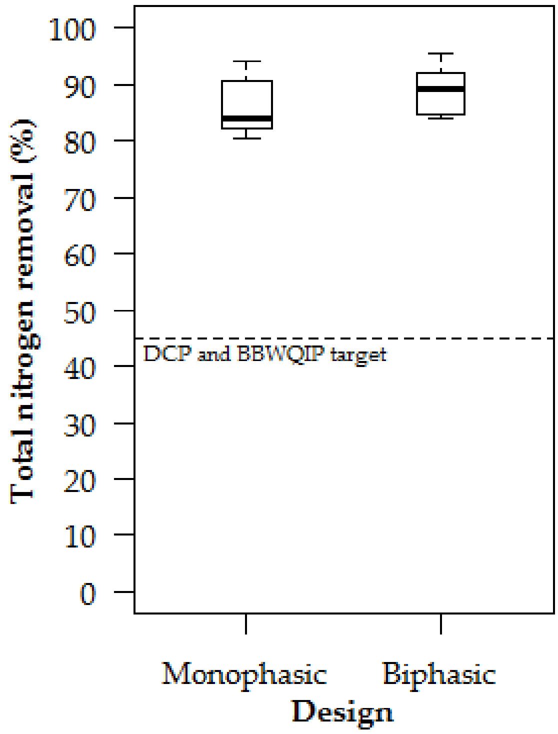


Figure 12: Total Nitrogen (TN) removal efficiency of monophasic and biphasic stormwater biofilter columns

The simulation columns achieved a median 84.0% and 89.0% TN removal efficiency for the monophasic and biphasic designs respectively, suggesting the achievement of the DCP and BBWQIP target of 45% to be well within reach for equivalent field biofilter units. The higher median nitrogen removal efficiency for the biphasic unit suggested that nitrification-denitrification had been initiated, although the difference was not statistically significant ($p = 0.17$).

Other studies have reported significant differences between monophasic and biphasic designs for TN, although these studies included plants and external carbon sources, which would enhance denitrification (Zhang et al., 2011, Nabiul Afrooz and Boehm, 2017, Yang et al., 2010).

Reasons for non-inclusion of wetland plants were discussed in chapter 2, section 3.3, and the biofilter column simulation was designed to rely on an internal carbon source to enable later comparison of fills, unlike other studies where carbon was sometimes added to water in terms of suspended solids, methanol or organics from harvested, natural stormwater.

The results of the present study, therefore, suggest that that the biphasic design should not be rejected but that further simulation research is needed, complemented with field research where higher levels of naturally occurring dissolved carbon would be encountered.

A comprehensive biphasic study elsewhere using rectangular soil columns of a larger cross-sectional area (460 × 610 mm) achieved very similar median TN removal efficiency (82%), suggesting the validity of using an economical, narrower-column simulation design (Ergas et al., 2010).

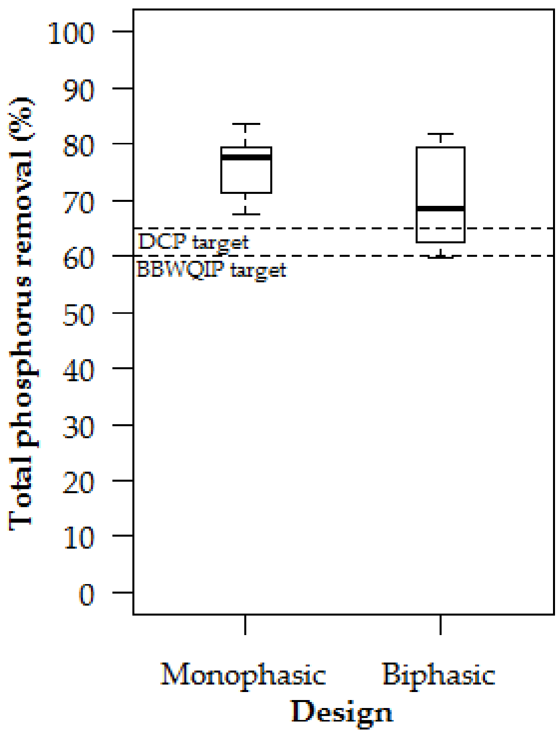


Figure 13: Total Phosphorus (TP) removal efficiency of monophasic and biphasic stormwater biofilter columns

For TP, the median removal efficiencies for the two designs were 77.8% and 68.5% respectively, with no statistically significant ($p = 0.26$) difference in TP removal between the two designs. Both designs complied with the City's DCP and BBWQIP removal targets for median TP removal (Figure 13). The full range of experimental results for the monophasic experiments complied with both targets (range = 67.6% to 83.8%), while some of the biphasic results in the interquartile range were non-compliant with the DCP target.

Stormwater biofilters have a limited phosphate retention capacity, which can be impacted by fill characteristics including initial phosphate concentration, fill depth, biochemical phosphate removal pathways, and the physical remobilization of phosphate bound to chemicals such as iron in the original fill (Glaister et al., 2014).

While biphasic TP removal efficiency was very similar to that achieved by larger rectangular columns (66%) (Davis et al., 2001), it was distinctly better than that achieved for small-diameter (64 mm) columns (58% median, 47% minimum) (Hsieh et al., 2007a). It is possible that where the column diameter is reduced below a critical level, factors such as edge effect and biofilm presence exert undue influence on removal efficiency.

Of interest was the increased median biphasic removal efficiency of TN, but not of TP when compared to that for monophasic units. Improved nitrogen removal over that of the phosphorus supports the existence of nitrification-denitrification in the laboratory monophasic units, given that there is no biochemical equivalent for phosphate removal under the required anaerobic conditions (Pelissari et al., 2017, LeFevre et al., 2014).

3.3.2. Heavy metal removal

The ecotoxicity of metals in stormwater relates in part to their field partitioning in the dissolved, suspended, or settled phase (Huber et al., 2016). Predominance in the dissolved-phase makes them readily bioavailable and hence more ecotoxic than those in suspended (particulate) or settled (sediment) phases, although metals readily cross these boundaries depending on the redox or pH status of the aquatic environment (Westerlund and Viklander, 2006). In making up the synthetic stormwater, metal salt compounds of high solubility were used to ensure availability of reactive ions in the columns.

3.3.2.1. Dissolved-phase heavy metal removal

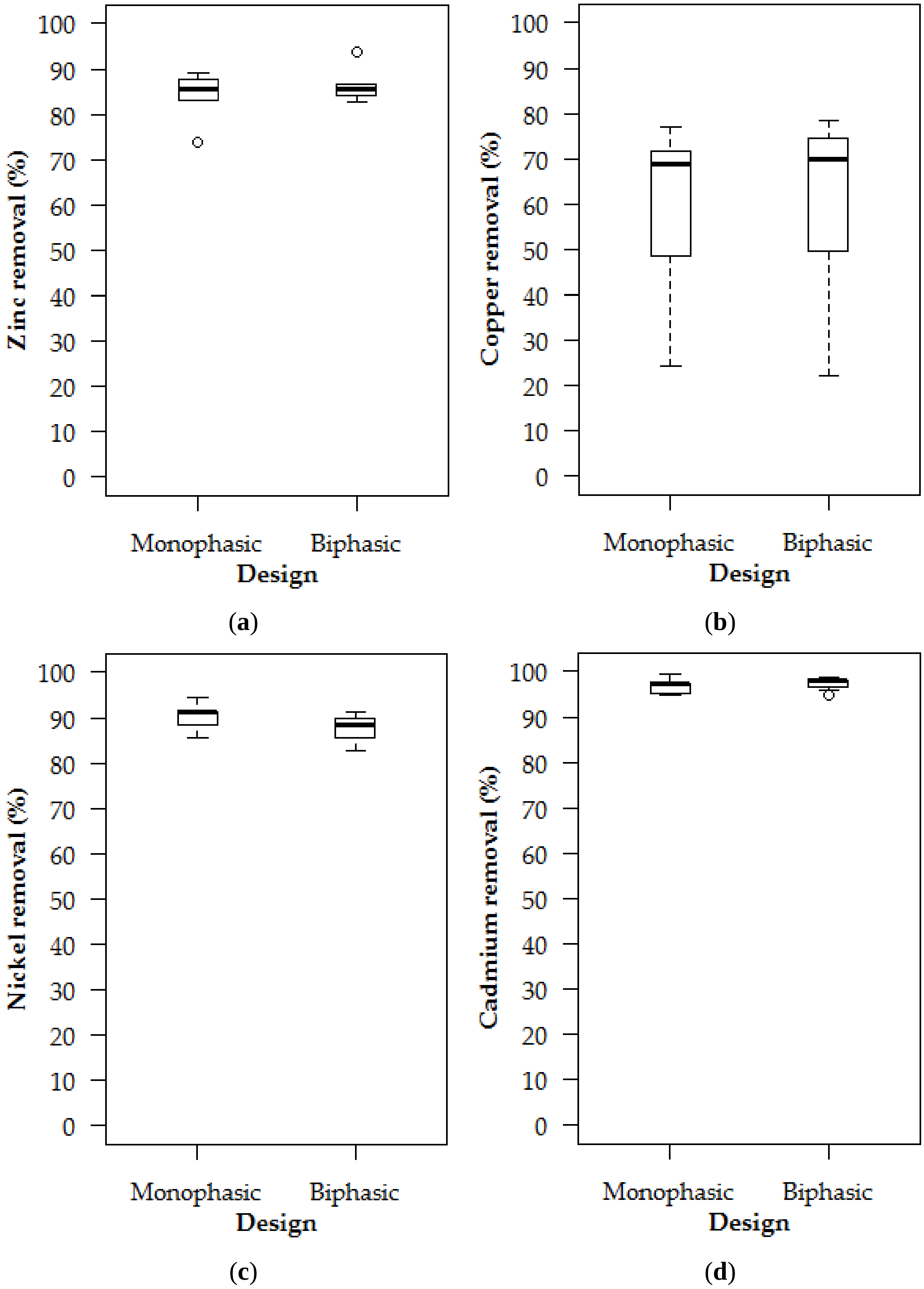


Figure 14: Dissolved-phase heavy metal removal efficiency by design type: (a) zinc (Zn); (b) copper (Cu); (c) nickel (Ni); and (d) cadmium (Cd). "○" indicates outliers

Zinc, copper, nickel, and cadmium are the most common dissolved ecotoxicants in stormwater, which through their bioavailability and bioaccumulation in aquatic and marine food chains, may result in a reduction of biodiversity and ultimately the contamination of human water and food supplies (Bennasir and Sridhar, 2013, Hrubá et al., 2012).

Zinc and copper have been shown to exhibit the highest intrinsic ecotoxicity in biomonitoring experiments using representative macroinvertebrates, fish and algae bioindicators, as based on a number of runoff stages during rainfall events (Kayhanian et al., 2008). In terms of intrinsic mammalian toxicity (LD50), zinc is not as poisonous as the other metals in the dissolved-phase, but occurs in much higher concentrations in road runoff than the other heavy metals, making it the most important ecohazard (Klaassen, 2013). It is released by a wide range of road infrastructural sources, including galvanised crash barriers (undergoing frequent gouging impact), fences, traffic light gantries and street lighting poles, as well as vehicular sources, including car bodies, automotive components and recycled oil. Zinc is also an important vulcanising agent in tyres, with deposits being left on the road in rubber globules causing a prolonged release, and is leached by soft rainwater from roofs, piping, and other infrastructure in urban areas (Kayhanian et al., 2008, Yuan et al., 2017). Given these factors, zinc deserves a high profile in research relating to urban stormwater contamination, whereas copper might be a preferred indicator for atmospheric-mediated stormwater pollution, particularly where smelting of associated heavy metals occurs.

In the simulations, median monophasic and biphasic removal efficiencies for metals were impressive; 85.5% and 85.7% for zinc, 67.9% and 68.6% for copper, 91.4% and 88.5% for nickel, and 97.3% and 98.0% for cadmium respectively (Figure 14). The simulation column biofilters, regardless of column design, was able to reduce median nickel and cadmium concentrations to below the 95% ecological protection level, while zinc and copper did not comply with the 90% ecological protection limit.

There was no statistically significant difference between monophasic and biphasic removals for any of the dissolved-phase metals ($p = 0.43, 0.73, 0.08$ and 0.21 respectively), whereas, in some simulation studies, the inclusion of a saturation zone improved removal efficiency for copper and zinc (Blecken et al., 2009b, Zhang et al., 2014).

Results for monophasic removal for zinc, copper and nickel were remarkably similar to those in earlier studies (84%, 67% and 95.9% respectively) (Hatt et al., 2009). Median cadmium removal (96.9%) was enhanced in comparison to the 85.2% removal efficiency previously reported for unvegetated monophasic biofilter columns (Vijayaraghavan and Praveen, 2016).

The concentration of copper in the stormwater discharged from the simulation biofilter columns was above the initial dosing concentration in three cases, with copper concentration increasing to 0.61, 0.89 and 0.23 mg/L. A leaching experiment, reported in chapter 6, showed that copper had a relatively high (compared to the other metals) rate of leaching (0.08 mg/L). Considering the relatively minute concentrations the column was dosed with (0.14 mg/L), even a small amount of copper leaching from the biofilter fill could have a major impact upon the biofilters copper removal performance. While the increased range of results produced by the leaching events are shown here, individual events were easily identifiable as outliers enabling stripping of these during statistical analyses involving this data set.

Copper leaching is known to occur in biofilter systems, with the relevant scientific literature indicating that dissolved copper is generally leached from the soil column complexed with dissolved organic matter (DOM) associated with organic compost in the biofilter fill (Li and Davis, 2009, Chahal et al., 2016, Mullane et al., 2015). It is possible that the copper leached from the biofilter may not cause any substantial ecological harm to downstream aquatic ecosystems, as copper-DOM complexes tend to be less ecotoxic than free copper ions (Chahal et al., 2016).

3.3.2.2. Suspended- or settled-phase heavy metal removals

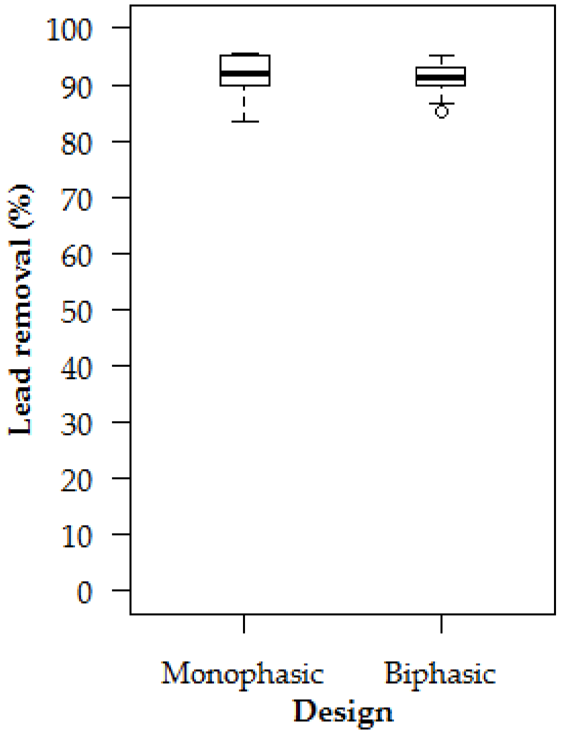


Figure 15: Lead removal efficiency by monophasic and biphasic stormwater biofilter columns. "○" indicates outliers

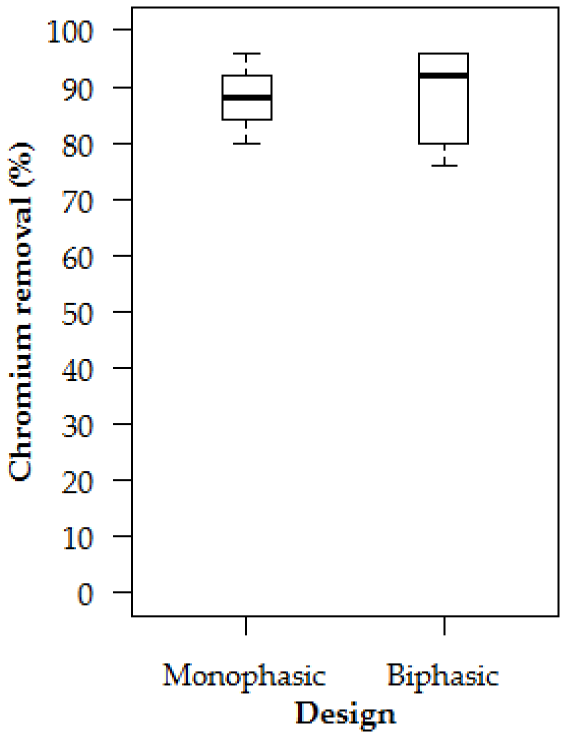


Figure 16: Chromium removal efficiency by monophasic and biphasic stormwater biofilter columns

Lead and chromium salts on road surfaces are mainly particle-bound, so TSS removal by stormwater biofilters may be an important strategy in avoiding an accumulation of these substances in receiving water sediments (Gunawardena et al., 2015). Tetraethyl lead was liberally used (up to 0.15 g/L) as an anti-knock ingredient in Australian petrol from 1921 to 2002, and chromium release still occurs from wear and tear to automotive steel, chromium plating, paints, corrosion coatings, brake linings, and catalytic converters. Certain industrial plating processes act as a potential source of carcinogenic hexavalent chromium compounds, and these could also be environmentally generated through the conversion of the non-carcinogenic trivalent form (Klaassen, 2013).

The simulation biofilters effectively removed the suspended phase heavy metals with greater than 75% removal for lead and chromium for all biofilter simulation columns tested. Median monophasic and biphasic removal efficiencies were 92% and 91% for lead (Figure 15), and 88.0% and 92.0% for chromium (Figure 16) respectively. There was no statistically significant difference between the design variations for lead ($p = 0.85$) and chromium ($p = 0.79$).

Lead concentration from both the monophasic and biphasic biofilter designs conformed to the 95% ecological protection guideline, while both designs conformed to the 90% protection level for chromium. Chromium did not conform to the 95% protection level; however, the 0.001 mg/L for the guideline is quite stringent. The biofilter retained proximately 90% of the chromium dosed, thus already providing substantial ecological protection.

3.3.3. Metalloid arsenic removal

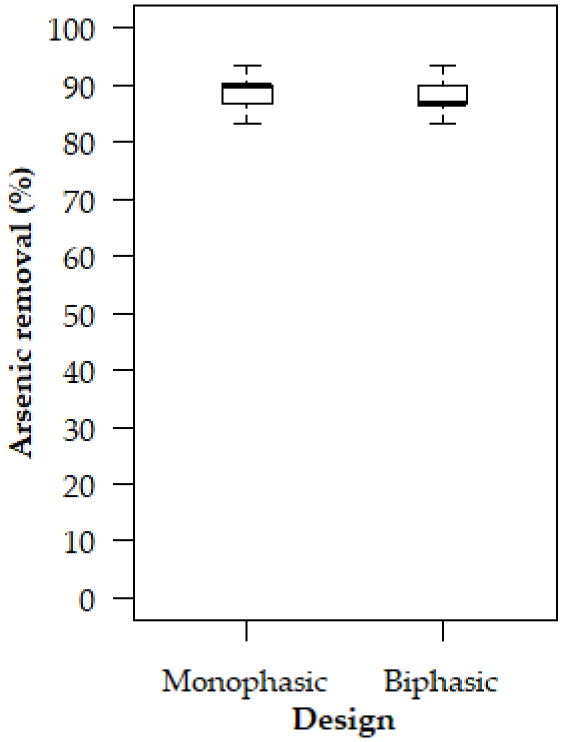


Figure 17: Metalloid arsenic removal efficiency of monophasic and biphasic stormwater biofilter columns

Arsenic enters urban stormwater primarily from leaching from arsenic containing soils, as arsenic naturally occurs in surface soils at median background concentrations of 4.8 mg/kg (Geoscience Australia, 2020) and higher concentrations (42 mg/kg) in contaminated soil from past industrial practices (Ying et al., 2009). In addition, arsenic can enter the environment by leaching from chromated copper arsenate pressure-treated wood, application of arsenic containing pesticides, the use arsenical animal drugs, and airborne deposition from industry (Erbanova et al. 2008).

Arsenic speciation primarily affects its toxicity, with arsenic (III) being the more toxic form. At stormwater concentrations, arsenic is potentially ecotoxic to phytoplankton and aquatic macroinvertebrates, however, the bioaccumulation of arsenic in aquatic and marine food chains, can lead to elevated arsenic concentrations in higher taxas, for instance 1 to 100 mg/kg dry weight of organoarsenic compounds have been found in the tissues of marine fish (ANZG, 2018).

The simulation columns achieved a median arsenic removal efficiency of 90.0% and 86.7% for the monophasic and biphasic designs respectively (Figure 17). There was no statistically significant difference ($p = 0.78$) between the two design treatments, which indicate that the inclusion of an anaerobic sump in biofilter design did not influence arsenic removal. Equally high removal in both biofilter design variations suggests that substrate properties were primarily responsible for arsenic retention (Szakova et al., 2009, Smith et al., 1999). The role of the filter fill upon arsenic removal performance being further explored in chapters 4 and 5.

Effective arsenic removal by both the monophasic and biphasic biofilter column designs meant that median arsenic concentrations in the treated stormwater conformed to the 90% ANZG (2018) default guideline, but not the 95% ecological protection level (Table 7). Dilution of the treated stormwater in the receiving waterways would likely mean that water quality would conform to the stricter 95% ecological protection guideline. Further improvements in arsenic removal by the biofilter system may be achieved, however, the effect of speciation and behaviour of arsenic in the soil matrix and aqueous solutions needs to be considered.

3.3.4. Total suspended solids

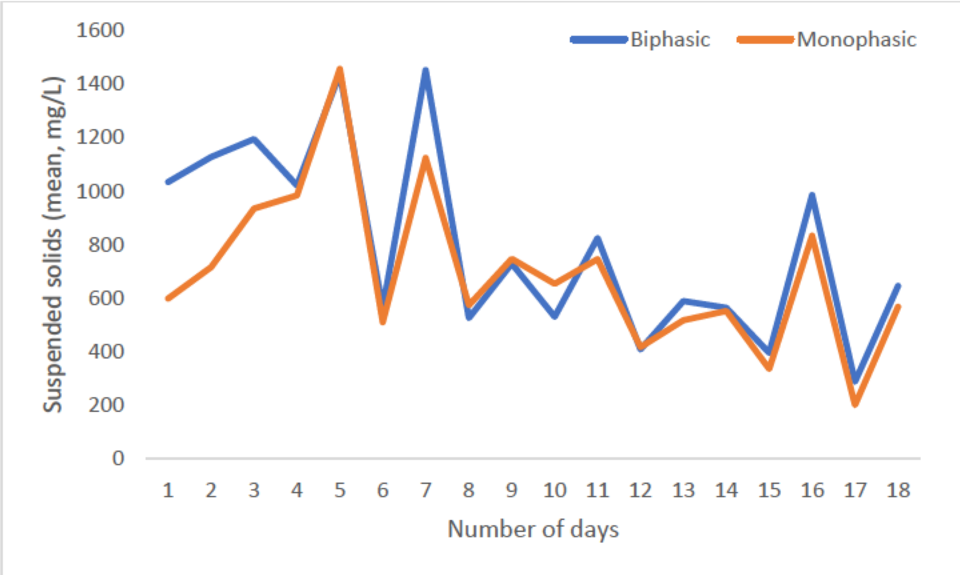


Figure 18: Mean total suspended solids release by monophasic and biphasic biofilters columns during 18 daily purge events

Despite omitting suspended solids from the synthetic stormwater, TSS was still discharged from the simulation biofilter columns, with between 1456 to 200 mg/L TSS being discharged during the 18 purge events (Figure 18). Suspended solids discharge generally declined over the successive purges, with the column simulation having a moderate negative correlation between TSS discharge and cumulative volume of purge water applied for the monophasic ($r = -0.40$) and biphasic ($r = -0.53$) design columns respectively.

There was no statistically significant difference ($p = 0.09$) in TSS release between the designs from individual purge events and collectively across the entire purge phase (Table 32 in appendix). The lack of difference in TSS release in the laboratory simulation was counter to field observations of the City's street biofilter systems. Preliminary field results indicate the City's field biphasic biofilter systems can discharge upwards 407 mg/L of SS, while monophasic systems discharge <25 mg/L of TSS (Derry et al., 2013).

The elevated TSS discharged from the saturated sump of the field biphasic biofilter was attributed to the production of "sludge" (biofilm and microbial spores) from anaerobic digestion during environmentally challenging conditions; i.e. low hydrological flows, low carbon availability. Organic sludge build-up was not observed in the simulation biofilters, likely due to the short-term nature of the experiment, and the uniform hydrological/environmental conditions the columns were operated under. Further column study with extended antecedent dry periods between wetting events, which puts the anaerobic microbes under environmental stress, is needed to evaluate the additional TSS discharge from biphasic designs saturation sump.

3.4. Conclusions

Through laboratory simulation, the performance of the two field biofilter designs was assessed in terms of a limited but locally relevant set of monitoring parameters.

Removal of TN by the simulation units was found to be highly efficient, with the results of all test runs showing compliance with the City's DCP removal target. The higher median nitrogen removal efficiency for the biphasic unit suggested that nitrification-denitrification had been initiated, although the difference between designs was not statistically significant ($p = 0.17$). The biphasic TN removal efficiencies by the simulations are likely to have been conservative in terms of that which might be obtained in the field, using fully functional planted units with external carbon source (derived from stormwater and breakdown of humic materials), which would promote greater denitrification and thus improve TN removal by the biphasic system.

The removal of TP by the units was less efficient with a few biphasic test runs failing to comply, although the median results for both monophasic and biphasic designs showed compliance. The target may be achieved in the field, as TP is progressively removed along the treatment train, of which stormwater biofilters are an integral part, but this will only be confirmed following further research of field units and the treatment train. Further research into optimizing TP removal by stormwater biofilters is needed, with this notion being explored in chapter 5, with substrate amendment tailored towards enhanced TP removal.

The biofilter system, regardless of design variation, had excellent pollution removal performance, with more than 75% of heavy metals except copper, being removed from the synthetic stormwater. High removal efficiency meant that metal and metalloid concentrations in the treated stormwater were equal or below discharge levels as set in the ANZG (2018) as per the established hardness level of the system, with all metals, again with the exception of copper and zinc, conforming to the 90% ecological protection level. Furthermore, the final median concentrations of cadmium, nickel and arsenic in the treated stormwater from the biofilter columns also satisfied the requirements of the more stringent 95% ecological protection guideline.

Despite omitting suspended solids from the synthetic stormwater, TSS was still discharged from the simulation biofilter columns. Biofilter design was not a factor for TSS release, with there being no significant ($p = 0.09$) difference in TSS release between designs. Field biphasic designs have been shown to discharge upwards of 400 mg/L of SS, due to production of biofilms and microbial spores in the anaerobic sump, which was not observed in the relatively short-term column experiment. Therefore, the TSS release was primarily from the leaching of fine particulates from the fills, with the impact of fill variation on TSS release being further studied in the following chapters.

Chapter 4: Simulation Experiment 2 – Biofilter fill performance with City fill specifications

4.1. Introduction

In the previous chapter, the simulation results demonstrated that the City's field biofilter designs operated effectively in terms of metal, metalloid and nutrient removal; however, the simulation experiment and field reports indicated that the biofilter fill was a persistent source of suspended solids during the start-up phase of earlier constructed field units (Derry et al., 2013). In response, the City introduced purchasing specifications for fill materials based on recommendations in the literature (FAWB, 2009). Table 9 shows that these were primarily related to physical particulate size, whereas it is known that several other factors can also influence TSS release and biofilter pollutant removal performance, which include; the nature of the organic matter (humus) added to the filtration sand required to sustain plant growth, the intrinsic hydraulic conductivity of the overall soil column, the chemical qualities of the soil and fill packing characteristics (Paus et al., 2014, Kraus et al., 2014, Clark and Pitt, 2010, Henderson et al., 2007).

Table 9: City of Sydney's fill purchasing specifications

Biofilter layer and liner	Specification (based on FAWB (2009) guidelines)
Mulch	Washed aggregate, 10 mm to 20 mm grade
Filter	Sandy loam mix Saturate hydraulic conductivity >100 mm/h to 300 mm/h Total clay and silt content <3% Organic content <5%
Transitional	Washed, recycled glass-sand or coarse washed river sand with little or no fines
Drainage	No-fines drainage gravel, 2 mm to 5 mm grade
Outer liner	Concrete

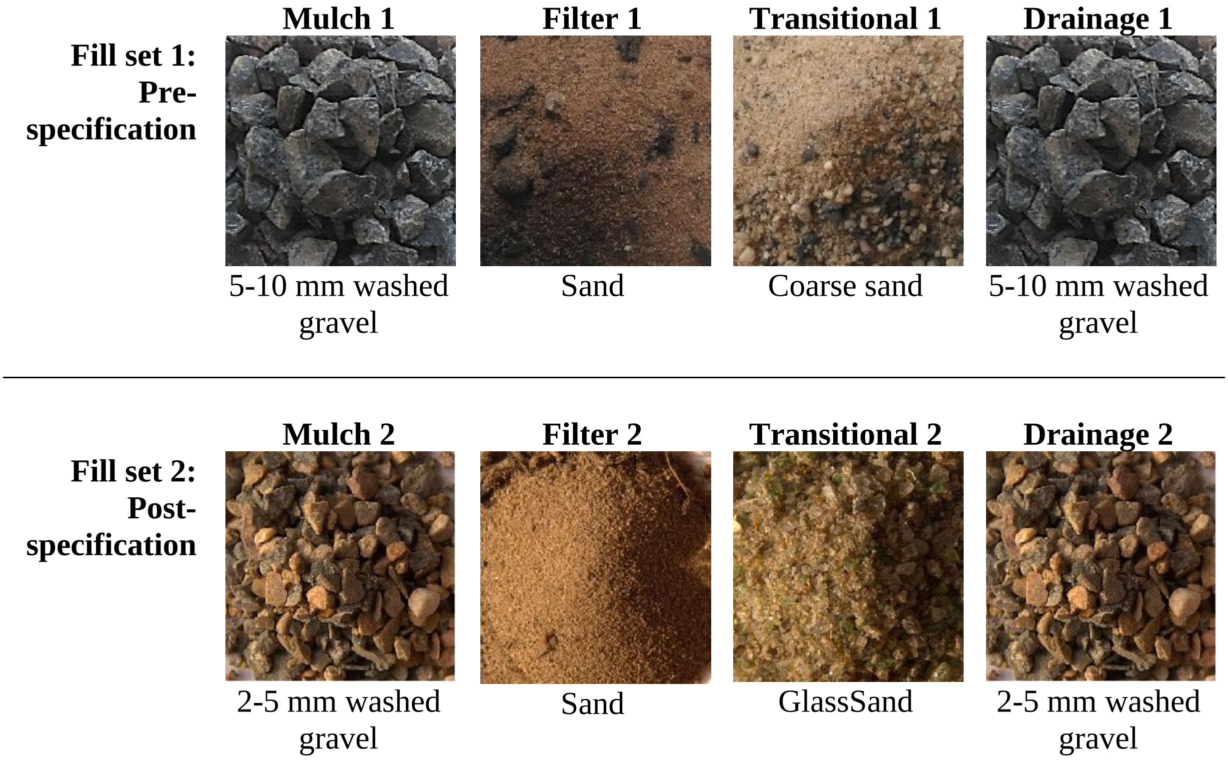


Figure 19: Fill materials used in the construction of field units in the City of Sydney, as comparatively studied

In order to study the implications of the purchasing specifications on fill quality and TSS release, a series of experiments were carried out on remnant stocks of fill in common use before the City's specifications were introduced (fill set 1, Figure 19), and a batch fill supplied by a large quarrying company in terms of the City's fill purchasing specifications (fill set 2, Figure 19). The objective of these tests was to gain further insight as to the outcomes and value of introducing physical controls (Table 9), as well as developing empirical testing strategies with the capacity to identity fill problems which lay outside the physical control parameters. In this way, the selection of an optimal fill could be achieved in terms of increasing pollutant removal performance, while reducing TSS release, and mitigating ageing fill clogging, which is the ultimate outcome of an incorrect fill composition of a commercial filtration mix. Although, this section is tailored towards the City, the understanding developed of what constitute good fill specifications, and how to test and measure the fill quality can be applied to broader biofilter management.

4.2. Fill characterisation sub-experiments

Biofilter fill variations were explored in five separate but inter-related sub-experiments in order to gain a robust understanding of how the City's fill specifications will impact field biofilter performance:

i. TSS release,
ii. hydrological assessment through fill infiltrometry,
iii. physical particle size analysis,
iv. chemical make-up characterisation, and
v. column simulation for pollutant removal performance assessment

In addition to the City's physical sizing specifications, the above fill characterisation experiments were compared against the physical, chemical and hydrological requirements of the adoption guidelines for stormwater biofilters developed by the Australian Cooperative Research Centre (CRC) for Water Sensitive Cities (Payne et al., 2015).

4.2.1. Sub-experiment 1 – Total suspended solids

The City's fill purchasing specifications are tailored towards limiting total suspended solids release from the biofilter system, by reducing the initial fine particulate availability within the fill matrix upon biofilter start-up. The migration of particles within the biofilter fill has profound effects on the fill stability (Dikinya et al., 2008), and the excessive release of sediment has a detrimental impact upon downstream water quality and the health of aquatic biota (Bilotta and Brazier, 2008).

In this section, the efficacy of the physical sizing specification upon fill quality was explored through the assessment of TSS discharge from soil column simulations. The column simulations allowed for a greater understanding of the behaviour of particle migration and release from the biofilter fill which would not otherwise have been gained from the physical sizing specifications alone.

4.2.1.1. Total suspended solids release column monitoring method

The laboratory simulation method, as described in chapter 2, formed the basis for determining the TSS release and pollutant removal performance of the biofilter fill variations from the introduction of the City's fill specifications. A single column monophasic design configuration (Figure 20) was adopted for the biofilter simulation experiments in this chapter and all subsequent experiments, as:

i. a monophasic field design was preferred by the City for promoting aquifer recharge, in which the limitation of TSS was of partial importance, and
ii. the following chapters were primarily aimed at investigating the influence of fill type and not design upon system performance. A monophasic column simplified the simulation model and minimised confounding influences of design variations.

Figure 20: Cluster of biofilter simulation column apparatus depicting single PVC monophasic column arrangement, underdrain tubing and effluent collection trays (Macnamara 2015)

4.2.1.2. Total suspended solids release results

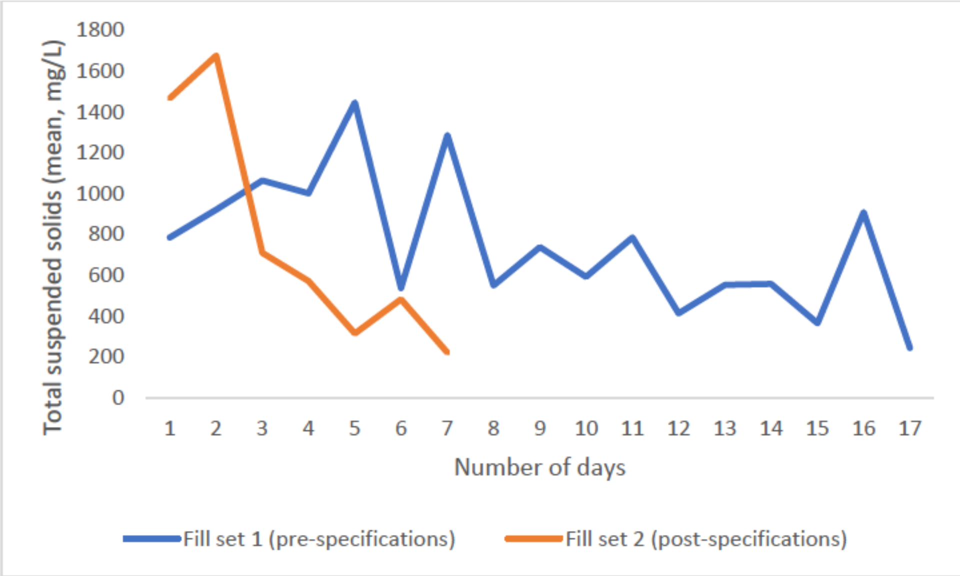


Figure 21: Mean total suspended solids (TSS) release between the pre- and post-specification fills during daily purging of the column biofilter simulations

Column simulation modelling demonstrated that the introduction of the City's fill specifications had a profound influence upon fill quality, especially in regards to TSS release (Figure 21). Despite the introduction of the fill specifications, TSS was still found to be discharged from the biofilter system; however, at a much-reduced rate than compared to the pre-specification fill (Figure 21). The reduction in TSS discharge was significantly ($p < 0.01$) different from the original level for both fill sets; however, the final levels at the end of the purge period remained above the ecological trigger value of <50 NTU (equivalent here to a TSS of 78.3 mg/L) (Figure 21) (ANZG, 2018).

Both fills showed a general downward trend in the release of TSS in the column effluent stream (Figure 21). Although fill set 2 had an initially high TSS release of 1467 mg/L, which was greater than the 785 mg/L released from fill set 1, the TSS in fill set 2 rapidly declined to approximately 220 mg/L in seven days, while fill set 1 had a more persistent release of TSS, taking an additional ten days to achieve a statistically ($p = 0.1$) equivalent release to that of fill set 2 (Figure 21). There was a statistically significant difference in TSS release between the two fill sets, with fill set 2 having higher TSS release than fill set 1 on days one and two, and a significantly lower release on days four, five and seven (Table 33 in appendix).

The persistence and variation of TSS released in fill set 1 was of concern, even if low absolute TSS levels were achieved at start-up, as the matrix might remain unstable in the long-term. The variation in TSS release could be attributed to a combination of several potential factors; 1) wetting and drying cycle from the daily purging, 2) available fine particulates in the fill media and 3) fill hydrology – hydraulic conductivity and tortuosity (flow path) through the substrate (Reddi, 1997).

Particle size analysis (section 2.3) indicates that <3% of the bulk mass of all substrates employed in the construction of the simulation biofilters was composed of fine particulates (<75 µm). There was, however, a difference in the availability/leachability of these particulates between the fills as indicated by turbidity released from a 1:10 suspension of fill sample in water (Table 10), where there was a 120 NTU and 659 NTU difference in between fills for drainage gravel and transitional sand respectively. No difference between the filter fill was detected, as both filter fills were highly heterogeneous with particle fractions which are readily suspended in water.

Table 10: Turbidity release of 1:10 suspension of the two fills in water

Biofilter Layer	**Turbidity (NTU)**	
	Fill set 1	**Fill set 2**
Filter	999	999
Transitional	999	340
Drainage	390	270

The variability in TSS release may also relate to fill hydrology, whereby the variable flow rate and tortuosity influence the migration of fines within the fill matrix. The action of the infiltrating stormwater passing through different flow paths on each subsequent purge event could expose new substrate and available fine particulates for leaching, therefore, causing the peaks in the TSS release that occur throughout the 17 purge events.

4.2.2. Sub-experiment 2 – Hydrological performance

Hydraulic conductivity is the rate at which water moves through the soil, with the City's fill purchasing specifications requiring a hydraulic conductivity of between 100-300 mm/hr, as per guideline recommendations (FAWB, 2009, Payne et al., 2015). This rate is needed in order to achieve an acceptable balance between the biofilters two opposing hydrological goals:

i. Retention of sufficient water to allow for a range of wetland plants to thrive and produce a root zone capable of filtering and retaining stormwater pollutants, and
ii. Allowance for the free passage of water through the substrate to act as a physical filter bed (Le Coustumer et al., 2009).

Problems arise when the biofilter fill's hydraulic conductivity is outside the optimal range:

i. Below 100 mm/hr, the biofilter can become clogged; where sediment deposition and soil compaction in the system can decrease the porosity of the soil and reduce the capacity of the biofilter to infiltrate stormwater (Liu et al., 2014), resulting in slowed drainage through the system, extended pooling of stormwater on the biofilter surface, system bypass, and plant damage from the prolonged inundation.
ii. Above the 300 mm/hr, stormwater may drain water too rapidly through the biofilter, resulting in ineffective pollutant retention, plant stress and dieback, as insufficient water is retained in the plants' root zone to maintain healthy plants.

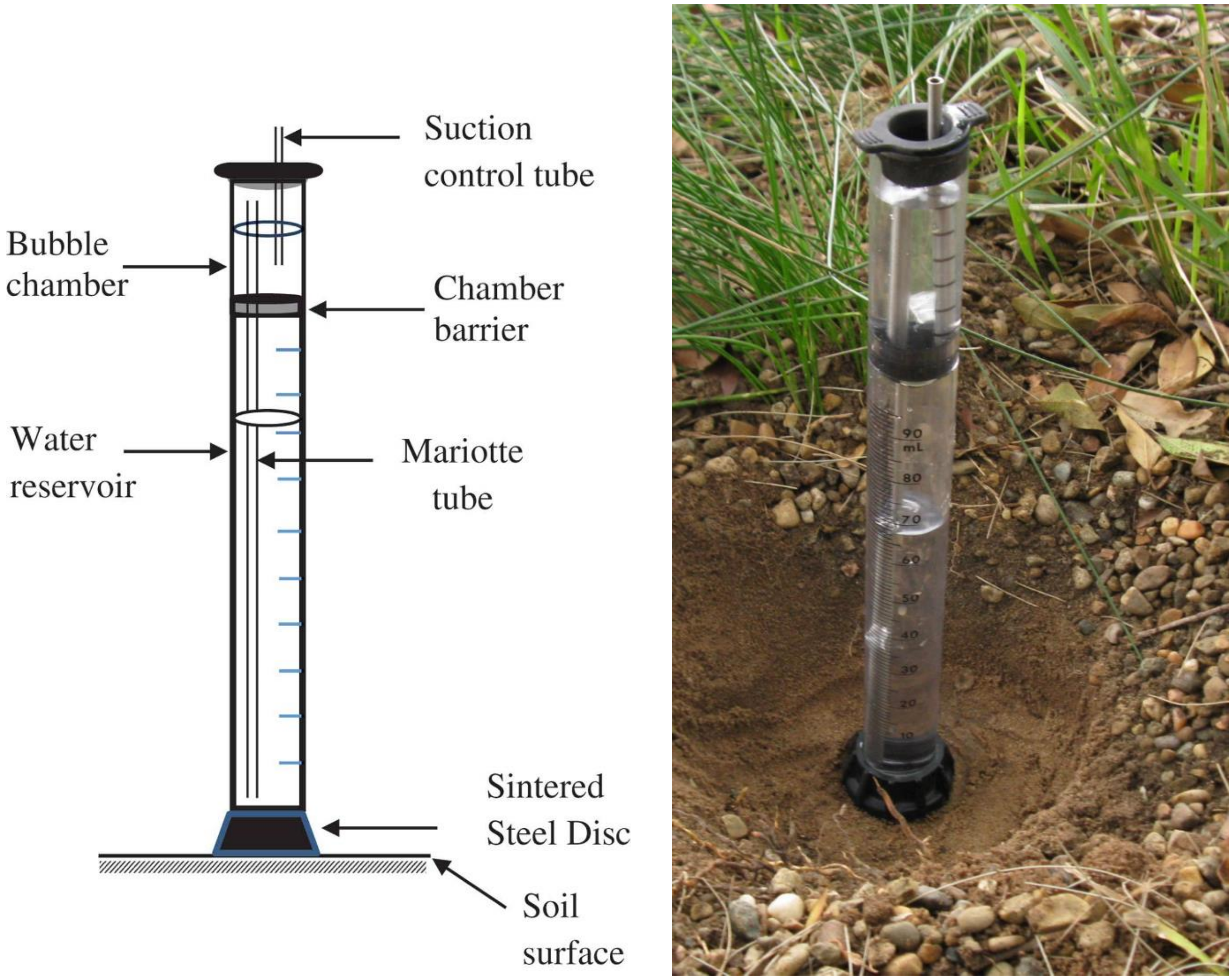
Difference in hydraulic conductivity between the pre- and post-specification fill variations may explain some of the TSS release and pollutant removal variability (chapter 3), as pollutant removal performance and TSS release is intrinsically linked to fill hydraulic conductivity (Kraus et al., 2014, Takaijudin et al., 2017).

In this section, the hydraulic conductivity of both biofilter fill sets were assessed through infiltrometry, in order to understand the impact of the physical sizing controls on biofilter hydrology, and how fill hydrology impacts biofilter performance in terms of TSS release and pollutant removal performance.

4.2.2.1. Hydrological assessment methods

4.2.2.1.1. Fill hydraulic conductivity – Mini-disk infiltrometry

A microflowmeter-tension disc infiltrometer, commonly known as a “mini-disk infiltrometer” sourced from Decagon Devices, was used to determine the hydraulic conductivity of the biofilter fills (Figure 22), as it is a common method in the literature for determining the hydraulic conductivity of surface soils (Naik et al., 2019, Kargas et al., 2017).



(a) (b)

Figure 22: Mini-disk infiltrometer a) Schematic diagram (Naik et al., 2019) and b) as operated in field stormwater biofilter unit (Derry et al., 2013)

The infiltrometer consists of a two-chambered column, an upper bubble chamber which controls suction and a lower water reservoir that provides water for infiltration (Naik et al., 2019, Kargas et al., 2017). Unlike other methods, the mini-disk infiltrometer is not reliant upon a constant hydraulic head to force water into the soil (Moret-Fernández et al., 2012) as it operates instead by virtue of adsorption of water into the soil via the sintered stainless-steel disk. An estimate of the soil column's ability to allow hydraulic flow can be gained, which is free from the influence of a potentially fluctuating hydraulic head.

The mini-disk infiltrometer was operated as per the manufacturer's instructions (Meter Group Inc., 2018). The suction control tube was set to 2 mm, and the initial water volume (typically around 90 mL) contained in the water reservoir was recorded for use in later calculations. The infiltrometer was placed flatly in the centre of the filled column, so that the infiltrating waterfront had no interaction with the column walls, thus eliminating any potential for an edge effect influencing the measured fill hydraulic conductivity. At the point of soil contact, a stopwatch was activated, and volume measurements were recorded every ten seconds until all water was drained from the water reservoir or two minutes of drainage time had elapsed.

4.2.2.1.2. Test column and fill

Fill samples were air-dried in a drying oven at 105°C for 5 hrs. Dry samples were used in order to remove the confounding influence of residual soil moisture, which can alter fill infiltration rates (Kirkham, 2014). A relatively dry soil was expected to be the predominant hydrological state in the biofilter system, given that the biofilter's sandy soil tends to have reduced water retention capacity, as there are strong infiltration and evaporation pressures extracting water from the sand matrix (Zhuang et al., 2013, Hess et al., 2017). Adding to this, Australia experiences prolonged drought conditions of low rainfall and high temperatures. Given the relatively dry state of the fill, the hydraulic conductivity calculated can be considered as the upper limit of potential hydraulic conductivity of the field biofilter system.

The pre-dried samples were used to fill a 400 mm internal diameter by 200 mm deep clear acrylic column to a depth of 100 mm. The column was sized to accommodate the approximately 150 mm diameter wetting front created by the mini-disk infiltrometer.

4.2.2.1.3. Hydraulic conductivity- Gravel

The hydraulic conductivity of the gravel fills was not assessed using the same method as that for other biofilter fills, as the distribution of the gravel pieces created inter-particulate pore spaces with sufficient volume to equal that of open air, with the increased air spaces reducing water flow potential and thus preventing the water from draining from the porous sintered stainless-steel disk of the mini-disk infiltrometer

To estimate the hydraulic conductivity of the gravel, a 104 mm by 480 mm PVC column was filled with the test gravel, and 500 mL of water was manually added to the gravel surface at a rate of approximately 30 ± 2.5 mL/second. The time taken for the infiltrating water to pass through the test gravel and drain from the column was recorded and used as a proxy for the gravel permeability/infiltration rate.

4.2.2.1.4. Data conversion and statistical analysis

Hydraulic conductivity was calculated by inputting the initial water volume in the water reservoir, volume per time increment, suction control, and soil type data into the provided Microsoft Excel worksheet from Decagon Devices. Soil type was set to sandy loam for all filter fill treatments, while it was set to sand for the transitional fills. The calculator produced a hydraulic conductivity value measured in cm/s, which was converted to mm/hr, as this was the more common unit reported in the scientific literature (Takaijudin et al., 2019, Payne et al., 2015).

Standard statistical analysis using Kruskal-Wallace test and Pearson's R correlation were performed on the hydraulic conductivity data as per the standard methods described in chapter 2.

4.2.2.2. Hydrological characterisation results and discussion

4.2.2.2.1. Filter fills

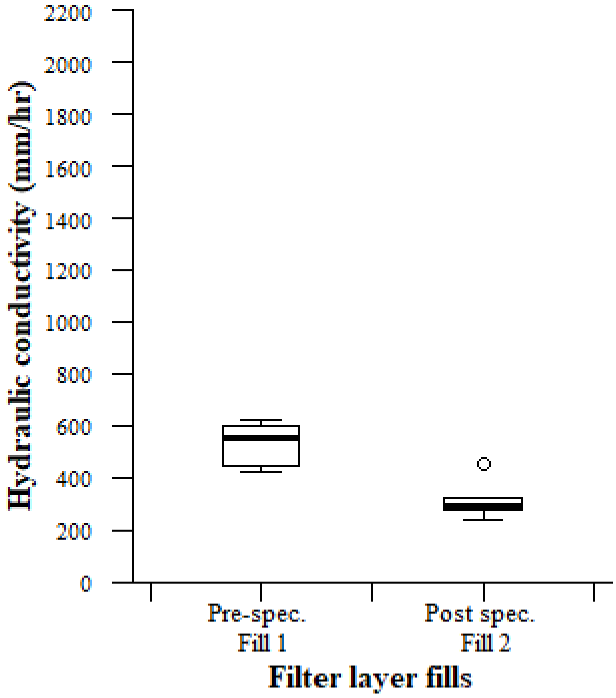


Figure 23: Boxplot of the hydraulic conductivity of the sand-based filter fills pre- and post-introduction of the City's fill specifications. "○" indicates outlier

The introduction of the fill specifications by the City was seen to have a statistically significant ($p = 0.01$) impact upon the hydrological performance of the biofilter system, with median hydraulic conductivity reducing from 582 mm/hr to 288 mm/hr between the pre- and post-specification filter fills respectively (Figure 23).

In all cases, filter fill 1 exceeded the recommended hydrological limit of 300 mm/hr for biofilters operated under temperate climatic conditions; while the median hydraulic conductivity of filter fill 2 conformed to this specification.

The difference in hydraulic conductivity between the fills may explain the differences in TSS release and pollutant removal performance observed. To dislodge particles from the filter fills, the infiltrating stormwater must have a sufficient hydrodynamic force (corresponding to a flow velocity) to overcome the inter-particulate bond between particulates in the fill matrix. The required force is dependent upon flow rate, particle size and elasticity, ionic strength and pH of the fill, with fills with an abundance of fine particulates and fast subsurface flow rates having greater sediment erosion (Reddi, 1997). As filter fill 1 had greater fine particulates and faster hydraulic conductivity that filter fill 2, there was a greater release of TSS. Hydrological effect on TSS is supported in the literature where it has been shown that reduced hydraulic conductivity from 250 mm/hr to 159 mm/hr increases TSS removal up to 98.5% (Goh et al., 2015). Furthermore, the faster flow rate would also limit contact time between the stormwater and the filter material, and thus may limit pollutant removal by the biofilter system (eWater, 2016).

4.2.2.2.2. Transitional fills

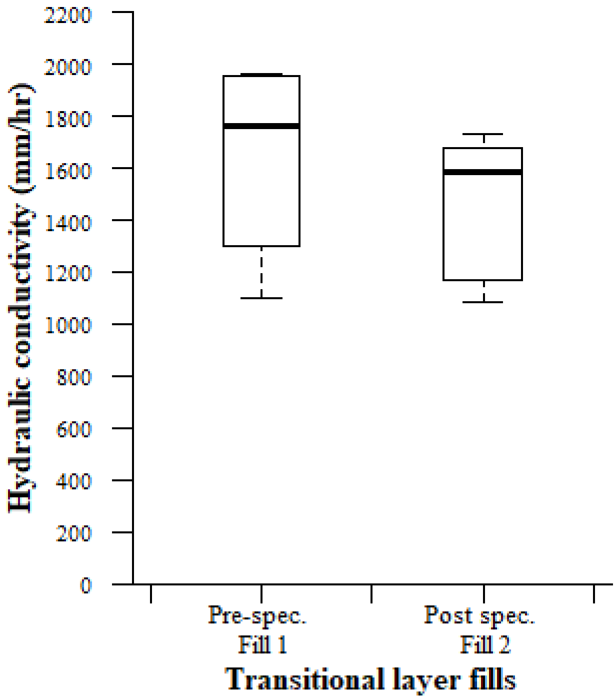


Figure 24: Boxplot of the hydraulic conductivity of the sand-based transitional fills pre- and post-introduction of the City’s fill specifications. “○” indicates outlier

There were no hydrological requirements under the City's purchasing specification for the transitional fill, while the CRC (2015) guidelines only required the transitional fill to have a greater hydraulic conductivity to that of the filter fill. Both fills conformed to the CRC requirement, having significantly ($p < 0.001$) greater hydraulic conductivities to that of their respective filter fill (Figure 24). Transitional fill 1 had a median hydraulic conductivity of 1759 mm/hr while transitional fill 2 had a median of 1583 mm/hr, which was a 202 and 450 percent increase on the filter fill respectively.

There was no significant difference ($p = 0.25$) between the two transitional fills, as the distribution of the two fills were similar, although transitional fill 2 had a slightly lower and more restricted range than transitional fill 1 (Figure 24).

4.2.2.2.3. Drainage fills

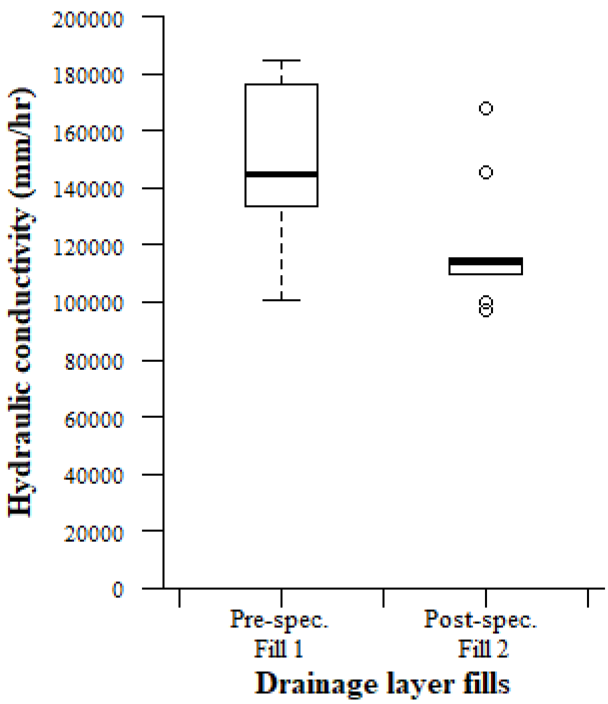


Figure 25: Boxplot of the hydraulic conductivity of the gravel drainage fill pre- and post-introduction of the City's fill specifications. "○" indicates outlier

There was a significant ($p = 0.02$) difference in hydraulic conductivity between the drainage gravel fills, with median infiltration of 144605 mm/h for drainage fill 1 and 113765 mm/hr for drainage fill 2 (Figure 25). The drainage gravel hydraulic properties were significantly higher ($p < 0.001$) than the transitional fills, which conforms to the CRC (2015) guidelines; whereby, the drainage fill was required to have a greater hydraulic conductivity to that of the overlying transitional fill.

4.2.3. Sub-experiment 3 – Physical characterisation

Although the City's fill purchasing specifications are predominately physical sizing based, they are quite limited in what they require, mostly restricting fine particulate concentrations in order to avoid excessive TSS release (Table 9). The physical structure of the biofilter fill is influential in determining the hydrological and pollutant removal performance, particularly in terms of soil infiltration, hydraulic conductivity, water holding and soil pollutant retention properties (Reza Mazaheri and Mahmoodabadi, 2012, Gunawardana et al., 2012).

In this section, the particle size variation of the biofilter fills were analysed, in order to gain a greater understanding of the physical nature of the fills, and how particle size influences TSS release, hydrology and chemical pollutant removal properties.

4.2.3.1. Particle size analysis method

The physical structure of the fills was characterised through sieve-method particle size distribution (PSD) analysis (based on the standard method ASTM D6913).

Ten 50 g subsamples of each of fill were randomly collected from the bulk fill stores and later combined to form a 500 g sample for PSD testing, which involved passing each fill sample through a series of sieves with aperture diameters of 2000, 1000, 850, 425, and 75 µm. The collected material in each sieve was weighed, and the percentage composition of each particulate fraction was determined.

The particle size distribution analysis was performed in order to detect undesirable fill variations which were not detectable using the City's fill specifications alone, with the physical characteristics being compared against the CRC (2015) guidelines.

4.2.3.2. Physical characterisation results

4.2.3.2.1. Filter fills

Filter fill 1 was sourced from the City of Sydney's works depot and was composed of 96% sand, 2% gravel and organic debris, and 2% silt and clay, and was classed as a 'sand' under the

United States Departments of Agricultures (USDA) unified soil classification system (Victorian State Government, 2019). Filter fill 2 was sourced from Benedict Industries who described it as a sand-based bioretention filter media (M165) and was composed of 94% sand, 4% gravel and organic debris and 2% silt and clay, and was also classed as a ‘sand’ as per the USDA soil classification (Victorian State Government, 2019).

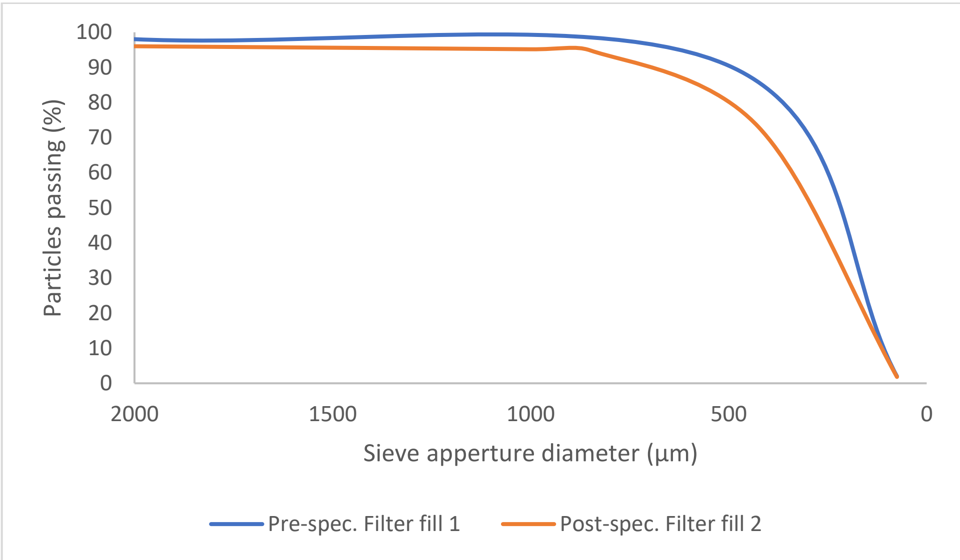


Figure 26: Percentage of fill particulates passing through sieve apertures of between 2000 and 75 µm for pre- and post-specification filter fills

Both fills were heterogeneous in particle size distribution with a dominant sand component and less than 3% silt/clay and a smooth grading between the particle classes (Figure 26), which roughly conformed to the CRC (2015) and City’s physical sizing specifications.

The City’s fill specifications are geared towards limiting fine particulate fractions in order to mitigate against excessive TSS release upon start-up, however, the fine clay and silt particulates are essential for the retention of pollutants, as stormwater pollutants tend to bind to the clay particulates (Uddin, 2017). Biofilter guidelines generally recommended against high clay contents for promoting pollutant removal, as this may lead to excess release of TSS, and high clay soils (>3%) tend to have a detrimental impact upon hydrological permeability (Li et al., 2007, Abdulgawad et al., 2009, Payne et al., 2015, Liu et al., 2014). An important finding is therefore that a balance is needed between the retention properties, TSS mitigation and detrimental hydraulic influences of the fine particulates in order to ensure the satisfactory operation of the biofilter system, supporting earlier work by Hsieh and Davis (2005).

Filter fill 1 was composed of approximately 9.5% of particulates of >2mm, mainly bulky organic and rocky fragments, whereas filter fill 2 was composed of about 4% bulky fragments. Differences in coarse particle structure likely explain the difference in hydraulic conductivity between the two fills. The presence of these particulates potentially contributed to the variation in fill hydraulic conductivity by creating macrospores within the soil matrix and localised preferential flow paths that allowed for an altered hydrological performance (Zhang et al., 2016), hence, the higher hydraulic conductivity in filter fill 1 than in filter fill 2 observed in section 2.2.2.1.

4.2.3.2.2. Transitional fills

Transitional fill 1 was a coarse sand sourced from Turtle Sand and Soil supplies, which had a textural breakdown of 10% gravel, 87% sand, and 3% silt/clay, while transitional fill 2 was a washed, recycled glass sand sourced from Benedict Industries (GTrans GlassSand) and was composed of 20% gravel (>2 mm glass fragments), 78% sand, and 2% silt/clay.

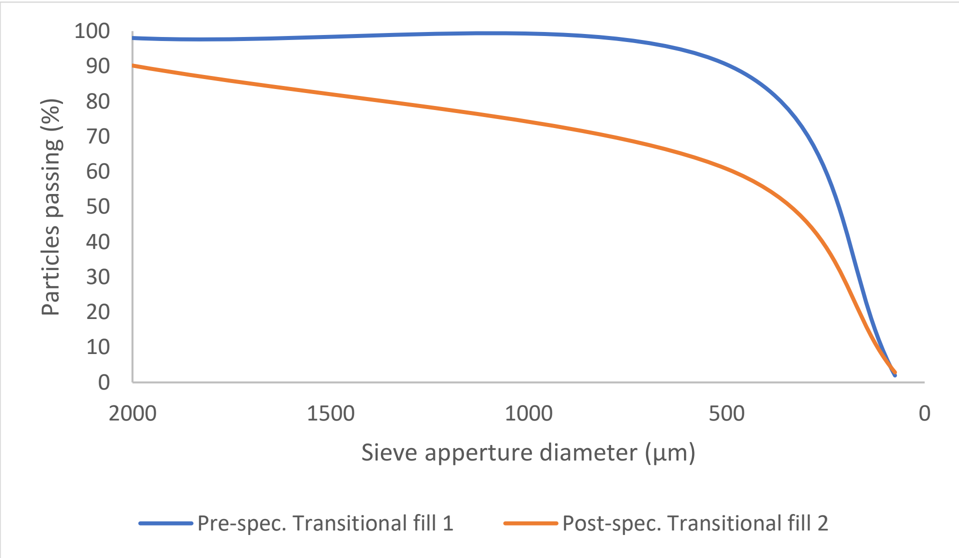


Figure 27: Percentage of fill particulates passing through sieve apertures of between 2000 and 75 µm for pre- and post-specification transitional fills

Both fills complied with the City's fill specifications, whereas the CRC (2015) guidelines were less stringent in their specifications for the transitional fills than that of the filter media, with the only requirements relating to hydraulic conductivity and particle size distribution. Texturally, both fills were suitable; however, fill 1 did exceed the 2% fine particulates limit set in the CRC (2015) guidelines (Figure 27).

4.2.3.2.3. Mulch fills

Fill 1 was a 5-10 mm blue metal gravel sourced from Turtle Sand and Soil Supplies and fill 2 was a 2-5 mm washed river gravel supplied by Benedict Industries.

Neither mulch fill complied with the City's mulch specifications (Table 9), as a smaller particle-sized drainage gravel was used as the surface mulch. The deviation from the specification was not perceived to be an issue as the mulch layer was not chemically or hydrologically influential upon the performance of the simulation biofilter, but was merely included (as with street biofilter systems) as a protective and distribution layer for the filter media to minimise surface scouring from stormwater dosing; a role in which both gravel mulch fills performed well in the benchmarking experiment.

4.2.3.2.4. Drainage fills

Fill 1 was a 5-10 mm blue metal gravel sourced from Turtle Sand and Soil Supplies and fill 2 was a 2-5 mm washed river gravel supplied by Benedict Industries.

There were limited guideline specifications for the drainage fill, with the drainage media only having to conform to physical sizing and bridging criteria. Fill 1 did not comply with the City's fill specifications, while fill 2 conformed to the drainage layer fill criteria.

4.2.4. Sub-experiment 4 – Chemical characterisation

There are no chemical requirements for fill in the City's fill purchasing specifications. A recommendation from this thesis is that fill chemical makeup should play a greater role in the selection of biofilter fill, as various chemical parameters, pH, CEC, nutrient TN and TP concentrations, hardness and organic carbon concentrations have been demonstrated to impact the pollutant removal performance of soil (Blecken et al., 2011, Clark and Pitt, 2010).

In this section, the chemical makeup of the biofilter fill was analysed in order to gain an understanding of how fill chemistry influences biofilter pollutant removal performance and to determine whether any chemical parameters could be added into the City's mandatory fill specifications.

4.2.4.1. Chemical characterisation methods

In order to gather a representative sample of each fill, ten 10 g subsamples were randomly collected from the bulk fill stores. The subsamples were combined to form a 100 g sample for testing, which was bottled, stored and transported for analysis as per standard methods (American Public Health Association et al., 2005). The chemical makeup of the fill samples was analysed by the NATA accredited soil laboratory at the Department of Primary Industries, Wollongbar, NSW (Table 11). Only the filtration and transitional fills were analysed, with the gravel drainage layer material and mulch excluded as they were assumed to be relatively chemically inert.

4.2.4.2. Chemical characterisation results

Table 11: Chemical makeup of pre- and post-specification filter and transitional layer fills, and compliance with the Australian Cooperative Research Centre (CRC 2015) guidelines

Parameter	Filter fill		Transitional fill		CRC (2015) guidelines
	Pre-spec. Fill 1	Post-spec. Fill 2	Pre-spec. Fill 1	Post-spec. Fill 2	
Electrical conductivity (dS/m)	0.052	0.097	0.12	0.28	<1.2
pH ($CaCl_2$)	6.7	5.5	8.4	9.9	5.5-7.5
pH (water)	7.5	6.3	9.2	10	5.5-7.5
Phosphorus Colwell (mg/kg)	39	16	6.6	8.7	<80
Phosphorus buffer index (L/kg)	21	22	16	62	
Organic carbon (%)	0.64	0.41	0.21	0.11	≤ 5
Total nitrogen (mg/kg)	330	<200	<200	<200	<1000
Hardness (Ca:Mg)	5.2	3.2	21	10	
Aluminium (cmol(+)/kg)	<0.01	<0.01	<0.01	<0.01	
Calcium (cmol(+)/kg)	3.6	1.2	3.3	1.7	
Potassium (cmol(+)/kg)	0.35	0.31	0.054	0.093	
Magnesium (cmol(+)/kg)	0.69	0.38	0.15	0.16	
Sodium (cmol(+)/kg)	0.041	0.14	0.064	1.3	
Cation exchange capacity (CEC) (cmol(+)/kg)	4.8	2.1	3.6	3.2	

4.2.4.2.1. Filter fill

Chemical characterisation of both biofilter fills showed that the physiochemical makeup conformed to all CRC (2015) criteria (Table 11).

There are no Australian guidelines that specify CEC requirements for the filter fill; however, the Washington State guidelines recommended a biofilter media with a CEC of >5 meq/100 g, and the City of Toronto, Canada guidelines recommends a CEC of ≥ 10 meq/100 g, which means that the CEC of both filter fills were low in regards to international fill specifications (Ewing, 2013). As fill CEC was low, means to improve this chemical parameter were explored in this research, with substrate amendment with zeolite being explored in chapter 5, section 3.4.

Differences in chemical parameters likely explain some of the variations in pollutant removal performance between the filter fills (section 2.5.2). Of the chemical parameters investigated, the pH, organic carbon and initial fill pollutant concentrations have been demonstrated in the literature to influence pollutant removal of soil-based systems. For instance, pH plays a role in nearly all pollutant (particularly metal removal mechanisms in the biofilter system; including chemical speciation of pollutants, flocculation of clay particles, sorption, cation ion exchange and precipitation of pollutant ions with clay particulates (Matagi et al., 1998, Blecken et al., 2011). Organic carbon plays a role in promoting denitrification and sorption of some metals like copper and nickel (Kavehei et al., 2019). The influence of these chemical parameters on pollutant removal performance will be highlighted in section 2.5.2 below.

4.2.4.2.2. Transitional fill

There were no specific chemical specifications for the transitional fill in the CRC (2015) guidelines; however, it would be safe to assume that the chemical specifications of the filter fill could be applied to the transitional fill. As such, both transitional fills conformed to the filter fill chemical parameters, except for the pH, which was alkaline and exceeded the CRC maximum of pH 7.5 for both the transitional fills (Table 11).

The pH increased by 1.7 and 3.7 units between the filter and transitional fills for fill 1 and 2 respectively. It is suggested that the elevated pH of the transitional fill was likely due to the presence of calcium salts within the sand matrix, indicated by high exchangeable calcium (1.7 cmol(+)/kg) and hardness (calcium:magnesium ratio) of 10:1.

4.2.5. Sub-experiment 5 – Pollutant removal performance

The quality of biofilter fill in which the City's fill specifications governs, is crucial for the successful operation of the biofilter systems, as it determines the pollutant removal, biochemical processes and hydrological properties of the biofilter (Barrett et al., 2013). In this section, the two fill sets were compared through laboratory column simulation in order to assess whether the introduction of the City's fill purchasing specifications had any impact upon the biofilter pollutant removal performance.

4.2.5.1. Column simulation method

Column method (single monophasic column modification as described in section 2.1.1), stormwater sample collection and chemical analysis were undertaken as per standard methods and benchmarking experimentation in chapter 2, except for nitrogen analysis.

Nitrogen in aquatic ecosystems exists in several redox states including inorganic dissolved nitrogen: nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+). In addition, a variety of dissolved organic compounds, amino acids, urea, composite dissolved organic nitrogen (DON) in association with ammonia nitrogen are measurable in terms of Total Kjeldahl Nitrogen (TKN) (Rabalais, 2002). In order to gain an understanding of the different nitrogen species in the stormwater and the effect of biofiltration upon their removal, three measures of nitrogen speciation were employed; nitrate and nitrite-nitrogen (NOx) and Total Kjeldahl Nitrogen (TKN), which extend the nitrogen analysis beyond the minimum total nitrogen (TN) as set by the City's decentralised water master plan (Table 1).

4.2.5.2. Pollutant removal results

Simulation column testing of the biofilter fills generally showed high pollution removal performance, regardless of whether the fill set used complied with the City purchasing specifications or not (Table 12). For this reason, all tabulated items are discussed, while those showing a statistically significant variation between different fill results have been highlighted as a point of interest.

Table 12: Pollutant concentrations and removal efficiency of pre- and post-specification fill variations

Pollutant parameter	Source compounds in synthetic stormwater	Pollutant conc. in synthetic stormwater (mg/L)	Pollutant conc. (median) after biofiltration (mg/L)		Removal efficiency (median) for biofilter simulation (%)	
			Pre-spec. Fill set 1	Post-spec. Fill set 2	Pre-spec. Fill set 1	Post-spec. Fill set 2
Total Nitrogen (TN)	Ammonium, nickel and lead nitrates	18.7	**2.4**	**6.5**	**85.3**	**60.0**
Total Kjeldahl nitrogen (NH_4^+)	Ammonia nitrate	2.3	0.04	0.36	98.1	84.1
Nitrite- and nitrate nitrogen (NOx)	Ammonium, nickel and lead nitrates	16.4	4.7	4.9	71.4	70.0
Total phosphorus (TP)	Trisodium phosph56ate	10.0	**2.2**	**0.8**	**78.3**	**94.2**
Zinc	Zinc chloride	0.69	0.1	0.08	86.2	87.9
Copper	Copper sulphate	0.14	0.07	0.08	51.8	44.1
Nickel	Nickel nitrate	0.07	**0.01**	**0.01**	**84.4**	**88.7**
Cadmium	Cadmium chloride	0.013	0.0002	0.0004	98.3	97.3
Lead	Lead nitrate	0.30	**0.04**	**0.01**	**86.7**	**96.1**
Chromium	Potassium chromate	0.05	0.007	0.01	85.6	71.8
Arsenic	Arsenic trioxide	0.03	0.002	0.001	93.3	95.3

***RED** highlighted cells represent a significant difference between the pre- and post- specification fill variations*

4.2.5.2.1. Total Kjeldahl nitrogen

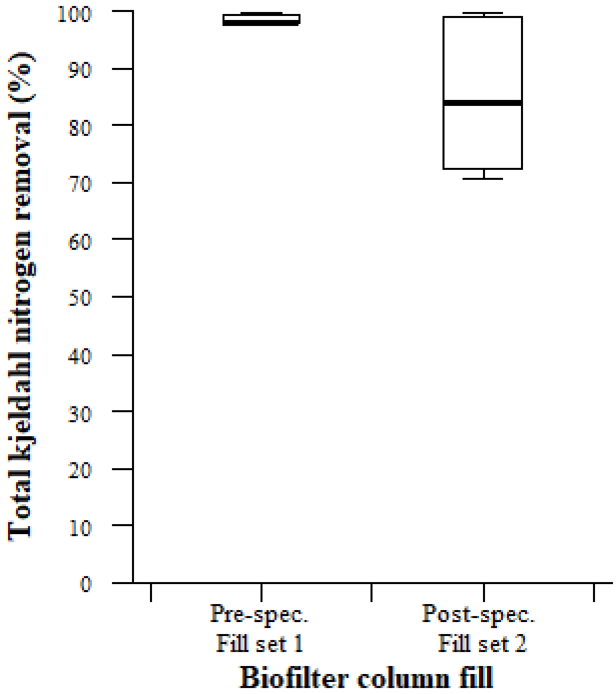


Figure 28: Total Kjeldahl Nitrogen removal efficiency by simulation columns filled with pre-and post-specification fill variations

The biofilter column simulations for both fills showed a high removal efficiency for the removal of TKN, achieving median removals of 98.1% and 84.1% for fill set 1 and 2 respectively (Figure 28). Median TKN concentration in the biofilter column outflow was reduced to 0.04 mg/L for fill set 1 and 0.36 mg/L for fill set 2, which complied with 0.9 mg/L trigger value for the 95% ecological protection target (Table 7). The two fill sets had equivalent TKN removal, as there was no statistically significant ($p = 0.08$) difference in removal between fill sets.

Column removal results for both fill sets were consistent with past studies which reported 95–97% NH_4^+-N removals (Zhou et al., 2016), with the literature indicating biofilter systems tend to have effective NH_4^+-N removal through ion exchange and denitrification mechanisms on the surfaces of clay and organic particulates (Abdulgawad et al., 2009).

4.2.5.2.2. Nitrate- and nitrite-nitrogen removal

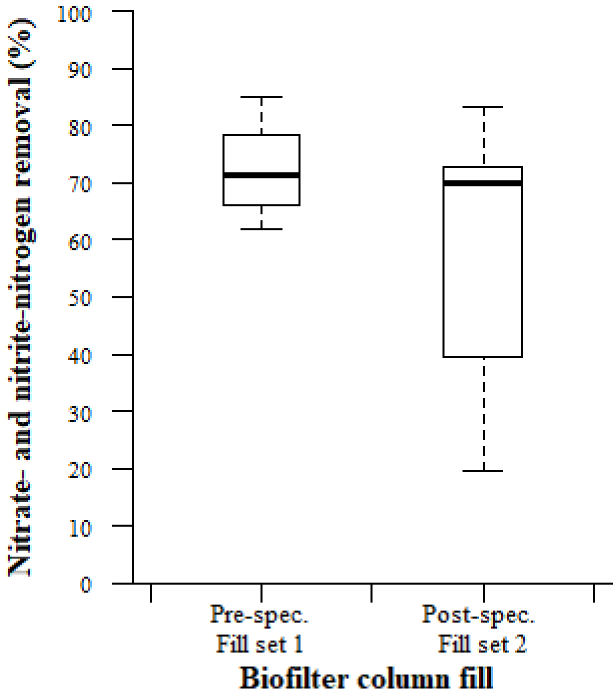


Figure 29: Nitrate- and nitrite-nitrogen (NOx) removal efficiency by simulation columns filled with pre-and post-specification fill variations

There was no statistically significant ($p = 0.4$) difference between the fill sets for NOx removal, with the simulation biofilters showing a median removal of 71.4% and 70% for fill set 1 and 2 respectively (Figure 29). Fill set 2 had a greater spread of NOx removal results than fill set 1, with an interquartile range of 33.6 and a moderate negative skew (-0.6) towards lower NOx removal performance (Figure 29).

Regardless of fill set used, the NOx concentration discharged were higher than the 3.8 mg/L limit recommended for a 90% ecological protection (Hickey, 2013), with fill set 1 and 2 reducing concentrations to 4.7 mg/L and 4.9 mg/L respectively.

The high but variable NOx removal efficiency was consistent with prior studies, which showed retention rates of 42.5-91.8% (Wang et al., 2017b). Under the aerobic conditions available in the surface fills in the simulation biofilter system, NO_2-N readily experiences oxidisation to

NO_3-N (Hatt et al., 2008), and the nitrification of NH_4-N produces NO_3-N (Tang and Li, 2016). In soil systems, NO_3-N is highly mobile and not readily captured, and subsequently leaches from the biofilter system (Dietz and Clausen, 2005, Davis et al., 2006). This NO_3-N leaching from the fill matrix may have given rise to variations in removal efficiencies, observed here.

4.2.5.2.3. Total Nitrogen

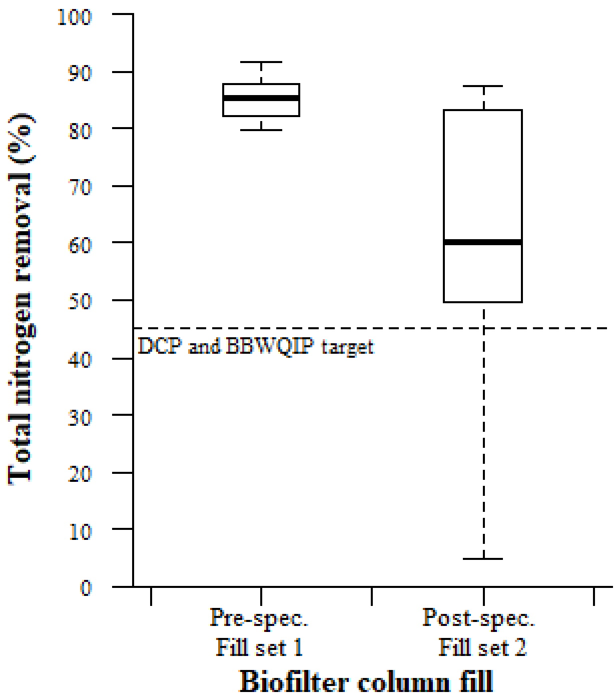


Figure 30: Total Nitrogen (TN) removal efficiency by simulation columns filled with pre-and post-specification fill variations

The simulation biofilters achieved a median 85.3% and 60.0% TN removal efficiency for fill set 1 and 2 respectively, demonstrating that regardless of the fill set employed, the DCP and BBWQIP target of 45% would be achievable for the equivalent street units (Figure 30). There was a significant ($p = 0.01$) difference between the fill sets, as the larger range of NOx removal results for fill set 2 resulted in a similarly large range in TN removals with some of column replicates having TN removal which did not meet the DCP and BBWQIP reduction targets. Difference in TN removal between the two fills is likely due to higher CEC in fill 1, with it having almost twice the CEC than fill 2 (Table 11). The higher CEC allowed for more effective capture of NH_4 from the simulated stormwater with a very consistent removal of 98.1% for TKN. Also, fill 1 had greater and more consistent removal efficiency for NOx (Figure 29, which when included with the TKN results would explain the greater and more consistent TN removal observed for fill 1 in comparison to fill 2.

4.2.5.2.4. Total Phosphorus

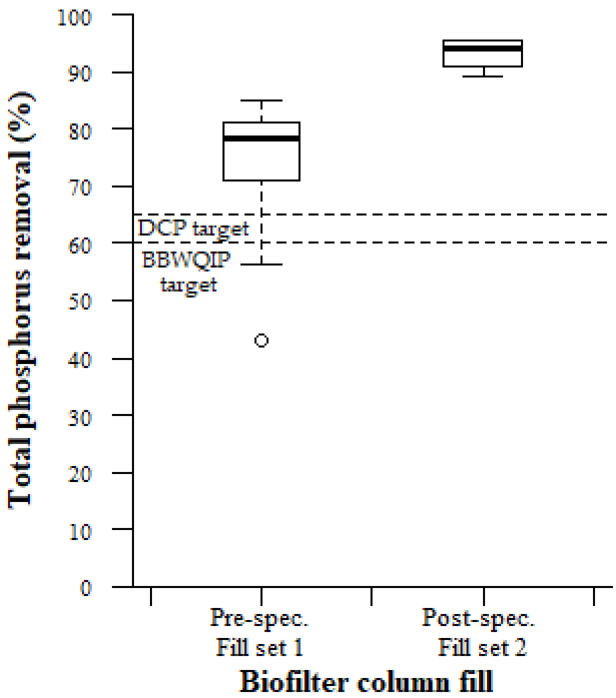


Figure 31: Total Phosphorus (TP) removal efficiency by simulation columns filled with pre-and post-specification fill variations. "○" indicates outliers

There was a significant ($p < 0.001$) difference between the pre- and post-specification fill sets for total phosphorus removal, with fill set 2 having a greater TP removal performance (median 93.3%) than fill set 1 (median 78.3%). The medians of both fills complied with the City's DCP and BBWQIP targets for total phosphorus removal, however, some of the results for the pre-specification fill did not meet the City's targets (Figure 31).

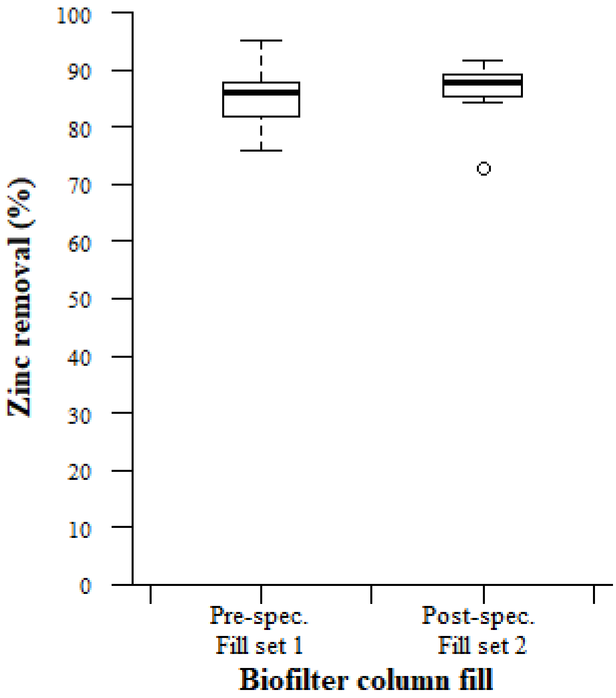
Initial phosphorus concentrations in the filter fill are influential in determining biofilter TP removal performance, as fills with elevated nutrient levels are suitable for promoting plant growth, but may already be approaching nutrient saturation, and so will not be able to capture additional nutrients from the infiltrating stormwater effectively.

The significant difference in phosphorus removal performance between the fill variations was most likely due to differences in the initial phosphorus content of the soils, as filter fill 1 had 39 mg/kg of available phosphorus, which was 2.4 times more than filter fill 2 (16 mg/kg). As filter fill 1 had a higher initial phosphorus concentration than filter fill 2, more of the fills maximum sorption capacity was already occupied. Therefore, there were fewer available adsorption sites for binding with the influent phosphorus, resulting in a lower removal efficiency than that of fill set 2.

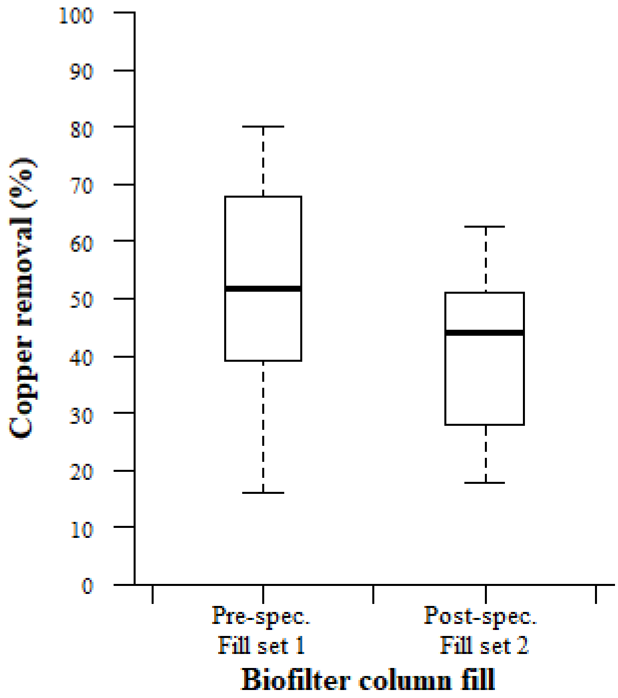
Both filter fills had equivalent maximum adsorption capacities for phosphorus (approximately 210-220 mg/kg), indicated by having similar phosphorus buffering indices (Table 11), which is a measure of the amount of phosphorus sorbed from the 100 mg/L phosphorus solution added to the test soil at a 1:10 ratio (Mason 2010). Under the classification system proposed by Moody (2007), soils with buffering indices of less than 35 L/kg are classed as having a ‘very low’ phosphorus adsorption capacity, with substrates of low phosphorus retention capacity often being reported in the literature as being problematic for stormwater biofilter systems (Berretta et al., 2018, Shrestha et al., 2018, Hunt et al., 2008, Komlos and Traver, 2012).

Substrate amendment with materials with known high phosphorus adsorption capacity, such as blast furnace slag and gypsum, were trialled in chapter 5, in order to optimise the filter fills’ TP removal performance.

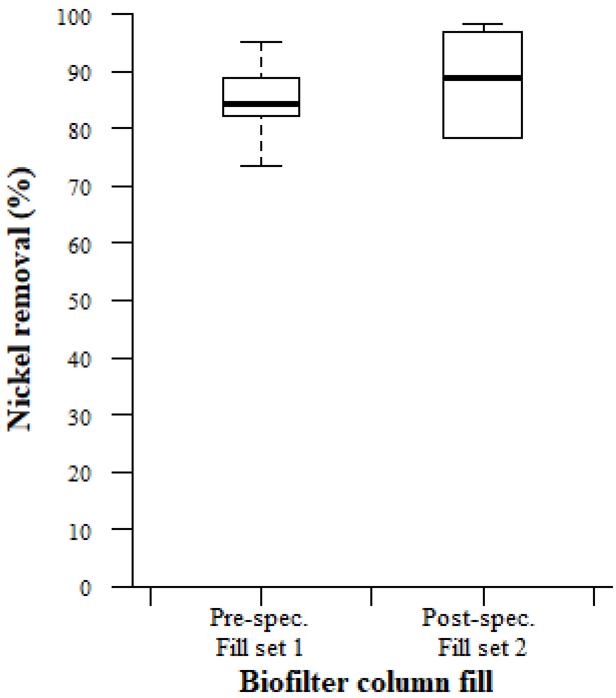
4.2.5.2.5. Dissolved-phase heavy metals



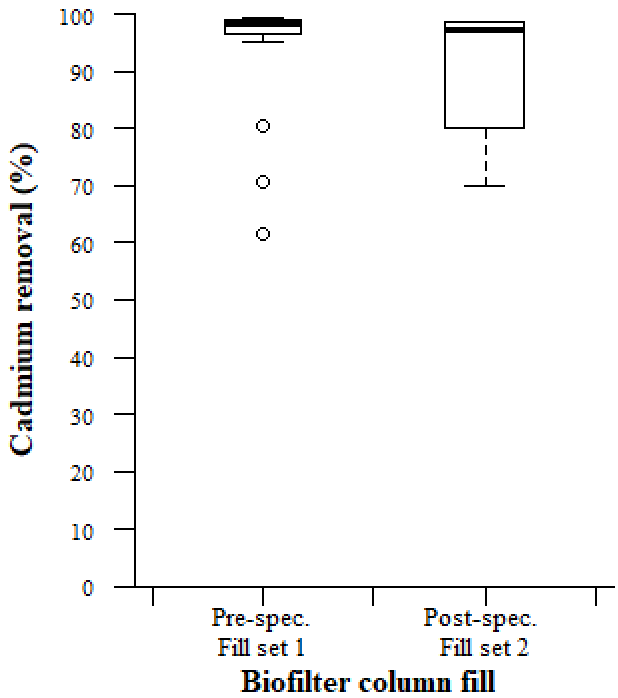
(a)



(b)



(c)



(d)

Figure 32: Dissolved-phase heavy metal removal efficiency (a) zinc; (b) copper; (c) nickel; and (d) cadmium by simulation columns filled with pre-and post-specification fill variations. "○" indicates outliers

The simulation biofilter columns, regardless test fill used, removed the dissolved-phase heavy metals with a median removal of greater than 80%, with the exception of copper.

Nickel removal was the only dissolved-phase metal to have a significant difference ($p = 0.002$) between the pre- and post-specification fill sets, with fill set 1 having a median removal of 84.4% and fill set 2 having a median removal of 88.7% (Table 12). There was also a difference in the interquartile range of the nickel removal efficiency from 6.6% to 45.5% in the two fills (Figure 32c). Despite the difference in nickel removal performance, both fill sets reduced median nickel concentration to approximately 0.01 mg/L, which was well below the 0.052 mg/L default value for the 95% ecological protection.

The variance in nickel removal efficiency between the fill sets was most likely due to the differences in chemical properties which promoted different predominant nickel sorption pathways. Nickel is removed through several kinetic mechanisms depending upon the soil and influent solution properties including soil/water pH, soil organic carbon (SOM) and soil available aluminium and iron (Zhang et al., 2015, Shi et al., 2012, Liao et al., 2013). At a soil pH <7, nickel weakly complexes with SOM, while at pH >6.5 nickel can form layered double hydroxide (LDH) precipitates in relation with Al/Fe oxides on soil particulate surfaces. As the filter fill 2 matrix was slightly acidic (pH 5.5-6.3) nickel complexation with SOM, a kinetically fast mechanism, would be the main means for nickel sorption, while in filter fill 1 which was more neutral to weakly alkaline (pH 6.7-7.5), the kinetically slower Ni-LDH mechanism would be favoured. The LDH mechanism may not have been as effectively achieved by the more rapidly infiltrating stormwater in filter fill 1 (Figure 31), which may explain the lower nickel removal performance (Figure 25c).

The simulation columns had equivalent cadmium removal performance between the pre- and post-specification fills, with a median removal of 98.3% and 97.3% for fill 1 and 2 respectively, although there was a disparity in the interquartile distribution of the cadmium removal between fills with IQR of 2.2 and 18.2 for fill set 1 and 2 respectively (Figure 32).

Despite the difference in the distribution of cadmium removal, there was no statistically significant difference between pre- and post-specification fills ($p = 0.2$). The simulation columns, regardless of fill specification, were able to lower the cadmium concentration to 0.0002 and 0.0004 mg/L for fill set 1 and 2 respectively, which was well below the 0.001 mg/L guideline for 95% ecological protection.

There was no statistically significant ($p = 0.4$) difference between the pre- and post-specification fills for zinc, with fill set 1 and 2 having median zinc removal of 86.2% and 87.9% respectively. Despite effective zinc removal by the simulation biofilter columns, median zinc concentrations were reduced to 0.1 and 0.08 mg/L, which exceeded the 0.071 mg/L limit for 90% ecological protection. The relatively high zinc concentrations were most likely due to the high initial zinc concentrations in the synthetic stormwater (0.69 mg/L), based on the knowledge that zinc is the predominate metal in urban stormwater owing to its owing to its common use in degradable transportation surfaces such as vulcanised tyres, brake linings, clutch plates, and galvanised crash barriers and vehicle components (Gobel et al., 2007). The similarity in removals between the fills was most likely due to both fills having similar silt/clay concentration and the primary adsorption mechanism of zinc adsorption on clay particulates within the fill matrix (González Costa et al., 2017, Behroozi et al., 2020).

Copper had the lowest removal efficiency of any of the dissolved-phase metals with a median of 51.8% and 44.1% for fill 1 and 2 respectively (Table 12 and Figure 32). The simulation biofilter columns may have lower copper removal, because other metals like zinc may be preferentially absorbed over copper (González Costa et al., 2017). The simulation columns reduced median copper concentrations in the treated stormwater to 0.07 and 0.08 mg/l respectively, which were non-compliant with the 90% ecological protection guideline of 0.002 mg/L.

Although not statistically significant ($p = 0.4$), there was a general drop in median copper removal efficiency in fill set 2, compared to that of fill set 1; which may be due to the relatively lower pH and SOM in the filter fill 2 (Table 11).

Studies have shown that aqueous copper ions have a strong affinity for soil organic carbon, with sand-based media showing an increased affinity for dissolved-phase copper with increased SOM (Li and Davis, 2009, Díaz-Barrientos et al., 2003). The lower SOM in the filter fill 2 was addressed in chapter 5, through substrate amendment with biochar, which increased the availability of organic carbon within the biofilter fill and aided copper removal.

4.2.5.2.6. Suspended- or settled-phase heavy metals

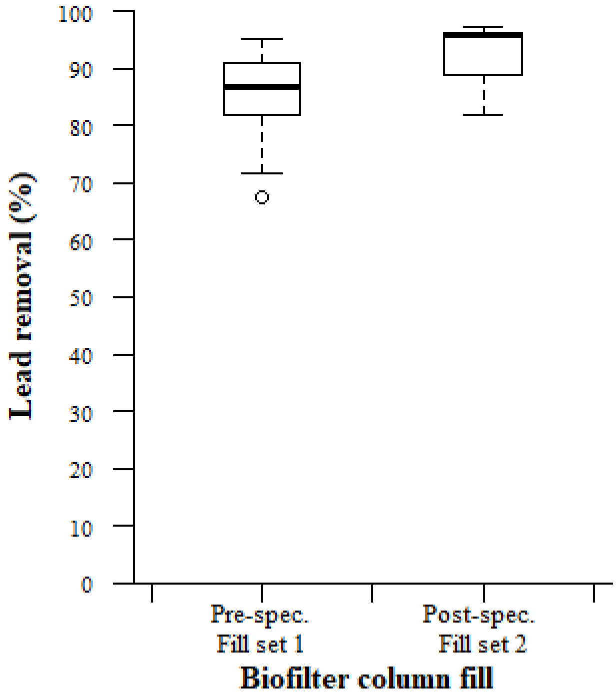


Figure 33: Lead removal efficiency by simulation columns filled with pre-and post-specification fill variations. "○" indicates outliers

Lead removal was significantly ($p = 0.01$) different between the pre- and post-specification fills, as there was an almost 10% difference in median lead removal between the fill variations; 86.7% and 96.1% for fill sets 1 and 2 (Figure 33), which reduced the median lead concentration to 0.04 mg/L and 0.01 mg/L for fill sets 1 and 2 respectively. When compared against the ANZG (2018) default discharge limits (Table 7), pre-specification fill set 1 were non-compliant with the 90% ecological protection guideline, while the post specification fill set 2 conformed with the 95% protection guideline.

The difference in lead removal between the fill variations was most likely due to the differences in hydraulic conductivity and the increased contact time present in filter fill 2 (Section 2.2.2, Figure 23). Lead adsorption shows a strong time dependence, with an alluvial soil in one experiment reaching an equilibrium adsorption in 45 minutes, with an initial rapid adsorption period of 25 minutes, with each 5-minute increment of contact time providing an approximately 10% increase in lead removal capacity (Das et al., 2014). If a similar trend was occurring for the biofilter fills in this experiment, then a 5-minute difference in contact time between fill set 1 and 2 would result in the observed 10% median increase in lead removal.

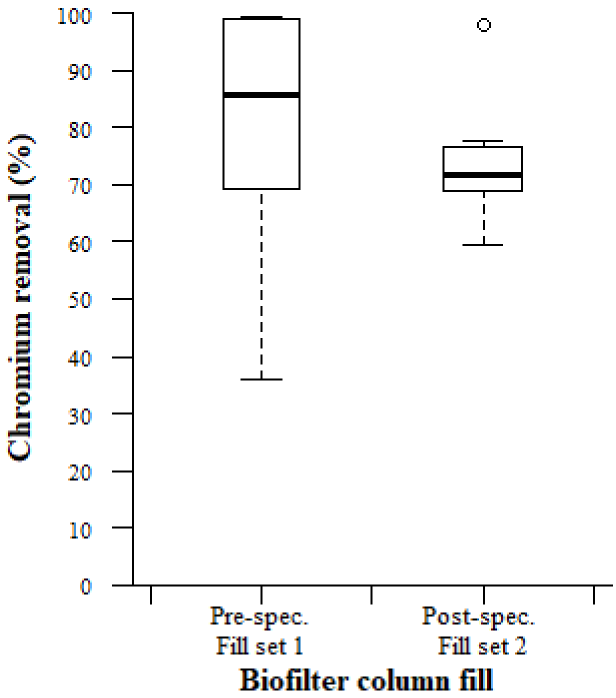


Figure 34: Chromium removal efficiency by simulation columns filled with pre-and post-specification fill variations

There were no statistically significant ($p = 0.3$) differences in chromium removal between the pre- and post-specification fill sets, as the fills achieved a median removal efficiency of 85.6% and 71.8% for fill sets 1 and 2 respectively (Figure 34). The removal results of the two fills overlapped, although fill set 1 had a wider range and interquartile range than fill set 2, with the IQR reducing from 31.3% to 8.5% respectively. Regardless of the effective removal performance by the simulation columns, the final median chromium concentration discharged was 0.007 and 0.01 mg/L respectively, exceeding the 0.006 mg/L limit for 90% ecological protection.

Environmentally, chromium is typically found in the cationic Cr (III) or anionic Cr (VI) forms (Rasoul Hoseini et al., 2015), with Cr (VI) being much more mobile and ecotoxic than Cr (III) (Khan et al., 2010, Ajouyed et al., 2010). Therefore, Cr (VI) in the form of chromate ion (CrO_4^{2-}) was the focus for removal performance.

Chromium removal is reliant upon soil pH, organic matter content, availability of aluminium and iron oxides and chromium speciation (Choppala et al., 2018, Jardine et al., 2011), with the variance in chromium removal between the fills most likely due to differences in how the chromate ions interreact with the above physiochemical fill parameters.

Filter fill 2 had lower pH than filter fill 1, with the increased H^+ promoting greater chromate retention, but it also had lower organic carbon than filter fill 1, which would reduce chromate sorption sites within the fill matrix. Therefore, a filter fill with a balance in physiochemical parameters which promote Cr (VI) sorption is required to meet the ANZG (2018) 90% ecological protection threshold. Further experimentation with substrate amendment which influences pH, sulphur and organic carbon content was trialled to promote greater chromium removal performance, as reported in chapter 5,

4.2.5.2.7. Metalloid arsenic removal

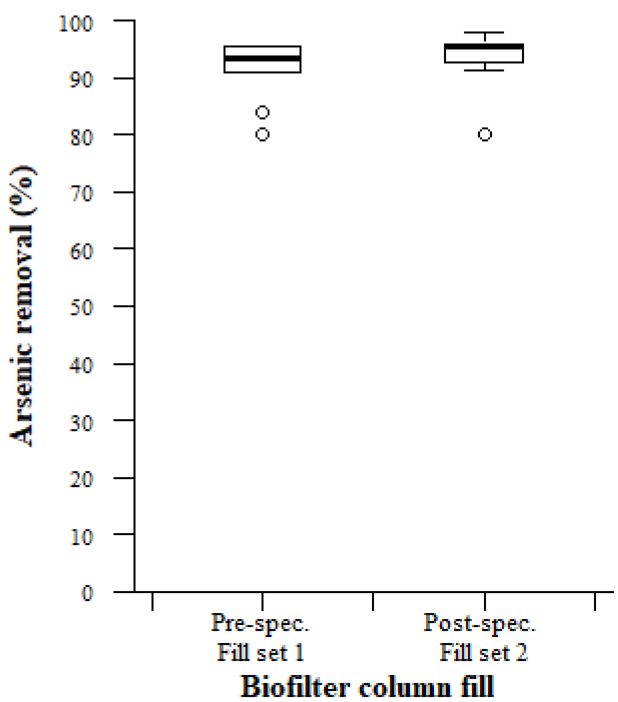


Figure 35: Metalloid arsenic removal efficiency by simulation columns filled with pre-and post-specification fill variations. "○" indicates outliers

There was no significant ($p = 0.05$) difference in metalloid arsenic removal efficiency between the pre- and post-specification fill sets, with median removals of 93.3% and 95.3% and an interquartile range of 4.4 and 3.9 respectively (Figure 35). Both fill sets reduced arsenic concentration in the biofilter effluent to around 0.002 and 0.001 mg/L, which was well below the 0.024 mg/L trigger value for the 95% species protection (Table 7) and below the 0.01 mg/L Australian drinking water guideline (NHMRC and NRMMC, 2018).

Arsenic sorption is primarily affected by the chemical redox state of arsenic (Smith et al., 1999) with arsenic being naturally found in one of four oxidative states (-III, III, 0, V), with arsenate (As (V)) and arsenite (As (III)) being most prevalent in aqueous and soil systems (Mamindy-Pajany et al., 2009). Arsenic trioxide (As_2O_3) was used in the preparation of the synthetic stormwater, which meant that arsenic was present in the system as As (III).

Both fills have effective (>90%) removal of arsenic, with studies showing that arsenic is rapidly bound to soil particulates, with up to 86% of available arsenic being absorbed in the first 2 hours through coprecipitation with metal oxides (Al, Fe, Ca and Mg) (Yang and Donahoe, 2007, Raposo et al., 2004, Aguilar-Carrillo et al., 2006).

4.3. Conclusions

The results of this chapter clearly showed that the introduction of fill purchasing specifications by the City was an important step in achieving improvements in fill quality and biofilter hydrological and pollutant removal performance. Improving the quality of fill purchased also resulted in a substantial decrease in the recognised problem of suspended solids load on start-up, with a reduction in both quantity and persistence of TSS released.

There was significantly improved total phosphorus, nickel and lead removal with the introduction of the fill specifications. The outflow concentrations of nutrients from the simulation biofilter columns largely complied with local DCP and BBWQIP targets, while some metal parameters did not comply with the ANZG (2018) 90% ecological protection guidelines. The City's standards are based on eutrophication as a limiter on biodiversity, and not on toxicant levels (such as those for metals) which appear to be equally, if not more important than the nutrient parameters, and therefore metal parameters should be included in future council pollutant control targets.

During conductivity testing, filter fill 1 showed a hydraulic conductivity that was considerably higher than the City's 300 mm/hr fill specification, while filter fill 2 complied. An elevated hydraulic conductivity rate suggests accelerated flow and is prohibitive to biofilter pollutant removal performance, as contact time in the biofilter system is limited.

There are no chemical requirements in the City's fill purchasing specifications, and as such, the fills' chemical characteristics were compared against the CRC (2015) guidelines, or relevant international standards as stated. Both fill sets complied with all the CRC (2015) guidelines, except for pH of the transitional fills, which was more alkaline than the guidelines allow. In the experiments, differences in pH, CEC, and initial phosphorus levels between the fills were all demonstrated to determine biofilter pollutant removal performance, and therefore the CRC (2015) guideline values should be considered for inclusion in the City's mandatory fill specifications.

The introduction of fill purchasing specification with the inclusion of chemical and minimum pollutant removal performance is recommended for all future field biofilter projects; if operational issues such as the elevated release of TSS and non-compliance with local pollutant control guidelines are to be avoided.

Although this chapter examined the impact of change of local fill specification, it highlights the importance of fill quality on biofilter performance, and the impact that changes in fill specifications, like local and national guidelines could have on field biofilter performance. Changes in fill properties and impact upon biofilter performance is further explored through fill amendment in the following chapter.

Chapter 5: Simulation 3 – Pollution removal efficiency with biofilter filtration layer amendment

5.1. Introduction

In the previous chapter, fill quality was identified as playing a crucial role in determining pollutant removal and hydrological performance of the biofilter system, with the introduction of the City's physical sizing specifications improving some of the biofilter's pollutant removal performance. Potential for further enhancing pollutant removal performance through the addition of materials other than sand and organic matter to the filtration layer has been suggested, a process known as "amendment". Five amendment materials were selected to be investigated by simulation experiment in this chapter:

i. **Blast furnace slag (BFS)** – a waste product formed during iron and steel production, with potential metal and phosphorus sorption properties (Piatak et al., 2015, Hamdan and Mara, 2014)
ii. **Biochar** – a porous carbonaceous solid product made from the thermal decomposition of waste biomass in the absence of oxygen (pyrolysis), with potential water-holding, ion exchange and nutrient retention properties (Charman, 2014, Sohi et al., 2010)
iii. **Crushed concrete –** a hard composite construction material derived from over 22 million tonnes of demolition waste concrete produced annually in Australia (Edge Environment Pty Ltd, 2011). It has potential metal and phosphorus sorption properties (Sonderup et al., 2014, Muthu et al., 2018).
iv. **Gypsum** – a calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) mineral derived from mining or as an acid neutralisation by-product with phosphorus and metal sorption properties (Lee et al., 2018, Liu et al., 2018). Around a million tonnes of demolition waste gypsum (plasterboard and gyprock) produced annually in Australia (Regyp, 2012).
v. **Zeolite** – a highly porous aluminosilicates crystalline material consisting of TO_4 tetrahedra that is derived from either a mining or synthetic source, with potential cation exchange and metal sorption properties (Li et al., 2019, Sancho et al., 2017).

The notion of substrate amendment has been included in the design considerations of biofilter systems from their earliest inception (Bitter and Bowers, 1994), but it was not a serious academic consideration until the late 2000s. Since then, it has been suggested that a variety of fill amendments could be used in stormwater bioretention systems to promote enhanced onsite pollution retention; which include zeolite, granulated activated carbon, blast furnace slag

(BFS), biochar and water treatment residuals (Berretta et al., 2018, Sakadevan and Bavor, 1998, Rodríguez-Jordá et al., 2010, Ulrich et al., 2017, O'Neill and Davis, 2012).

The objective of this experimental phase was to explore fill amendment in terms of the City's biofilter designs as operating in a warm temperate climatic area, in order to enhance the baseline pollutant removal performance of the City's field biofilter as determined in chapters 3 and 4.

5.2. Methods

The biofilter column simulation experiments in this chapter followed the established procedures outlined below:

i. The general study design in chapter 2; in terms of simulation columns and operational procedures,
ii. The single-column monophasic design configuration as used in chapter 4, and
iii. The hydrological assessment through mini-disk infiltrometry as outlined in chapter 4.

The experimental differences that were unique to this phase are described below, which primarily relate to the additional assessment of column outflow time and the fill amendment method.

5.2.1. Hydrological methods

In addition to the assessment of fill conductivity through mini-disk infiltrometry, column outflow time was measured in order to understand the impact of fill amendment on overall biofilter performance. Column outflow time was based on the start of dosing event to the appearance of stormwater at the base outlet. Each column discharge experiment was repeated five times, with a three-day interval between measurements, to allow for columns to return to a field capacity state.

5.2.2. Fill amendment

There were two methods used for amending the filtration layer fill, based on the physical (Table 36 in appendix) and hydrological characteristics of the amendment material and the expected impact of these materials on the fill's properties.

5.2.2.1. Discrete layer method

Fill amendment was introduced into the biofilter column simulation as a discrete layer of between 20, 40, 60, 80 and 100 mm which equated to amendment concentrations from between 5% to 25% weight of amendment substance to total weight of the filter bed. The method assumed that a homogenous amendment layer would result in consistent contact between the contaminated stormwater and the amendment media, as the stormwater had to physically pass through the amendment layer to discharge from the column.

Initially, the discrete layer method was employed for the investigation of zeolite and BFS as part of a preliminary honours study (Macnamara, 2011). The discrete layer method is a common practice in the relevant scientific literature, although there is no agreement on the placement of the amendment material, which ranged from surface placement to 400 mm below the surface (Berretta et al., 2018, Asuman Korkusuz et al., 2007, Sakadevan and Bavor, 1998). A depth of 100 mm was selected so it would not interfere with the biofilter's surface infiltration and or be flushed from the filtration layer.

5.2.2.2. Mixture method

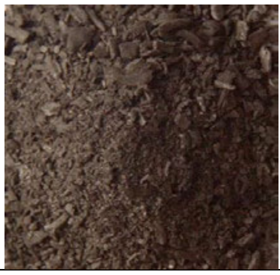
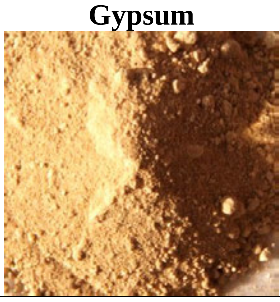
The mixture method integrated the amendment materials uniformly into the filtration layer to achieve amendment rates of between 0.38-30% w/w (Table 13) were selected for the stormwater biofilter system based on the literature (Sakadevan and Bavor, 1998, Shainberg et al., 1989, Kookana et al., 2011, Egemose et al., 2012) and the following local considerations:

i. **Economy**: Recyclable materials were readily available in comparison to specialised filtration media, such as diatomaceous earth or fibre filters.
ii. **Environmental sustainability:** Presently unwanted materials would be disposed of while removing pollutants from the environment which could then be possibly collectively sequestrated to a safe site (e.g. clay-lined landfill) at the end of the service life of the biofilter.

Amendment material was measured by weight and was manually stirred into the sand-based filter fill to produce one-kilogram batches of amended fill, as derived from methods established in the literature (Lucas and Greenway, 2011). The mixture method was adopted for biochar, gypsum and crushed concrete, based on preliminary infiltration experiments which suggested that these substances might impede flow if consolidated in a single layer.

5.2.2.3. Amendment materials and application rates

Table 13: Fill amendment rates (% w/w) for, biochar, blast furnace slag, crushed concrete, gypsum and zeolite

Fill amendment material	Characteristics	Applied amendment rate (% w/w)
Biochar 	<2 mm *Eucalyptus* woodchip derived fast (5 minutes) high temperature (750°C) pyrolysis biochar, sourced from Better Earth Products	1.88, 3.76, 5, 15, 30
Blast Furnace Slag 	<2 mm coarse grade granular blast furnace slag, sourced from Rootzone Australia	5,10,15,20,25
Crushed Concrete 	<2 mm crushed construction aggregate (predominately concrete), sourced from Turtle Sand and Soil supplies	5, 15, 30
Gypsum 	<2 mm natural gypsum Composed of ~ 95% calcium sulphate ($CaSO_4.2H_2O$) dihydrate, 3% calcite ($CaCO_3$) and 2% quartz (SiO_2), sourced from Bunnings	0.38, 5, 15, 30
Zeolite 	<2.2 mm natural zeolite composed of ~85% clinoptilolite, 15% mordenite with traces of Quartz and Feldspar, sourced from Castle Mountain Zeolite	5,10,15,20,25

5.2.3. Data analysis

For each amendment material trialled, statistical analysis was applied as per the methods outlined in chapter 2. The pollutant removal results for the amendment rate treatments were pooled to produce medians for comparison with the unamended control (fill set 2) as established in chapter 4.

5.3. Results and discussion

The effect of each amendment material on the pollutant removal and hydrological performance of the simulated biofilter columns in terms of conductivity as measured by surface infiltrometry and overall column performance is presented in the following sections, with a summary of median pollutant removal performance reported in Table 14 below and Table 35 and Table 37 in appendix.

Table 14: Removal efficiency (median) of amended monophasic stormwater biofilter simulation columns

	Removal efficiency (median) of amended biofilter simulations (%)					
Pollutant Parameter	**Unamended control (fill set 2)**	**Biochar**	**Blast furnace slag**	**Crushed concrete**	**Gypsum**	**Zeolite**
Total nitrogen	60	46.9	60.3	44.2	50	57.4
Nitrate- and nitrite-nitrogen	70	52.2	75.5	**20.0**	31.2	82.1
Total Kjeldahl nitrogen	84.1	**41.7**	**28.6**	79.6	80.9	28.6
Total phosphorus	94.2	**64.1**	**52.7**	91.5	95.2	**76.2**
Cadmium	97.3	98.3	87.5	**99.6**	97.9	98.1
Copper	44.1	**72.8**	47.3	67.4	**80.7**	57
Nickel	78.3	88.9	88.9	93.2	91.1	83.3
Zinc	87.9	**95.9**	80.7	98.3	**93.8**	82.8
Chromium	71.8	**35.9**	80	58.9	94.4	78.8
Lead	95.9	**99.5**	97.2	**99.3**	**99.5**	95.8
Arsenic	95.3	**70.0**	**90.0**	**71.4**	**71.4**	**80.0**

***RED** highlighted cells represent a significant difference between the amendment and unamended control treatments*

5.3.1. Gypsum

5.3.1.1. Nutrient removal: nitrogen and phosphorus

5.3.1.1.1. Total Kjeldahl Nitrogen

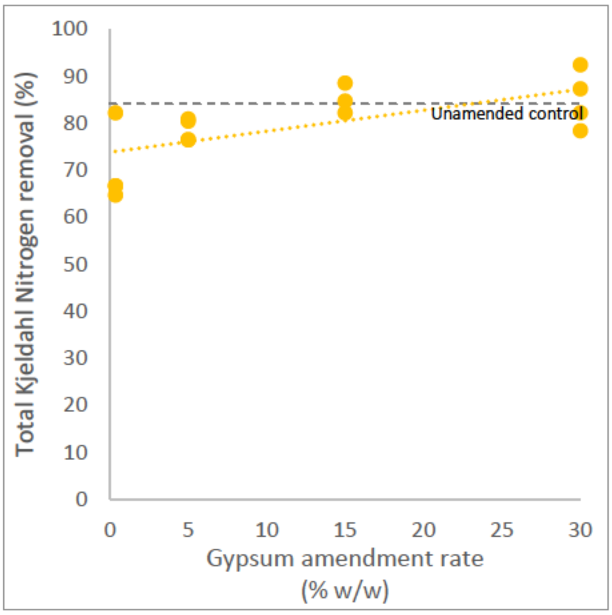


Figure 36: Total Kjeldahl Nitrogen (TKN) removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

There was a high positive correlation (r = +0.66) between the TKN removal and the amount of gypsum added, with the removal efficiency increasing with amendment rate. It can be seen in Figure 36 that the added gypsum enhanced performance with an amendment rate higher than about 22% w/w, when the unamended control removal rate was exceeded. This is an important finding because it informs biofilter managers that gypsum can improve pollutant removal in terms of TKN, and would likely improve the pollutant retention and service life of the biofilter system. The demonstrated removal efficiency means that gypsum could be an effective amendment material in biofilters, and offers the potential to recycle waste gypsum from the contruction industry into biofilter designs.

Gypsum's mechanism for enhancing the filtration layers TKN removal performance is most likely related to the release of calcium ions as the infiltrating stormwater partially dissolves the added gypsum (Equation 3).

Equation 3

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{\ 2-}$$

The freed Ca^{2+} ions have a strong affinity for negatively charged clay minerals and are rapidly absorbed onto the surface of these particulates (Ockert et al., 2014). Ammonium (NH_4^+) ions from the stormwater then preferentially exchange for the calcium ions on the clay, and are therefore removed from the stormwater (Ockert et al., 2014).

The reason why amendment at a lower level did not achieve that observed for the unamended control may relate to the mandated low clay concentrations (3% w/w) in the filter fill, and limited Ca^{2+} concentration released when low rates of gypsum amendment are applied, which meant that the exchange of Ca^{2+} with the NH_4^+ ions was not as efficient with lower gypsum application rates.

5.3.1.1.2. Nitrate- and nitrite-nitrogen

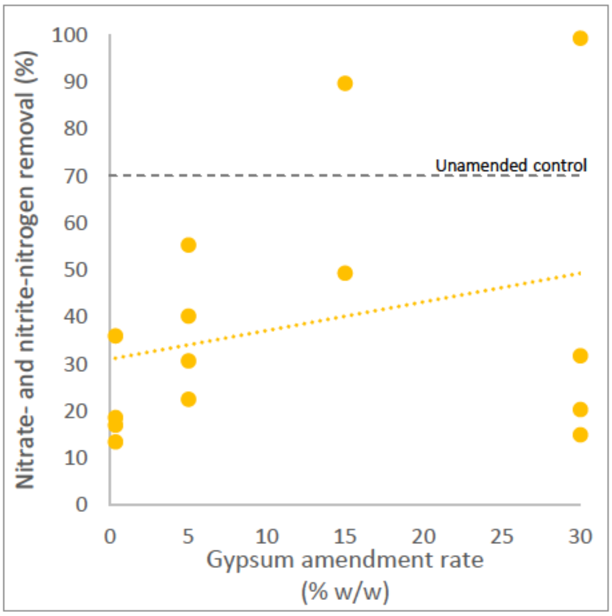


Figure 37: Nitrate- and nitrite-nitrogen (NOx) removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

Gypsum amendment had no affinity for NOx removal with there being no significant ($p = 0.51$) difference in removal performance between the gypsum rate treatments, and a low positive correlation ($r = +0.28$) between the amount of gypsum added and NOx removal efficiency (Figure 37). As such, NOx removal performance for the gypsum amended columns was lower than the level set by the unamended control; however, this difference was not statistically significant ($p = 0.14$). Past studies have also demonstrated that gypsum amendment has a limited influence upon nitrate runoff concentrations coming off gypsum amended soils (Favaretto et al., 2006, Norton, 2008).

5.3.1.1.3. Total Nitrogen

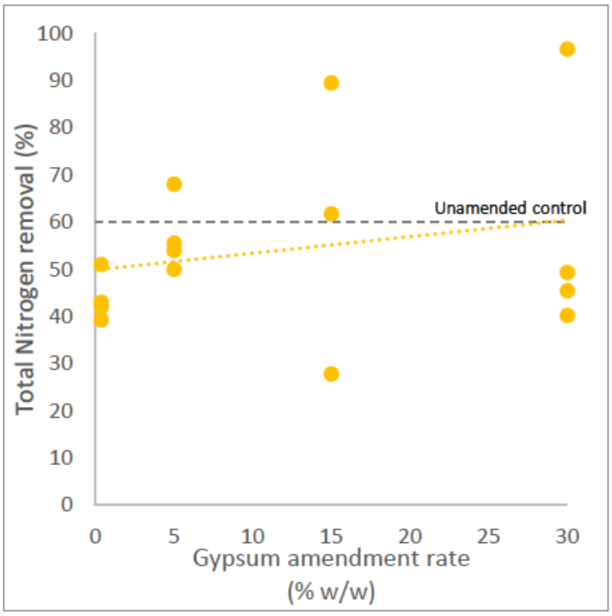


Figure 38: Total Nitrogen (TN) removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

Variability in TKN and NOx removal by the gypsum amended columns resulted in a low positive correlation ($r = +0.23$) in TN removal performance between the gypsum dosage rates (Figure 38). Gypsum amendment overall had a median TN removal of 50% which was statistically ($p = 0.40$) equivalent to that of the unamended control and was compliant with the City's DCP and BBWQIP guidelines (Table 1).

5.3.1.1.4. Total Phosphorus

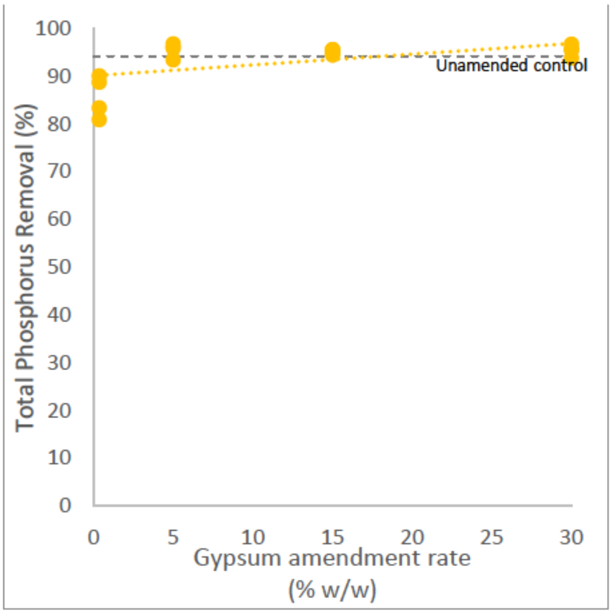


Figure 39: Total phosphorus (TP) removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

Gypsum amendment had a rate specific influence upon total phosphorus removal; with a significant difference ($p = 0.02$) in removal performance between the gypsum rate treatments and a moderate positive correlation ($r = +0.55$) between gypsum amendment and TP removal efficiencies (Figure 39). It can be seen in Figure 39 that the added gypsum enhanced performance with an amendment rate higher than about 18% w/w, at which point the unamended control removal rate was exceeded. This result is important because it again demonstrates the removal efficiency of gypsum, with extension to recycled gypsum, to enhance the phosphorus removal of the biofilter system. It also highlights to the biofilter operators what rate of gypsum amendment can improve filter bed performance.

The amended biofilter systems all had effective TP removal performance, with the pooled amendment results having a median 95.2% removal efficiency, which easily complied to the City's DCP and BBWQIP TP reduction targets (Table 1).

Gypsum has a two-stage sorption kinetic for phosphorus, with a relatively rapid first stage sorption through calcium precipitation reactions, which accounts for the majority (86-95%) of phosphorus sorption in the first 24 h of contact (Cheung and Venkitachalam, 2006). Calcium derived from gypsum reacts with the soluble reactive phosphorus within the soil pores, which is converted to insoluble calcium phosphate compounds in the soil matrix; altering the ratios of Ca_2-P (dicalcium phosphate), Ca_{10}-P (hydroxylapatite) and Ca_8-P (octacalcium phosphate) in the soil (He et al., 2017). The gypsum aided precipitation of phosphorus to calcium phosphate provides a relatively stable storage of phosphorus in the biofilter, improving the retention of phosphorus, as the captured phosphorus would not be readily leached out of the biofilter, and by enhancing the P retention pathway in the filter media, would improve the overall service life of the biofilter.

Regardless of the changes in soil phosphorus fractions, gypsum amendment does not impact the availability of phosphorus in the soil matrix, as gypsum amendment (5 t/ha) has been shown not to affect Bray-1 P levels; a soil test for plant available phosphorus (Brauer et al., 2005). Despite being relatively insoluble under the general alkaline conditions of gypsum amended soil, Ca_2-P and the slow-release Ca_8-P can be utilised by plants during active growth. Vegetation in the street biofilters, therefore, provides an avenue for the continual removal of phosphorus from the soil system via plant uptake and incorporation into plant biomass, following phosphorus immobilisation in the gypsum amended filter fill matrix due to the 0.38% w/w treatment having a significantly lower TP removal efficiency to the ≥5% w/w treatments.

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5.3.1.2. Heavy metal removal: dissolved-phase heavy metals

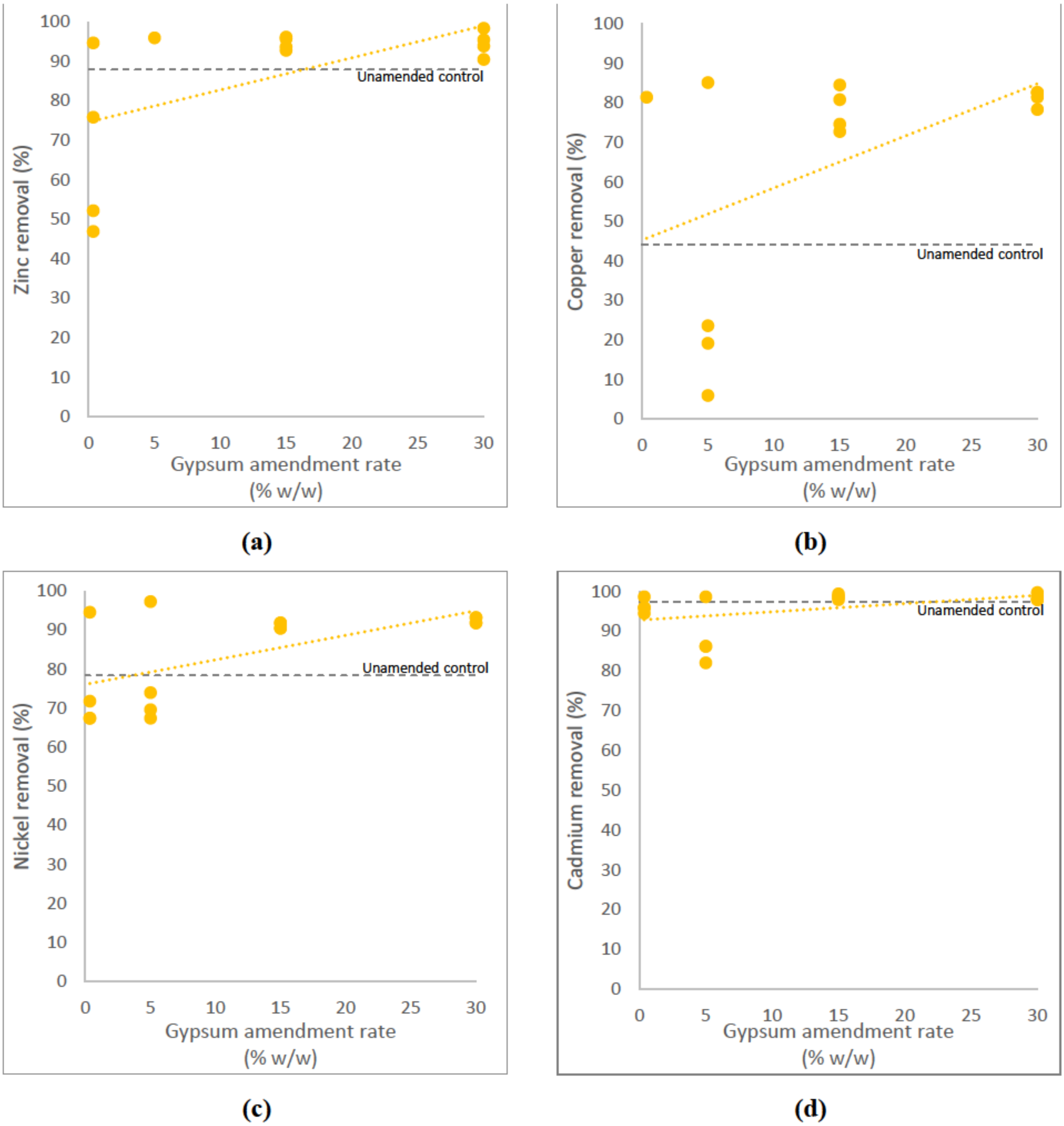


Figure 40: Dissolved-phase heavy metal removal efficiency: (a) zinc, (b) copper, (c) nickel and (d) cadmium removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

Gypsum amendment increased the dissolved-phase heavy metal removal, with higher gypsum amendment rates, especially at rates above 15% w/w, where performance was enhanced in comparison to the unamended control (Figure 40). As such gypsum's influence on the dissolved-phase heavy metal removal was rate-specific, with there being a high positive correlation ($r = +0.63$) for nickel removal, and a moderate positive correlations ($r = +0.44$, $+0.52$ and $+0.59$ respectively) for cadmium, copper and zinc removal with increased gypsum dosage rates (Figure 40).

Gypsum amendment significantly ($p = 0.03$ and 0.04 respectively) increased copper and zinc removal performance in comparison to the unamended control (Table 14 below and table 35 and 37 in appendix). Copper removal performance almost doubled with higher gypsum amendment rates, increasing median removal from 44.1% for the unamended control to 80.7% with the pooled gypsum amendment treatment. The enhanced copper removal performance was most likely due to gypsum adding fine particulates (Table 36 in appendix) and sulphate ions into the fill matrix, which the copper tends to bind to forming ternary cation-anion (SO_4^{2-}) complexes with Fe and Al oxy-hydroxides functional groups (Kumpiene et al., 2008).

The gypsum amended biofilters increased median zinc removal performance from 87.9% for the unamended control to 93.8% for the pooled gypsum amendment treatment. From all accounts, the gypsum amended biofilters should have had lower zinc removal than the unamended control, as the additional Ca^{2+} in the fill matrix should interfere with ion exchange by displacing or outcompeting zinc for exchange sites on organic matter and clay particulates within the fill matrix (Schomberg et al., 2018, Zhu and Alva, 1993).

The gypsum amendment had two factors which could have promoted the improvement in zinc removal:

i. Elevated fill pH which creates negative charges on the fill particulate surfaces, resulting in higher zinc adsorption (Casagrande et al., 2005), and

ii. The addition of small quantities of calcite and quartz (<5% w/w composition of the gypsum product), which adds carbonate ions into the fill matrix which can precipitate with the zinc (Kumpiene et al., 2008).

Effective removal by the gypsum amended simulation columns resulted in the median discharge concentrations of cadmium, nickel and zinc (Table 35 in appendix) that were compliant with the 95% ecological guidelines (Table 7) for all gypsum amended treatments, whereas, all copper results were non-compliant with the 90% ecological protection guideline

(Table 35 in appendix). Effective reduction of metal concentrations to below the ANZG (2018) guidelines is an important finding because these metals are road runoff pollutants of major concern, where the judicious amendment with gypsum which can remove these dissolved-phase heavy metal effectively and thus aid in protecting downstream water quality and ecological health. The enhanced removal of these dissolved-phased metals by the gypsum amended biofilters, further raises the possibility of applying gypsum in field biofilters, with the option of diverting waste gypsum from the landfill stream for reuse as an amendment in biofilter construction. The improved field biofilter performance, will aid in reducing these ecotoxic metals in urban waterways, providing public health and ecological improvements.

5.3.1.3. Heavy metal removal: dissolved-phase Heavy metal removal: suspended- or-settled-phase heavy metals

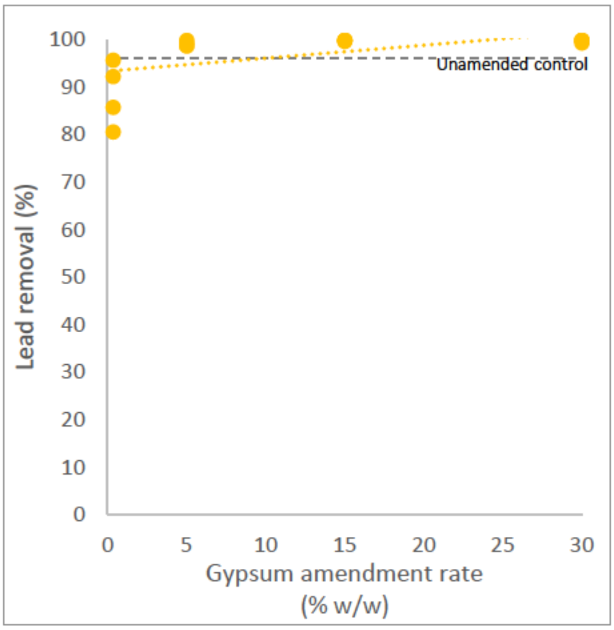


Figure 41: Lead removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

Gypsum amendment of the stormwater biofilter simulation columns had a positive effect upon the suspended-or-settled phase heavy metal removal; with there being a moderate positive correlation (r = +0.55) between lead removal and amendment rate (Figure 41. Median lead removal also significantly ($p = 0.02$) increased to 99.3% for the pooled amendment treatment in comparison to the unamended control (Table 14 below and Table 35 and 37 in appendix), as the ≥ 5 % w/w rate treatments all had higher removal than the median of the unamended control (Figure 41). All gypsum amended biofilter column treatments had greater than 90% lead removal efficiency (Figure 41), which meant that the lead concentrations discharged (Table 35 in appendix) were well below the 0.015 mg/L limit for the 95% ecological protection guideline (Table 7).

Lead is removed from the synthetic stormwater by a precipitation mechanism with the lead reacting with the sulphate ions (SO_4^{2-}) from the gypsum forming $PbSO_4$ (Koralegedara et al., 2017). Gypsum has been demonstrated in laboratory batch experiments to effectively remove lead from aqueous solutions, with a synthetic flue gas desulphurisation (FGD) gypsum showing up to 96.7 mg/g sorption capacity (Yan et al., 2015), and in soil systems at a rate of 5% w/w FGD gypsum amendment of a lead-contaminated sandy loam soil resulted in a lowering of lead leaching compared to that of the unamended soil (Koralegedara et al., 2017).

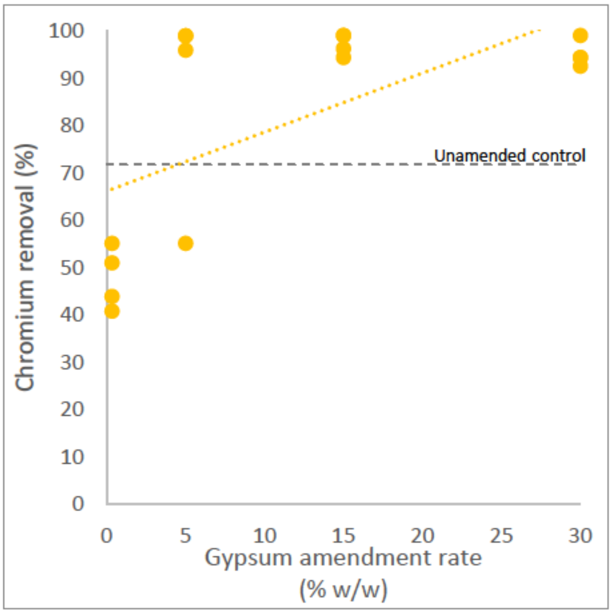


Figure 42: Chromium removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

There was a high positive correlation ($r = +0.64$) between the chromium removal and the amount of gypsum added, with the removal efficiency increasing with amendment rate. It can be seen in Figure 42 that amendment rates higher than 5% w/w significantly ($p = 0.08$) enhanced performance in comparison to unamended control, with the gypsum amended columns increasing median removal efficiency to 94.4%. All chromium discharge concentrations from the gypsum amended treatments were compliant with the 90% protection target (0.006 mg/L), except for the 0.38% w/w treatment (0.0265 mg/L).

5.3.1.4. Metalloid removal: arsenic

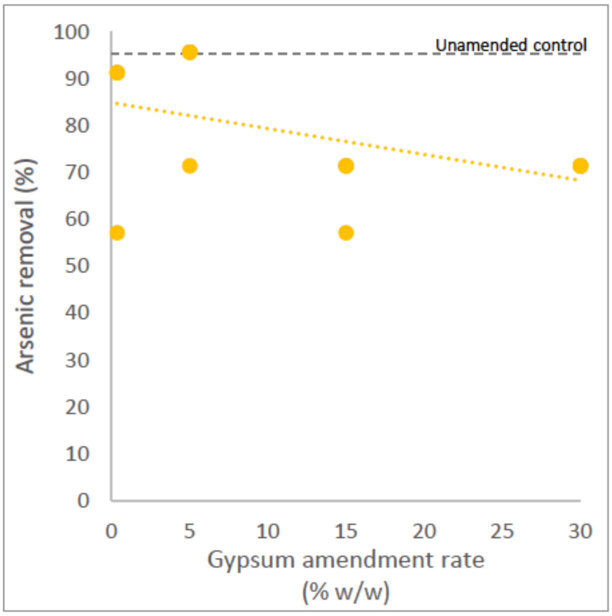


Figure 43: Metalloid arsenic removal efficiency with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

Figure 43 shows that the gypsum amended biofilters have reduced performance in comparison to the unamended control. Removal efficiency by the amended columns was significantly ($p = 0.005$) reduced, with median removal dropping from 95.3% for the unamended control to 73.4% for the pooled gypsum amended treatment. Fortunately, environmental arsenic is not predominant in the soils or general environment in the Sydney region.

Gypsum had limited capacity for arsenic removal, as indicated by moderate negative correlation ($r = -0.48$) with gypsum amendment, with removal performance decreasing with the increased application of gypsum (Figure 43). Despite the lower removal performance, all gypsum treatments reduced the arsenic concentration to below the 0.024 mg/L limit of the 95% ecological protection guideline.

Past studies have indicated that gypsum amendment has no significant effect upon the retention of arsenic in agricultural soils (Torbert et al., 2018, Aguilar-Carrillo et al., 2006). As the gypsum has limited absorptive capacity for arsenic, the decreased removal performance by the amended biofilter columns was due to the gypsum partly replacing the sand-based filter fill, reducing the availability of binding sites in the filter matrix.

3.5.1. Total suspended solids

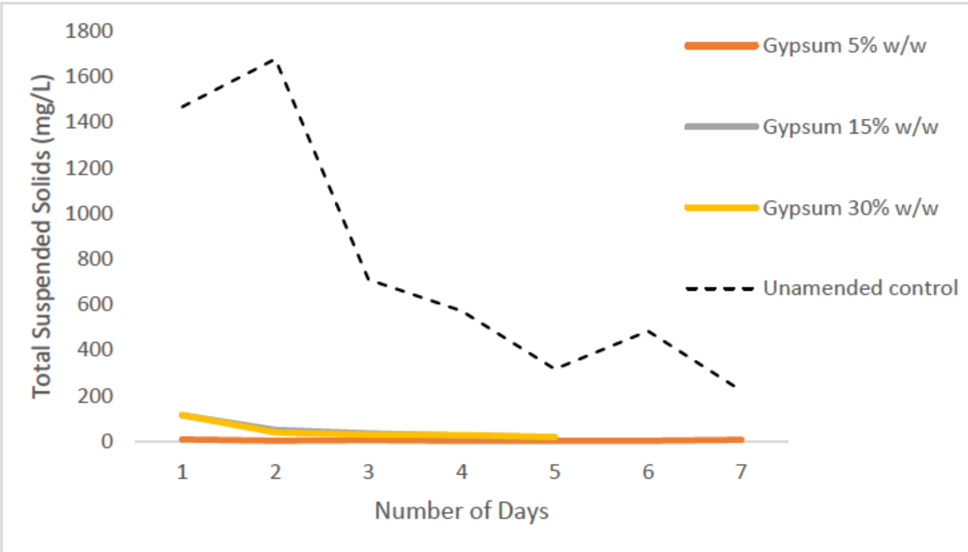


Figure 44: Mean total suspended solids discharged with gypsum amendment in comparison to the unamended control (dotted line)

Gypsum amendment significantly ($p < 0.001$) reduced the amount of suspended solids released by the biofilter columns upon start-up in comparison to the unamended control (Figure 44), with a median reduction of 97.1% across all rate treatments and purge days. After one day of hydraulic purging, there was a maximum release of 114 mg/L of TSS, which was a significant ($p < 0.001$) reduction of 1353 mg/L, as compared to the unamended control (Figure 44).

Gypsum amendment has a beneficial impact upon sediment discharge from soil-based systems, with studies demonstrating decreased suspended solid loads in the runoff from gypsum amended fields (Ekholm et al., 2012). The mechanism for gypsum enhanced TSS was most likely related to increased Ca^{2+} concentrations within the filter fill, with chemical testing showing gypsum had an exchangeable calcium concentration of 91 cmol/kg, which was substantially higher than the 1.2 cmol/kg of the sand-based unamended control.

The increased Ca^{2+} availability in the filtration layer promoted the flocculation of fine clay particulates (Przepiora et al., 1997). The flocculated clay aggregates may be better filtered and retained in the biofilter, thus limiting total suspended solids discharged in the gypsum amended treatments compared to the unamended control. Gypsum stabilisation of filter fill fine particulates is an important finding for improving fill stability and minimising sediment release which is a recognised problem with the City's field biofilters.

The 5% w/w treatment had the lowest TSS release of less than 7 mg/L. Interestingly, as the amendment rate increases to 15 and 30% w/w there is a slight increase of upwards of 20 mg/L in total suspended solids released. The increased TSS may be due to the change in the particle size distribution of the filter fill, with the added gypsum tending to have a high proportion of fine particulates (Table 36 in appendix), that may not be well captured by the sand-based filter fill or by the gypsum aided flocculation mechanism.

3.5.2. Hydrological performance

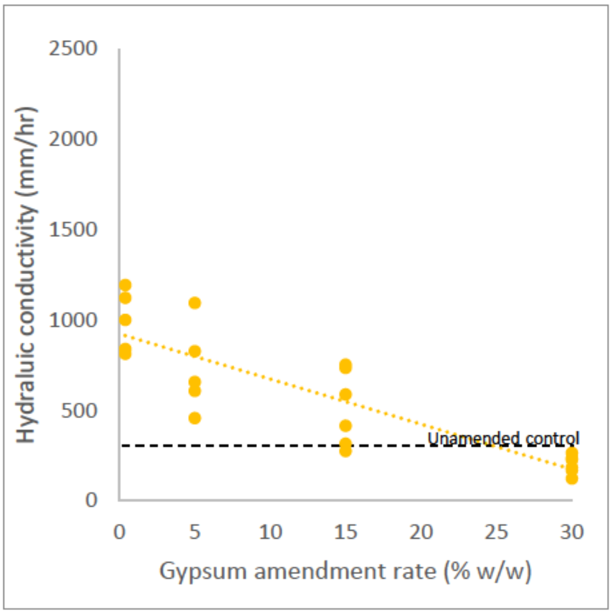


Figure 45: Hydraulic conductivity with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

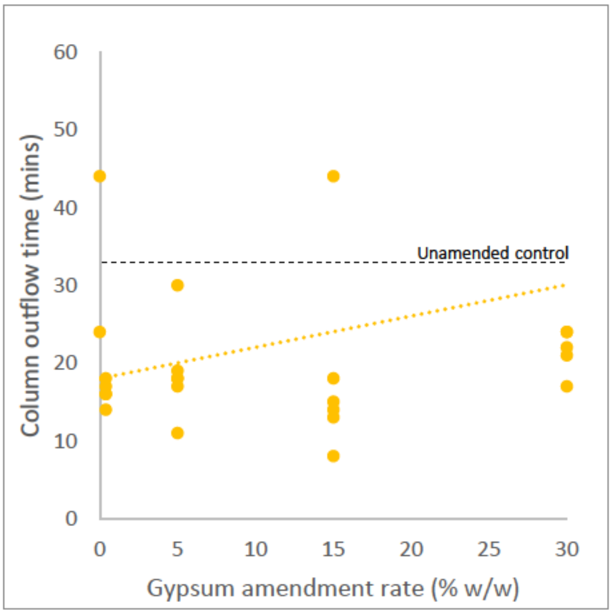


Figure 46: Column outflow time with gypsum amendment showing trend with gypsum dosage (dotted line) against unamended control (dashed line)

Gypsum amendment at low levels initially increased flows through the filter bed as shown in Figure 45 and 46, with high conductivities being potentially detrimental for optimal performance of the biofilter, although a point was reached at the 25% w/w amendment rate where flow performance was marginally slowed in comparison to that of the unamended control, and was within the optimal range of the CRC (2015) hydrological guidelines.

Compared against the unamended control, the 0.38 and 5% w/w significantly ($p = 0.008$ and 0.02 respectively) increased hydraulic conductivity, the 30% w/w treatment significantly ($p = 0.003$) lowered conductivity, and the 15% w/w gypsum amendment was statistically ($p = 0.3$) equivalent to that of the unamended control (Figure 45). Column discharge time was significantly ($p = 0.02$) different between the gypsum amendment rates (Figure 46), and overall significantly ($p = 0.002$) decreased discharge time in comparison to the unamended control.

Gypsum amendment had a very high negative correlation ($r = -0.86$) with fill hydraulic conductivity (Figure 45) and a corresponding low positive correlation ($r = +0.31$) with column discharge time (Figure 46). The low rate treatments of 0.38 and 5% w/w had median hydraulic conductivities of 1000 mm/hr and 657 mm/hr, which resulted in median column discharge times of 16.5 and 18 minutes respectively. In contrast, the high 30% w/w rate treatment had a median hydraulic conductivity of 204 mm/hr and produced slower column discharge times of 23 minutes. The relation between these two hydrological measurements was expected to be complementary because as the stormwater flows through the fill more efficiently, column outflow time would be faster.

Gypsum's hydrological influence was most likely to be physical in nature, through the alteration of the fill's particle and pore size distribution (Keren et al., 1980). The gypsum had a PSD that was dissimilar to that of the filter fill, with the amendment increasing the percentage composition of coarse particulates (<2 mm and 1-2 mm fractions) and the <75 µm fractions. The altered PSD and pore size distributions resulted in high hydraulic conductivities at low amendment rates, while as amendment rate increased so too did the concentration of fine particulates (Table 36 in appendix), which lead to the infill of pores and the progressive drop in hydraulic conductivity (Keren et al., 1980). Additionally, pure gypsum had a relatively restricted hydraulic conductivity, with a median of 73 mm/hr, which supports the notion of decreased hydraulic conductivity with greater gypsum amendment. Addition of recycled gypsum into the filter media could potentially be used to regulate fill hydraulic conductivity of field biofilters. Application of a low gypsum amendment rate which increases flow rate through soil, could open up the substrate of clogged biofilters by flocculating the fine clay particulates trapped in the biofilter media into larger particulate aggregates, thus shifting PSD to a larger diameter, and opening soil pores to more effective infiltration of water. A higher amendment rate of gypsum, could slow the flow to an optimal level in fast free flowing sandy soil biofilters. Correction of unsuitable system hydrology would ultimately extend service life, as poor hydrology is often reported as key reason for biofilter system failure.

5.3.2. Crushed concrete

5.3.2.1. Nutrient removal: nitrogen and phosphorus

5.3.2.1.1. Total Kjeldahl Nitrogen

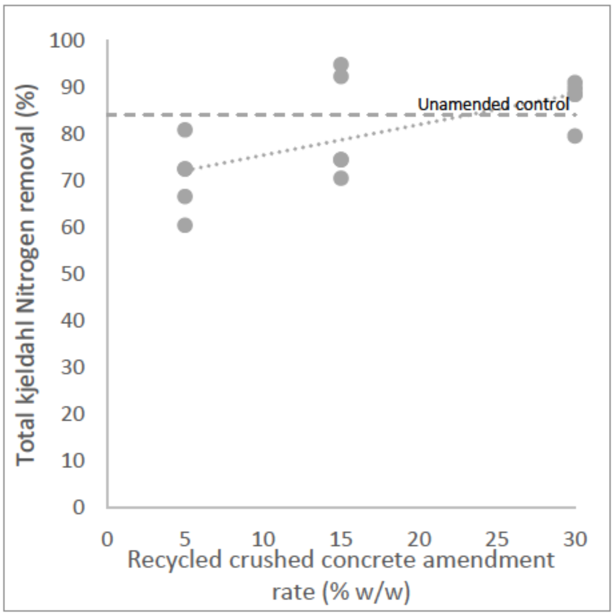


Figure 47: Total Kjeldahl Nitrogen (TKN) removal efficiency with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

The graph (Figure 47) shows that the amount of TKN removed increases with the amount of gypsum added, with a high positive correlation ($r = +0.66$) in TKN removal with the crushed concrete amendment. The concrete amendment enhanced performance at higher rates greater than about 25% w/w, when the unamended control removal rate was exceeded. This is an important finding relevant to biofilter designers and operators, as it shows an increase in removal of unstable organic nitrogen and ammonia from stormwater flows which is desirable in the interests of improving receiving water quality.

On the whole, crushed concrete had minimal impact upon the biofilter performance, with there being no significant ($p = 0.37$) difference between the pooled crushed concrete treatment and the unamended control, as removal performance was similar between the two groups, with median removal of 79.6% for the pooled crushed concrete treatment and 84.1% for the unamended control.

Crushed concrete has been demonstrated to have some capacity for NH_4^+ removal, with 2-5 mm crushed cement brick and porous concrete permeable pavement reducing column effluent concentrations by 58 and 36% respectively, however, once the ion exchange sites on the surface layers of the porous pavement become exhausted NH_4^+ concentrations gradually increased back up to 4.8 mg/L (Li et al., 2017). Crushed concrete's limited adsorption properties for NH_4^+ most likely explains the positive correlation and improved TKN removal with high amendment rates observed (Figure 47).

5.3.2.1.2. Nitrate- and nitrite-nitrogen

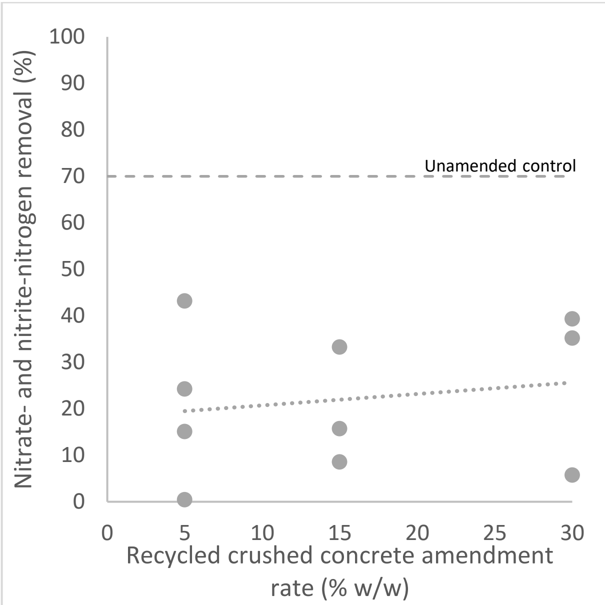


Figure 48: Nitrate- and nitrite-nitrogen (NOx) removal efficiency with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

All amended simulation biofilter columns had NOx removal efficiencies that were below the performance of the unamended control (Figure 48), with the pooled crushed concrete's median of 20.0% being significantly ($p = 0.01$) lower than the unamended control. Furthermore, there was no relationship between crushed concrete amendment and NOx removal, as there no significant ($p = 0.7$) difference between the rate treatments and only a low positive correlation ($r = +0.18$) between the crushed concrete amendment and NOx removal performance.

Cement brick and porous concrete have shown minor improvements in nitrate removal, with these materials reported to reduce NO_3-N concentration by 13% and 21% respectively (Li et al., 2017). It has been suggested that aggregates (zeolite, pumice, perlite) used in the production of concrete can have nitrate absorptive properties through anion adsorption on surface metal oxides, with maximum absorptive capacity of 70 mmol/g after 1 hr contact time (Mehrania et al., 2017). There was low availability of these concrete aggregates and limited contact time with the concrete amendment explains the limited NOx removal capacity for the amended biofilter columns.

5.3.2.1.3. Total Nitrogen

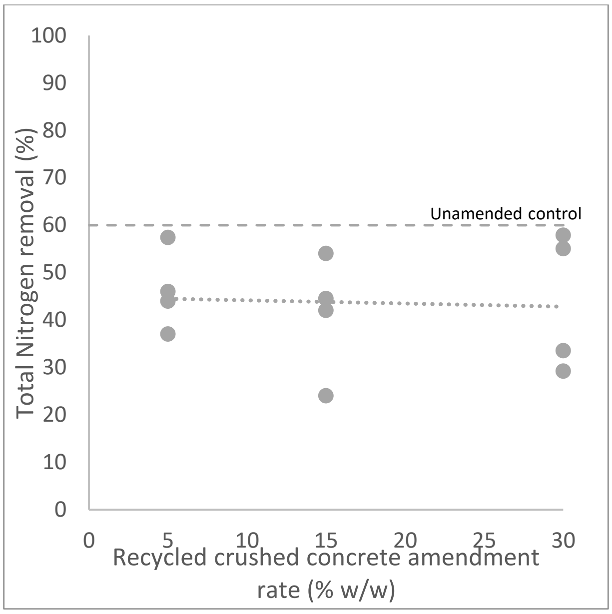


Figure 49: Total Nitrogen (TN) removal efficiency with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

All crushed concrete amended columns had TN removal efficiencies that were below the performance of the unamended control (Figure 49); however, there was no significant ($p = 0.63$) difference between the pooled crushed concrete amended and the unamended control treatments. Median TN removal of 44.2% for the crushed concrete amendment did not conform to local guidelines of the City's 45% TN reduction target, with median TN removal for all the crushed concrete amendment rate falling to just below the City's target.

The rate of crushed concrete amendment applied had limited impact upon TN removal, with there being no significant ($p = 0.06$) difference in TN removal performance between the crushed concrete amended column treatments, with all rates having nearly equal TN removal performance, and a very low negative correlation (r = -0.06) (Figure 49).

The literature indicates that concrete can have some capacity for TN removal, with studies showing that fly ash aerated crushed concrete can achieve 95.6% TN removal from sewage and landfill leachate (Li et al., 2017, Deng and Wheatley, 2018). However, the fly ash aggregate in the concrete material has specific TN removal capacity, and this may not be replicated in recycled concrete derived from ordinary construction waste.

5.3.2.1.4. Total Phosphorus

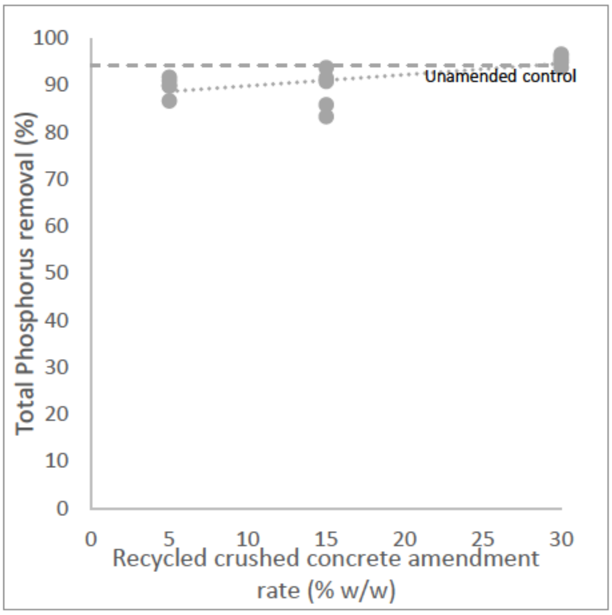


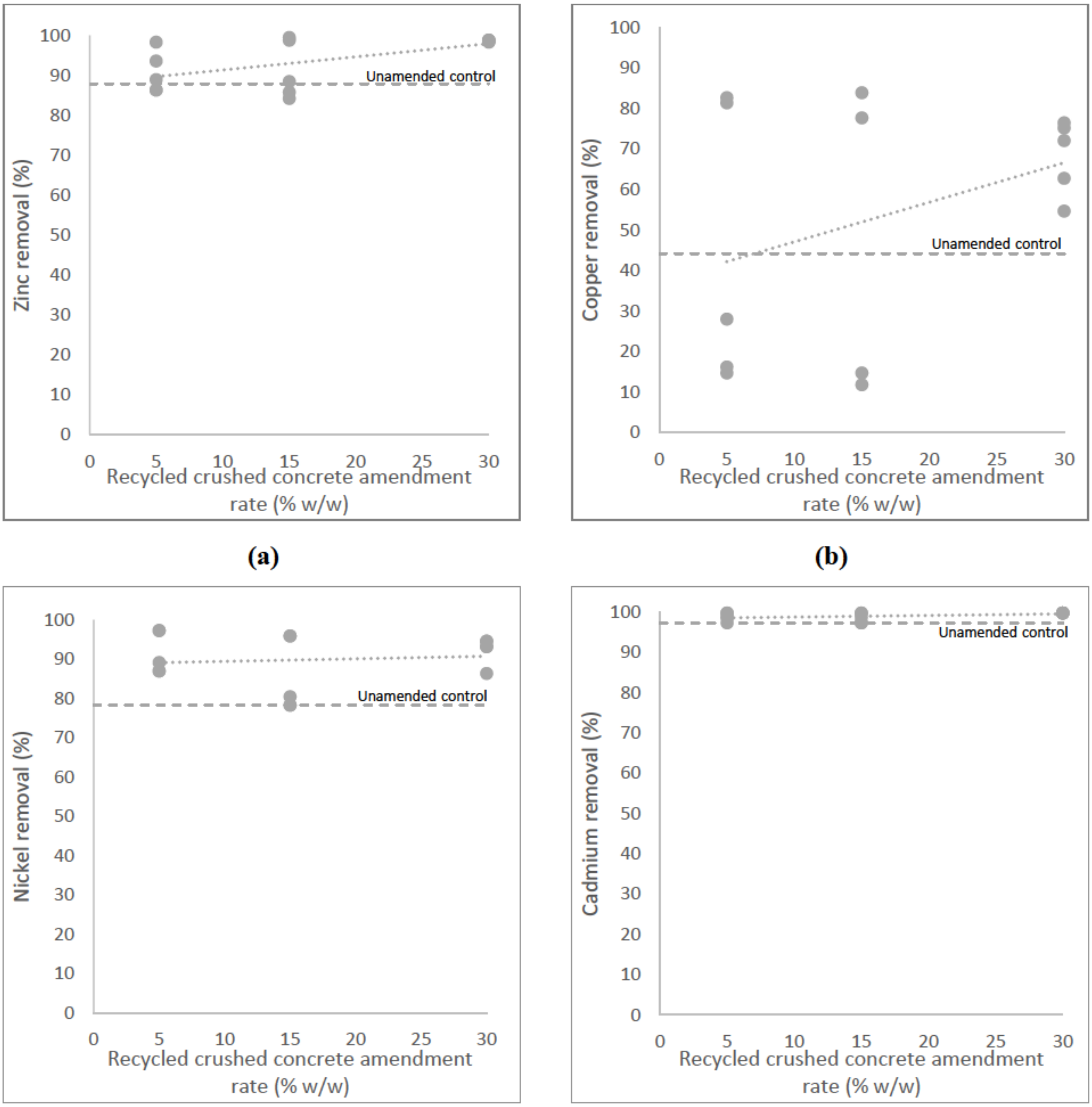
Figure 50: Total Phosphorus (TP) removal efficiency with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

Total phosphorus was effectively removed by the crushed concrete amended biofilter simulation columns, with a median removal of 91.5% across all the rates trialled. This high performance meant that all the crushed concrete amendment treatments had removal performances that complied with the City's TP removal targets (Table 1).

The biofilter column simulations had a high positive correlation ($r = +0.65$) between TP removal and crushed concrete amendment rate, with median removal significantly ($p = 0.01$) increasing from 89.8% for the 5% w/w biochar treatment to 95.4% in the 30% w/w biochar treatment (Figure 50). Despite the positive influence of crushed concrete amendment on removal performance, the pooled amended treatment had statistically equivalent ($p = 0.46$) removal performance to that of the unamended control.

Past studies have suggested that crushed concrete can be an effective TP absorbent (Deng and Wheatley, 2018, Bus and Karczmarczyk, 2017, Egemose et al., 2012), with batch experiments using 2-5 mm recycled concrete aggregate indicating maximum adsorption capacity of 6.88 mg/g and an over 80% removal performance from 20 mg/L P solution (Deng and Wheatley, 2018). The majority of past studies have investigated concrete's phosphorus removal under continually saturated hydraulic loading (Deng and Wheatley, 2018, Bus and Karczmarczyk, 2017, Egemose et al., 2012); therefore the application of crushed concrete in columns which experienced intermittent hydraulic saturation is novel, and the results of such would be expected to be dissimilar to the prior continuous saturation experiments.

5.3.2.2. Heavy metal removal: dissolved-phase heavy metals



(c) (d)

Figure 51: Dissolved-phase heavy metal removal efficiency: (a) zinc, (b) copper, (c) nickel and (d) cadmium with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

The crushed concrete amended biofilter column had enhanced dissolved-phase heavy metal removal performance in comparison to the unamended control, increasing median removal to 99.6%, 67.4%, 93.2% and 98.3% cadmium, copper, nickel and zinc respectively (Table 14 and Figure 51). High removal efficiencies meant that concentration of the dissolved-phase heavy metals in the stormwater conformed to the 95% ecological protection guidelines for all metals except copper.

Crushed concrete amendment, especially at higher rates, had a positive influence on metal removal efficiency, with zinc and cadmium both showing a moderate positive correlation ($r = +0.58$ and $+0.42$ respectively), while copper showed a low positive correlation ($r = +0.36$) and nickel had a very low positive correlation ($r = +0.10$).

There was limited research available on the interaction of concrete with aqueous metal solutions; however, a few studies have shown that concrete could influence metal ion sorption. For instance, 102 mm diameter porous concrete blocks reduced zinc and copper concentration in stormwater by 90% and 87% respectively (Haselbach et al., 2014). In comparison, a silica fume-based pervious concrete showed a 69% nickel and 84.5% copper removal efficiency; however, this concrete was customised to optimise its heavy metal adsorption properties, and such high adsorption capacity would not be likely to be representative of concrete derived from an industrial waste stream (Yousefi and Matavos-Aramyan, 2018).

The enhanced removal of dissolved-phase metals is an important result, as it supports the application of recycled concrete materials as an amendment material of biofilters. Application in field systems, could mean that these ecotoxic metals could be effectively removed, with the simulation results indicating that 95% ecological protection targets could be achieved. This would mean that health of receiving water ways could improve and be maintained for the benefit of the aquatic organisms that live in them. Also, with improved water quality, there is great opportunity social and recreational use of urban waterways as there is a reduced public health risk with the cleaner water ways.

5.3.2.3. Heavy metal removal: suspended- or-settled-phase heavy metals

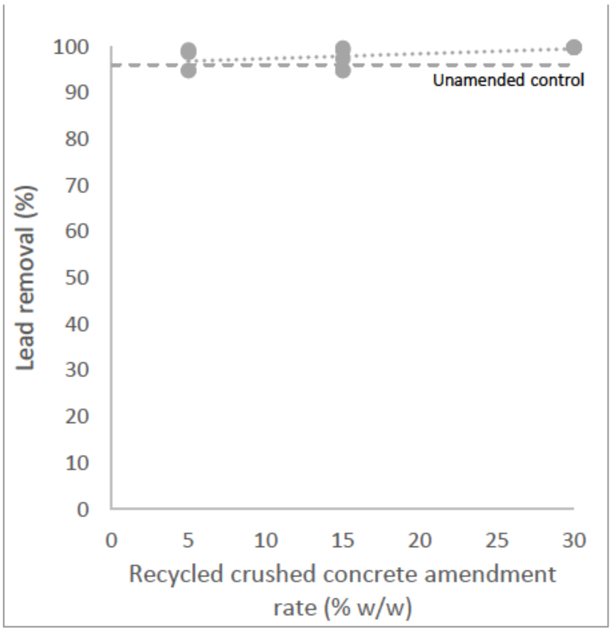


Figure 52: Lead removal efficiency with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

Crushed concrete amendment enhanced lead removal in comparison to the unamended control (Figure 52), with the amendment significantly ($p = 0.01$) increasing lead removal from a median of 96.1% for the unamended control to 99.3% for the pooled crushed concrete amended treatments. The influence of crushed concrete was rate-dependent, with there being a moderate positive correlation ($r = +0.52$) for lead removal efficiency with crushed concrete amendment. Overall, the high removal performance meant that all crushed concrete columns had lead concentrations in the stormwater discharge that conformed to the 95% ecological protection guideline level (Table 35 in appendix).

The literature supports that crushed concrete has some capacity for lead removal with a three-tiered pervious concrete filter demonstrating an up to 99.1% removal under a carbonized system (Muthu et al., 2018). Tier 1 alone achieved an 88% reduction (from 8 to 1 mg/L) after 3 minutes of hydraulic contact time (Muthu et al., 2018). The primary mechanism for lead removal by concrete is reported as lead complexation with hydrous silica gel from the hydrolysis of concrete.

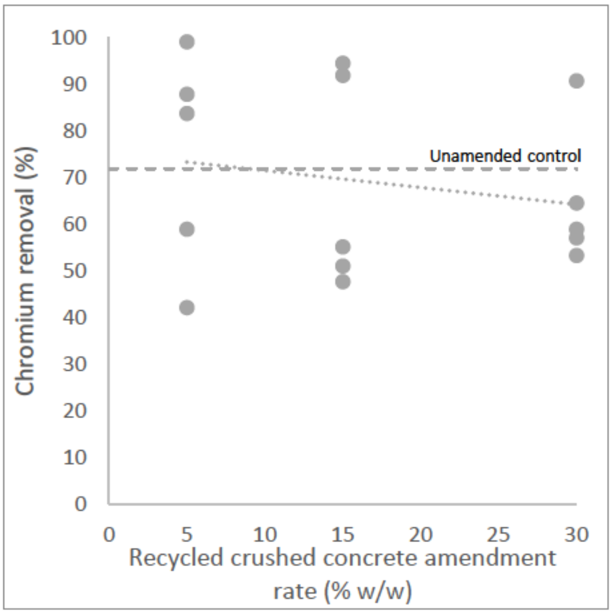


Figure 53: Chromium removal efficiency with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

The crushed concrete amended biofilter columns had a broad range (42-99%) of chromium removal efficiencies, with a median removal of 58.9% (Figure 53). There was a low negative correlation ($r = -0.20$) between chromium removal and crushed concrete amendment rate, and an 18% reduction in median chromium removal between the crushed concrete amended and unamended control. However, the difference in chromium removal between these treatments was not statistically significant ($p = 0.3$). The overall lower chromium removal efficiency by the crushed concrete amended columns meant that median chromium concentrations discharged by the amended columns were 0.022 mg/L, which were non-compliant with the 0.006 mg/L limit for 90% ecological protection.

There was no scientific literature available on the chromium absorptive properties of crushed concrete, however, given the negative correlation between chromium removal and crushed amendment it is safe to assume that crushed concrete had no or limited influence on chromium removal, hence the drop in chromium removal with the increased crushed concrete amendment.

5.3.2.4. Metalloid removal: arsenic

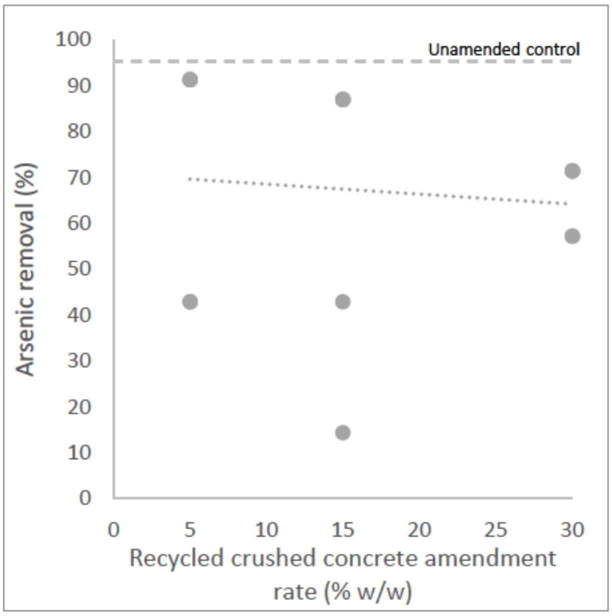


Figure 54: Metalloid arsenic removal efficiency with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

Crushed concrete amended biofilter columns had lower removal performance than the unamended control (Figure 54), with median removal for the pooled crushed concrete treatment significantly ($p < 0.001$) decreasing to 71.4%, in comparison to the unamended control. Despite the negative influence of crushed concrete on the arsenic removal performance, the median arsenic concentration (0.003 mg/L) discharged from the amended columns still complied with the 95% ecological protection guideline.

The rate of the crushed concrete amendment was not a determining factor for this decrease in arsenic removal, as there was a very low negative correlation ($r = -0.10$) and no significant ($p = 0.6$) differences in removal performance between amendment rate treatments.

The literature indicates that cement has some capacity for arsenic sorption (Sasaki et al., 2014, Kundu et al., 2004); with a 1:15 suspension of a hardened cement paste in a pH 4.5, 0.2 mg/L As (V) solution after 8 hrs reaction time having equilibrium sorption of 95%. A 5-10% cement amendment of an arsenic-contaminated soil showed a >90% retention of As (V) (Miller et al., 2000).

The arsenic removal results for the biofilter simulation columns were dissimilar to the positive performance reported in the literature. The biofilter simulations operated at a pH >7, had limited hydraulic retention times (<30 minutes) and was treating an As (III) solution, all these factors were beyond the optimal conditions required for cement materials to be absorptive for arsenic; hence the crushed concrete amendment had a negative impact on arsenic removal in the stormwater biofilter simulations.

5.3.2.5. Total suspended solids

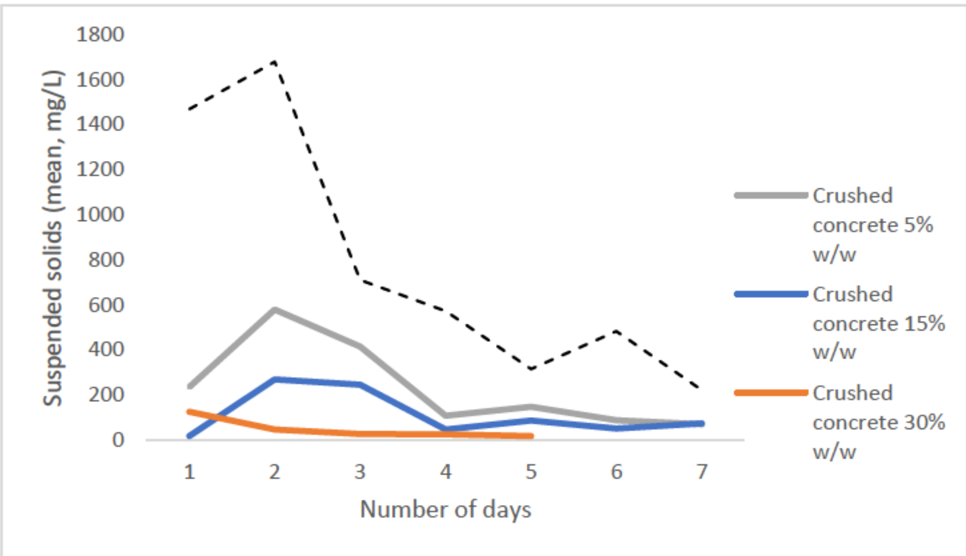


Figure 55: Mean total suspended solids discharged with crushed concrete amendment in comparison to the unamended control (dashed line)

Crush concrete amendment reduced TSS release in comparison to the unamended control, with a median reduction of 84% across all rate treatments and purge events. Furthermore, there was a significant (Table 38 in appendix) reduction in the amount of suspended solids discharged in comparison to the unamended control over the seven days of purging (Figure 55).

The 30% w/w treatment had the best performance, with a continual decline in TSS release by the simulation columns, and final minimum discharge of 23 mg/L of TSS at day 5. The TSS released from the 5 and 15% w/w crushed concrete amended biofilter column treatments rapidly declined after an initial peak, falling to 112 mg/L and 117 mg/L respectively, by day seven.

Both the 5% and 15% w/w treatments had a peak in TSS discharge of 446 mg/L and 968 mg/L respectively, on day two of purging. A day two peak was a similar trend to that of the unamended control, except that the crushed concrete amended columns had a significantly ($p < 0.001$) reduced peak, with the amendment reducing mean peak TSS discharge by 1230 mg/L and 708 mg/L respectively, compared to the unamended control (Figure 55).

Like gypsum, the expected mechanism for crushed concrete to suppress TSS release from the biofilter columns was through the partial dissolution of the concrete particles, which elevate available Ca^{2+} concentration within the filter fill. Elevated Ca^{2+} ions flocculate clay particles within the filter matrix, with the larger flocculated clay particles not being as readily dislodged by the infiltrating stormwater or they are better filtered by the biofilter matrix and thus retained. Crushed concrete is not as efficient in releasing Ca^{2+} ions as that of gypsum, and so the reduction in TSS by crushed concrete was less than that seen in the gypsum. Reduced TSS discharge is an important finding in the crushed concrete amendment of the column biofilters. It indicates that recycled concrete from the building industry could be an effective means of stabilising fill fine particulates, preventing excessive TSS discharge during biofilter establishment, which is a known issue with field biofilters.

5.3.2.6. Hydrological performance

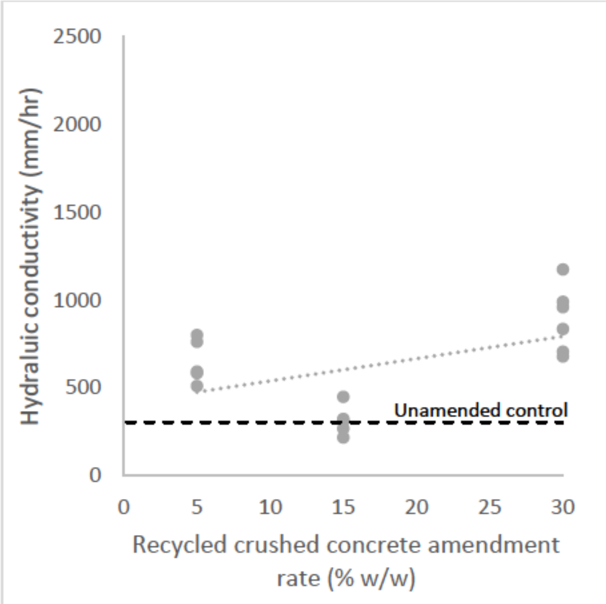


Figure 56: Hydraulic conductivity with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

Crushed concrete amendment tended to increased flows through the filter bed as shown in Figure 56 and 57, with the faster subsurface flow rates being potentially detrimental for optimal performance of the biofilter as per the CRC (2015) hydrological guidelines. Crushed concrete amendment tended to increase the hydraulic conductivity of the biofilter fill, as there was a moderate positive correlation ($r = +0.49$) between the amount of crushed concrete added and fill conductivity (Figure 56). There was a significant ($p = 0.003$) difference in hydraulic conductivity between amendment treatments and a significant ($p = 0.03$ and 0.01 respectively) difference between the 5% w/w and 30% w/w treatments and the unamended control. There was no significant ($p = 0.06$) difference between the 15% w/w treatment and the unamended control, as the median (310 mm/hr) of the 15% w/w treatment was equivalent to that of the unamended control (302 mm/hr).

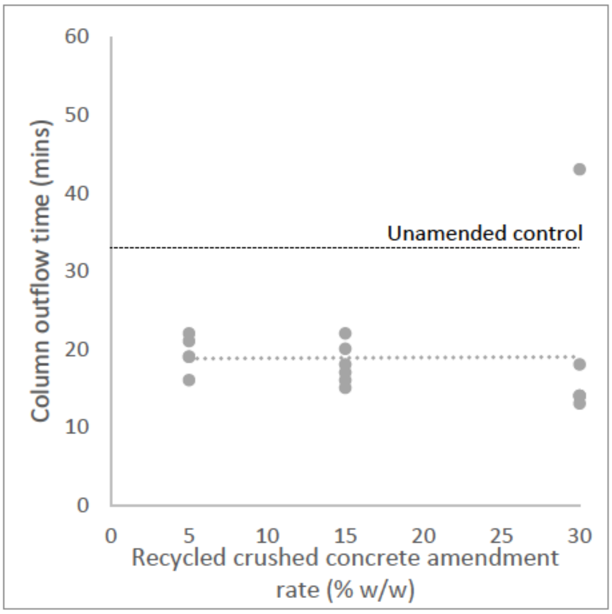


Figure 57: Column outflow time with crushed concrete amendment showing trend with crushed concrete dosage (dotted line) against unamended control (dashed line)

As expected from the hydraulic conductivity results, the crushed concrete amendment consistently and significantly ($p = 0.003$) lowered the outflow time of the amended biofilter columns as compared to the unamended control (Figure 57). Unlike the hydraulic conductivity results, amendment rate had no impact upon the systems discharge time, as there was a very low negative correlation ($r = -0.003$) between amendment rate and column discharge time. Despite the lack of correlation, there was a significant ($p = 0.02$) difference between the amendment rates, but this was primarily related to differences in the spread of discharge time values, as there was a 6-minute difference in median outflow time between the 5% w/w and 30% w/w treatments.

The use of crushed concrete as a soil amendment in stormwater biofilters is a novel application, with crushed concrete tending to be used as a road and pavement base or backfill material (Cardoso et al., 2016), as such there was limited relevant scientific literature about the influence of crushed concrete amendment on soil hydraulic properties.

According to the Minnesota Stormwater Manual, a sand/sandy loam fill has design infiltration rate of approximately 20.3 mm/hr (Minnesota Pollution Control Agency, 2018). Amendment of this soil with crushed concrete would likely alter soil texture, and move classification towards a gravelly sand class, with a design infiltration of 41.4 mm/hr (Minnesota Pollution Control Agency, 2018).

Understanding the impact of crushed concrete amendment on system hydrology is an important finding, if biofilter designers and operators were to consider recycled crushed concrete as a fill media for TSS and metal retention properties, it is essential to understand how this may impact other properties of the system. By understanding that crushed concrete tends to increase hydraulic conductivity, addition of gypsum could be paired with the crush concrete amended fill to counter this effect and to achieve optimal hydrological properties.

5.3.3. Blast furnace slag

5.3.3.1. Nutrient removal: nitrogen and phosphorus

5.3.3.1.1. Total Kjeldahl Nitrogen

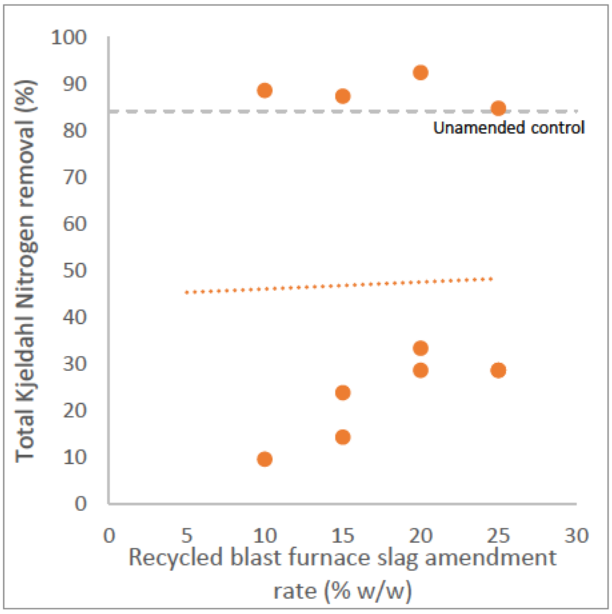


Figure 58: Total Kjeldahl Nitrogen (TKN) removal efficiency with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

There was virtually no relationship between BFS amendment and TKN removal performance, as indicated by a very low positive correlation between BFS amendment and TKN removal (r = +0.02) (Figure 58). Furthermore, there was a significant ($p = 0.03$) drop in median removal efficiency form 84.1% for the unamended control to 28.6% for the pooled BFS amended treatment (Figure 58).

Past batch experiments have shown that BFS has a low removal performance for NH_4^+; with an 89.21 cmol/kg CEC BFS demonstrating a 15.5% removal efficiency from a 100 mg/L NH_4^+ solution (Zhu et al., 2011). The BFS employed in the biofilter experiments had a comparatively low CEC of 1.8 cmol/kg, and therefore most likely had lower NH_4^+ removal efficiency than that report in the literature, which would explain the observed weak correlation and the significant decline in TKN removal performance in comparison with the unamended control.

5.3.3.1.2. Nitrate- and nitrite-nitrogen

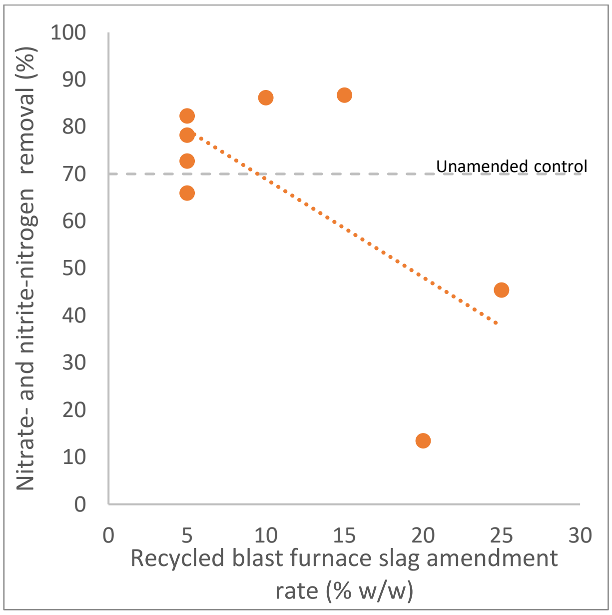


Figure 59: Nitrate- and nitrite-nitrogen (NOx) removal efficiency with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

Figure 59 shows that a 5% w/w BFS amendment enhanced NOx removal in comparison to the unamended control, increasing median removal to 75.5%. NOX removal performance then decreases with higher rates of fill amendment, as indicated by a high negative ($r = -0.65$) correlation between NOx removal and BFS amendment rate; however, this was derived from a limited dataset due to outlier removal (Figure 59). Although there was a considerable variation in data distributions between the pooled BFS amended and unamended control, overall, there was no significant difference ($p = 0.35$) between the two treatment groups, with only a marginal difference in median NOx removal between the two datasets (Table 14, and 35 and 37 in appendix).

Low sorption capacity of BFS for NOx would explain the negative correlation and overall low NOx removal with BFS amendment observed, with previous studies indicating that BFS has a low capacity for the sorption of the negatively charged nitrogen oxides, for instance, 1 g of steel slag achieved only 18% removal efficiency from a 20 mg/L NO_3 (pH 4) solution after 180 minutes of contact (Yang et al., 2017b). As an amendment, A 1:1 BFS/sand amended unvegetated bioswale reduced nitrate by 36% which was essentially equivalent to the 40% nitrate removal efficiency of the unamended sand-based bioswale (Li et al., 2016).

5.3.3.1.3. Total Nitrogen

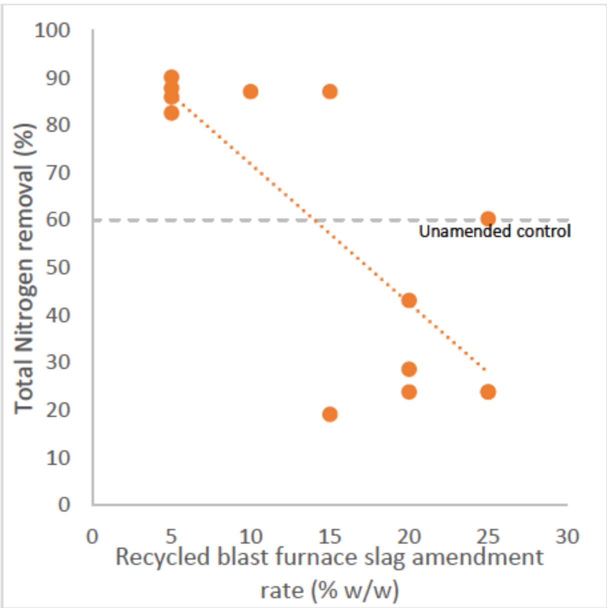


Figure 60: Total Nitrogen (TN) removal efficiency with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

Alike NOx removal, BFS enhanced TN removal for the 5% w/w treatment in comparison to the unamended control, but deceased performance for amendment rates greater than 15% w/w. There was a high negative correlation for TN removal ($r = -0.71$) between the BFS amendment rate treatments (Figure 60), due to absence of correlation for TKN and the high negative correlation for NOx removal results. There was no significant ($p = 0.91$) difference between pooled BFS treatment and the unamended control, with almost identical median removal for these two groups (Table 14 and table 35 and 37 in appendix). The BFS amended biofilter simulation columns had median removal of 60.3% which conformed to the City's TN reduction target of 45% (Table 1), however, the full range of experimental results for all the BFS amendment rates did not comply with the City's targets, especially with higher BFS amendment rates of ≥15% w/w.

There was limited literature on the impact of BFS on TN removal; with the available literature generally supporting this studies results, depicting that high amendment rate of a 1:1 BFS to sand ratio resulted in a 37% TN removal efficiency (Li et al., 2016).

5.3.3.1.4. Total Phosphorus

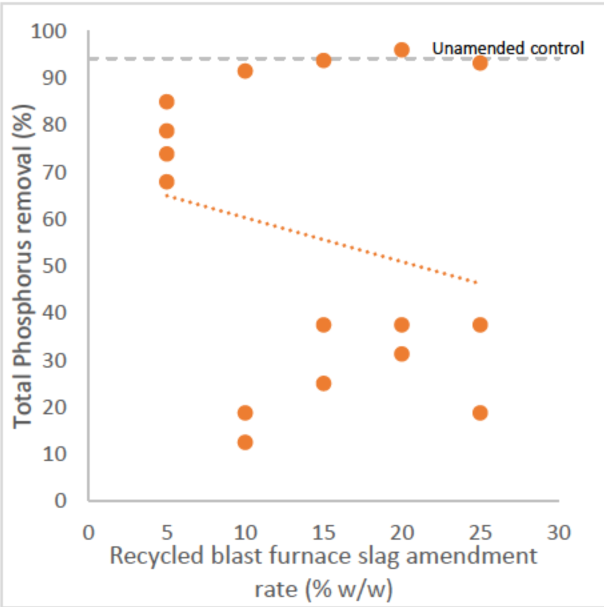


Figure 61: Total Phosphorus (TP) removal efficiency with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

There was a significant ($p = 0.01$) decline in TP removal with BFS amendment, with the pooled BFS treatments having a median removal of 52.7% which was far less than the 94.2% for the unamended control (Figure 61). Furthermore, TP removal decreased with increases in BFS amendment rate, as depicted by the low negative correlation ($r = -0.22$). Overall, the pooled BFS treatment was able to meet the City's TP reduction targets, with only the 5% w/w rate with a median of 76.3% complying with the 60% minimum reduction target.

The results of the biofilter column simulation experiment are in opposition to that of past scientific studies which generally report that BFS have high sorption capabilities for phosphate from aqueous solutions (Kostura et al., 2018). BFS has been shown to have kinetically fast adsorption rate for phosphorus, achieving equilibrium in only 20 minutes and a maximum retention capacity of between 2.1 mg P g^{-1} and 44.2 mg P g^{-1}, (Oguz, 2005, Oguz, 2004, Sakadevan and Bavor, 1998).

Past amendment studies have also shown that BFS can effectively control TP in wastewater; with up to 96.9 ± 1.7% TP removal reported for a horizontal flow constructed wetland amended with a 15 cm layer of BFS that was treating domestic wastewater with influent TP concentration of approximately 20 mg/L (Andreo-Martínez et al., 2017). In comparison, a 40 cm filter layer of BFS or 1:1 BFS to sand media amendment showed soluble reactive phosphorus removal of 76.3-83.2% and 76.3-88.2% respectively (Li et al., 2018a). Both these studies investigated BFS amendment at relatively high rates; however, at lower BFS rates phosphorus removal is limited. For instance, a 4.8% w/w amendment of BFS in a silt clay loam soil resulted in higher leaching of P than the unamended control, with BFS exporting a mean of 0.64 ± 0.07 mg/L, while the control released only 0.22 ± 0.06 mg/L of dissolved reactive phosphorus (Ahmad et al., 2012).

5.3.3.2. Heavy metal removal: dissolved-phase heavy metals

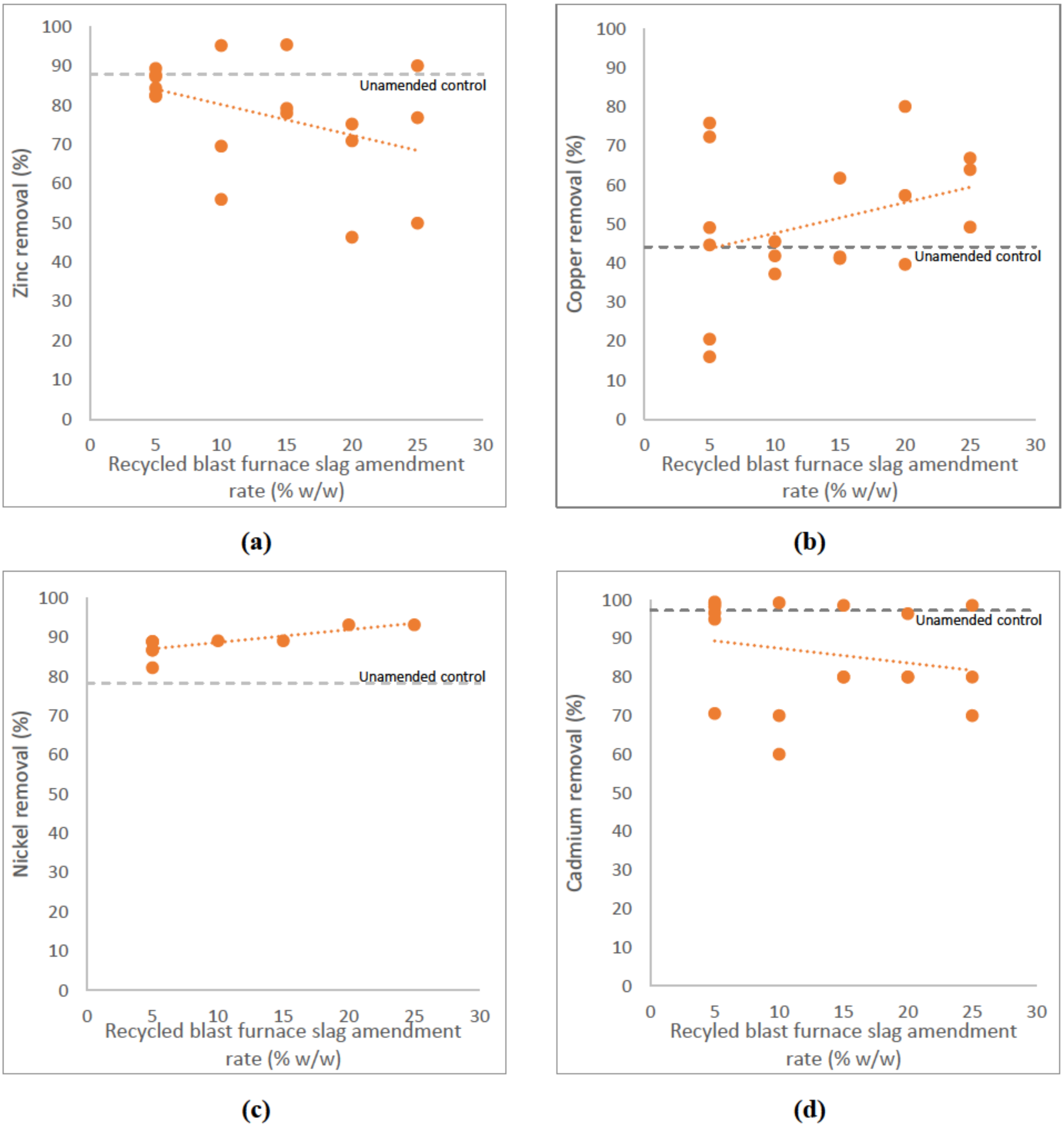


Figure 62: Dissolved-phase heavy metal removal efficiency: (a) zinc, (b) copper, (c) nickel and (d) cadmium with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

There were mixed results for dissolved-phase heavy metal removal performance by the blast furnace slag amended simulation columns (Figure 62), with copper and nickel having moderate and high positive correlations (r = +0.34 and +0.77), while zinc and cadmium had moderate and low negative correlations (r = -0.42 and -0.22). Zeolite amendment tended to enhance the removal performance of both nickel and copper, with Figure 62 showing that copper and especially nickel tended to have an enhanced removal performance in comparison to the unamended control. Median copper removal for the pooled BFS treatment was increased to 47.7%, while nickel had a median removal of 88.9%.

Zinc and cadmium tended to have lower removal than the unamended control (Figure 62); however, the difference between BFS amended biofilters and the unamended control was not statistically significant (p = 0.12 and 0.06 respectively).

The variable metal removal performance meant that there was a mixed result in discharge compliance with the local guidelines. The cadmium and nickel concentrations in the BFS amended columns outflow complied with the 95% ecological protection levels, regardless of amendment rate. Copper was non-compliant with the 90% guideline value for all BFS rates, while zinc complied with the 90% guideline for only the 15 and 30% w/w treatments.

The dissolved-phase heavy metal removal performance by the BFS is pH dependent. As the rate of BFS amendment increases, the BFS (pH 9.6) raises the pH of the sand-based filter fill (pH 6.3) into an alkaline state, which favour copper and nickel removal, over that of cadmium and zinc (Nguyen et al., 2018). Optimal sorption for cadmium and zinc by BFS occurs at a pH 5 and 6 (Gupta et al., 1997), whereas copper and nickel have optimal sorption at pH 8 and 10 (Dimitrova and Mehanjiev, 2000). Hence, the corresponding for the dissolved-phased heavy metals as the pH is shifted into and above the optimal range.

Past laboratory-scale (400 mm internal diameter high-density polyethylene column) studies on loamy sand constructed wetlands have shown a similar non-significant difference in dissolved-phase heavy metal removal with BFS amended (Lucas and Babatunde, 2017).

5.3.3.3. Heavy metal removal: suspended- or-settled-phase heavy metals

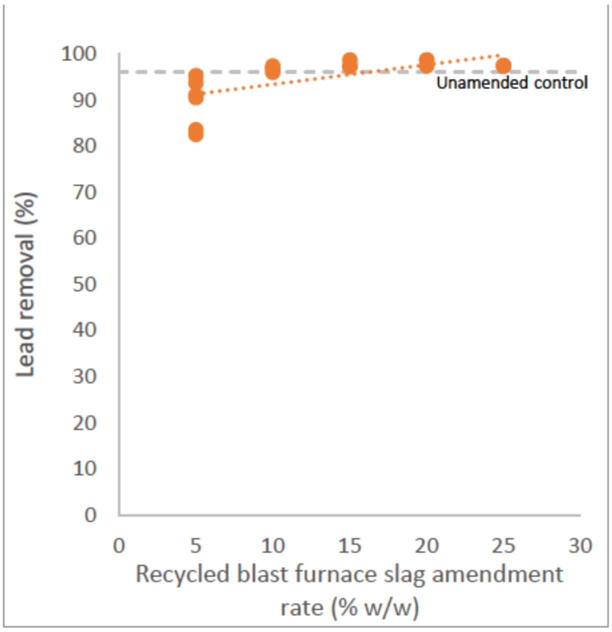


Figure 63: Lead removal efficiency with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

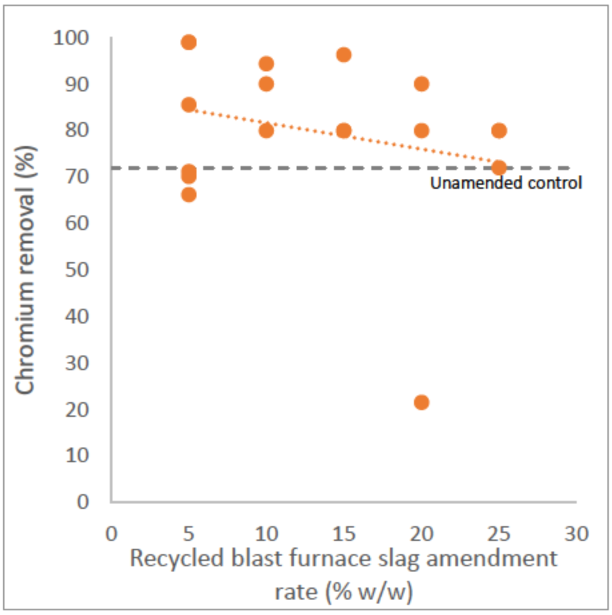


Figure 64: Chromium removal efficiency with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

BFS amendment had a mixed effect on the suspended phase heavy metal removal; with lead removal having a high positive correlation (r = +0.66), while chromium removal had a low negative correlation (r = -0.25) with BFS amendment rate (Figure 64). Figure 64 shows that for BFS amendment rate of ≥10% w/w had lead removal efficiencies which were greater than the unamended control, however, median removal for the pooled treatment of 95.8% was almost identical to the 96.1% median removal of the unamended control. All amendment rate treatments had some chromium removals that surpassed the unamended control, as such the pooled BFS treatment had a median chromium removal of 78.8% which was greater than the 71.8% for the unamended control.

The generally high suspended phase heavy metal removal of greater than 70% by the BFS amendment treatments resulted in median concentrations in the stormwater being reduced to 0.006 and 0.002 mg/L for lead and chromium respectively. Overall, the BFS amended biofilter columns were able to comply with the 95% guideline value for the lead and the 90% discharge level for the chromium. Although some of the BFS rates were not able to fully comply, with the 5% w/w BFS treatment only complying with 90% discharge target for lead, and the 5% w/w BFS treatment was not able to comply to the 90% level for chromium.

BFS has been demonstrated to effectively remove lead from solution, with removal performance of upwards of 98% achievable, through precipitation and complexation with OH^- to form weakly soluble PbOH complexes on the slag surface (Dimitrova and Mehandgiev, 1998). Absorption of both lead and chromium are strongly pH dependent, with lead having optimal removal at higher pH's of between 4 to 6, while chromium was most effectively removed at a rate of 58% at a pH of 1(Srivastava et al., 1997). The pH of the biofilter system therefore favours lead removal over that of chromium, which may explain the differences in correlation between the two suspended-phased heavy metals.

Instead of directly absorbing the Cr (VI), the BFS amendment may have had some influence on the REDOX state of the chromium in infiltrating stormwater. The scientific literature indicates that BFS amendment may aid in immobilization of captured chromium, through reduction of Cr (VI) with sulphur compounds to Cr (III) (Equation 4) (Tae and Morita, 2017, Hassan, 2011).

Equation 4 $$8CrO_4{}^{2-} + 3S^{2-} + 20H_2O \rightarrow 8Cr^{3+} + 3SO_4{}^{2-} + 40OH^-$$

An 80% w/w BFS amendment reduced 98.7% of the Cr (VI) in solution to Cr (III) after seven days contact time (Hassan, 2011). A less profound influence on Cr (VI) reduction would be expected in the BFS amended stormwater biofilter columns, due to the shorter contact time and lower BFS amendment rates than the study mentioned above. The analysis technique (inductively coupled plasma mass spectrometry) employed was unable to distinguish between the chromium redox species. So, the extent of Cr (VI) reduction to the less toxic Cr (III) in the biofilter system was not able to be assessed.

5.3.3.4. Metalloid removal: arsenic

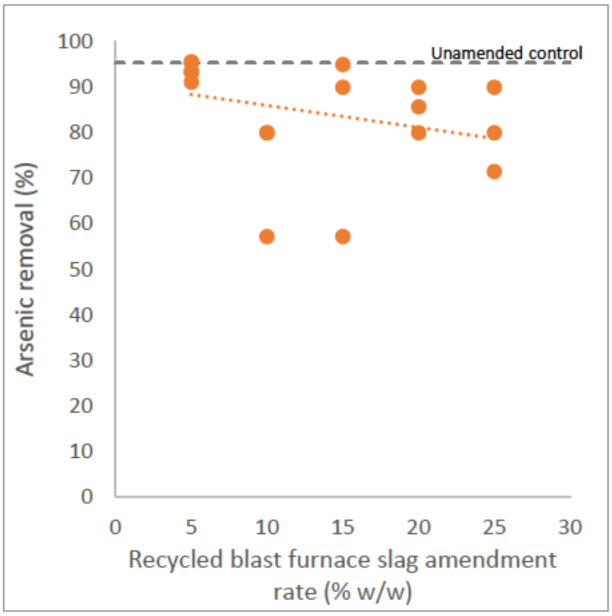


Figure 65: Metalloid arsenic removal efficiency with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

BFS amendment significantly ($p = 0.008$) decreased arsenic removal in comparison to the unamended control, with median removal dropping from 95.3% for unamended control to 70.0% for the pooled BFS amended treatment (Figure 65). Median arsenic concentration discharged from the BFS amended biofilter columns increased to 0.002 mg/L compared to the 0.001 mg/L for the unamended control. Regardless, all BFS amended rate treatments still discharged arsenic to levels that complied to the 95% ecological protection guideline.

Higher rates of amendment also tended to have lower arsenic removal performance, with there being a low negative correlation ($r = -0.31$) between arsenic removal and BFS amendment rate.

Reduced performance by the BFS amended biofilter is mostly related to BFS arsenic removal capacity being highly pH dependent. BSF has a 70% relative adsorption at pH 7, but at a pH 8 electrostatic repulsion of $HAsO_4^{2-}$ ion means there is a rapid decline in arsenic removal to practically 0% adsorption (Hua et al., 2015). Furthermore, at a pH 7, BFS has a competitively high maximum sorption capacity of 0.82 mg/g and 4.04 mg/g for As (III) and As (V) respectively, compared against a variety of alternative waste industrial by-products (Lekić et al., 2013).

The BFS used had a pH of 9.6, therefore, as the rate of BFS amendment increase, the BFS would exert a greater influence upon fill pH, shifting the biofilter soil pH from neutral were greatest arsenic sorption occurs to more alkaline were absorption is limited. The pH-dependency of arsenic removal by BFS explains the negative correlation and the consistently high performance by the 5% w/w BFS amendment (Figure 65).

5.3.3.5. Hydrological performance

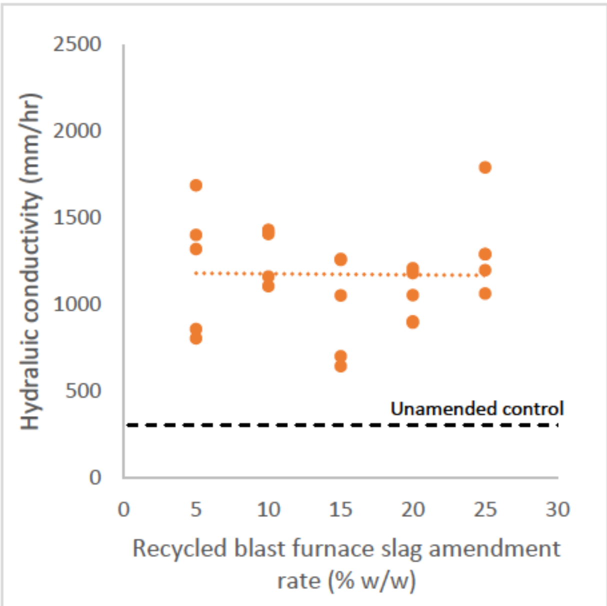


Figure 66: Hydraulic conductivity of a sand-based filter fill amended with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

Blast furnace slag amendment consistently and significantly ($p < 0.001$) increased the hydraulic conductivity to above that of the unamended control (Figure 66). There was no significant ($p = 0.16$) differences in hydraulic conductivity between BFS amendment rates and a very low negative correlation ($r = -0.02$) between amendment rates and hydraulic conductivity. Overall, the pooled BFS amendment increased hydraulic conductivity to a median of 1196.7 mm/hr, which was a 295% increase in comparison to the unamended control.

The granular blast furnace slag had a coarse grade, with 82% of particulates having a size greater than 425 µm, with the greatest particulate fractions being the 850-425 µm fractions (38.5%), followed by the 1-2 mm (27.6%) (Table 36 in appendix). The loose packing of these coarse particles most likely explains the shift in PSD towards the large particulate fractions with BFS amendment, and associated formation of greater inter-particulate spaces would explain the increased flow rates observed in the BFS amended fills.

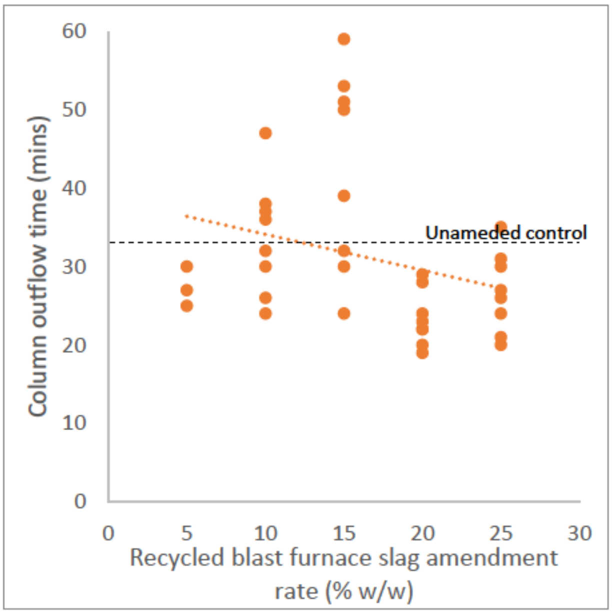


Figure 67: Column outflow time with BFS amendment showing trend with BFS dosage (dotted line) against unamended control (dashed line)

Blast furnace slag amendment of the biofilter columns resulted in a general decreasing of outflow time (Figure 67), with a low negative correlation (r = -0.29) and a significant (p = 0.01) difference in discharge times between the rate treatments. Due to large variations in outflow times for each BFS amendment rate (Figure 67), there was no significant (p = 0.84) difference in discharge times between the unamended control and the pooled BFS treatment, or between the 5% or 25% w/w BFS amendments (p = 0.59 and 0.57 respectively).

The subsurface flow rate of the BFS amended columns results from two factors:

i. **High hydraulic conductivity of the BFS** – The BFS fill alone had a hydraulic conductivity of 1359 mm/hr, which was greater than the unamended control, as such the discrete BFS amendment layer had a higher hydraulic conductivity to that of the rest of the filtration layer fill which promoted the faster subsurface flow rates. This explains the general declining trend in column outflow time with BFS amendment.

ii. **Moderating effect of total column length** – the BFS layer only represented a small fraction of the total column length, so despite the higher hydraulic conductivity in the BFS, the hydraulic conductivity and subsurface flow rate remain similar in the rest of the column for both the rate treatments and the unamended control. This explains the similarity in subsurface flow rate and absence of significance observed between the BFS amended and unamended control.

5.3.4. Zeolite

5.3.4.1. Nutrient removal: nitrogen and phosphorus

5.3.4.1.1. Total Kjeldahl Nitrogen

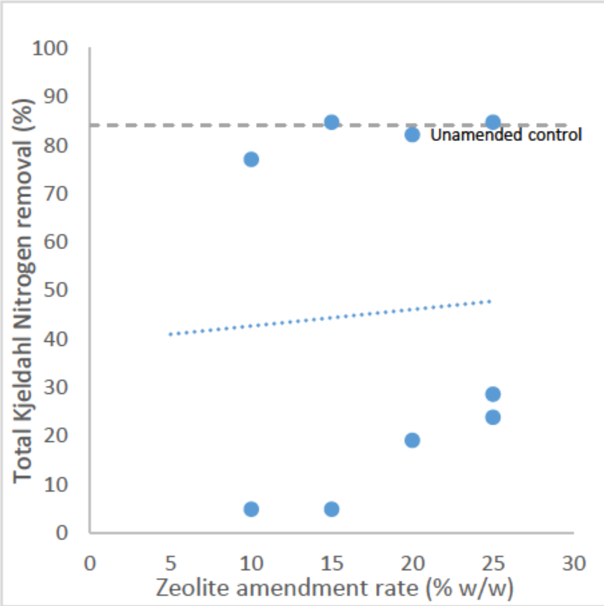


Figure 68: Total Kjeldahl Nitrogen (TKN) removal efficiency with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

Zeolite amendment tended to decrease TKN removal performance in comparison to the unamended control, with median removal efficiency decreased from 84.1% for the unamended control to 28.6% for the pooled zeolite amended treatments (Table 14, and Table 35 and 37 in appendix). The difference between the two treatment was however statistically not significant ($p = 0.37$), as there was a large degree of variation in both groups. TKN removal was supressed regardless of the zeolite amendment rate, as there was a very low positive correlation ($r = +0.06$) for TKN removal with zeolite amendment (Figure 68).

A greater positive influence by zeolite amendment on the stormwater biofilter simulation columns NH_4^+ removal was expected, given that the scientific literature often highlights zeolite's high cation exchange capacity for NH_4^+ removal (Cyrus and Reddy, 2011, Du et al., 2005, Sprynskyy et al., 2005). An Australian zeolite, which was chemically identical to the one used in this study, was shown to have a maximum absorptive capacity of 13.32 g NH_4^+ per kg when exposed to a 500 mg/L NH_4^+ solution (Millar et al., 2016).

Zeolite has been recommended for used in media-based stormwater control measures (Khorsha and Davis, 2017). A 5% and 10% w/w clinoptilolite amendment of an Inceptisol (coarse loam, non-acidic paddy soil) resulted in a significant ($p = 0.001$) increase in the retention of nitrogen (primarily NH_4^+) in the paddy soil, with batch experiments of zeolite alone showing that it was capable of a mean removal of 61% of NH_4^+-N (Lim et al., 2016a).

Unlike the scientific literature, a positive influence of zeolite amendment was not seen for TKN removal, which was most likely due to limited hydraulic contact time between the zeolite amended fill and the influent stormwater. The zeolite amendment may have inadvertently reduced contact time, by increasing hydraulic conductivity in the filter fill, in comparison to the unamended control (see the hydrological performance in section 3.4.5). The literature shows that zeolite's NH_4^+ removal efficiency is improved by 23% when contact time is increased from 10 to 47 minutes (Khorsha and Davis, 2017).

5.3.4.1.2. Nitrate and nitrite-nitrogen

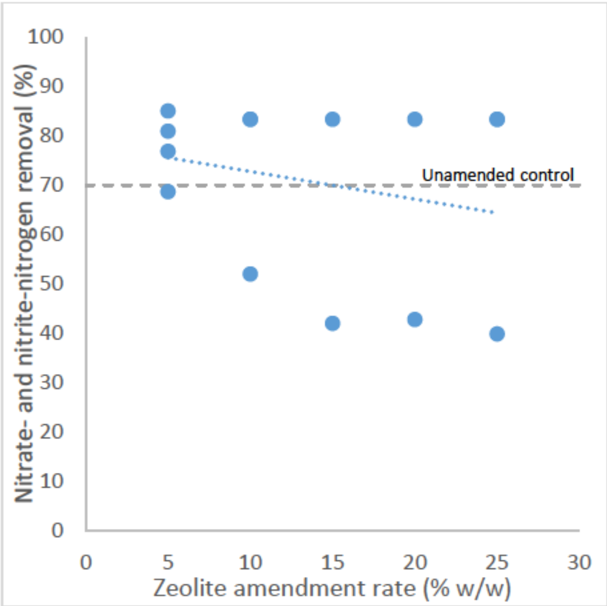


Figure 69: Nitrate- and nitrite-nitrogen (NOx) removal efficiency with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

The removal of NOx by the zeolite amended biofilter simulation columns generally decreased with an increased rate of amendment (Figure 69), with there being a low negative correlation ($r = -0.25$). Low rates of zeolite amendment enhanced the NOx removal performance of the biofilter system, with the 5% w/w amendment treatment having a median of 78.9% which surpassed the unamended control. Overall, the pooled zeolite treatment increased median NOx removal to 82.1%, which was greater than the 70.0% removal for the unamended control. However, the difference between the treatments was not statistically significant ($p = 0.1$), as there was a great deal of variation in both the zeolite and control datasets.

The literature shows that natural zeolite has limited sorption capabilities for negatively charged nitrogenous pollutants; for instance, under optimal batch sorption condition of 4 g adsorbent dosage, 60 min contact time, reaction temperature of 20°C, pH 5.5 and the initial NO_3 concentration of 100 mg/L; zeolite only had a maximum sorption of 8.7% (Asl et al., 2016).

This limited anion sorption capability explains the negative correlation with zeolite amendment, as zeolite amendment increases there is less capacity for NOx removal, with the sand-based filter fill performing the bulk of nitrate removal.

5.3.4.1.3. Total Nitrogen

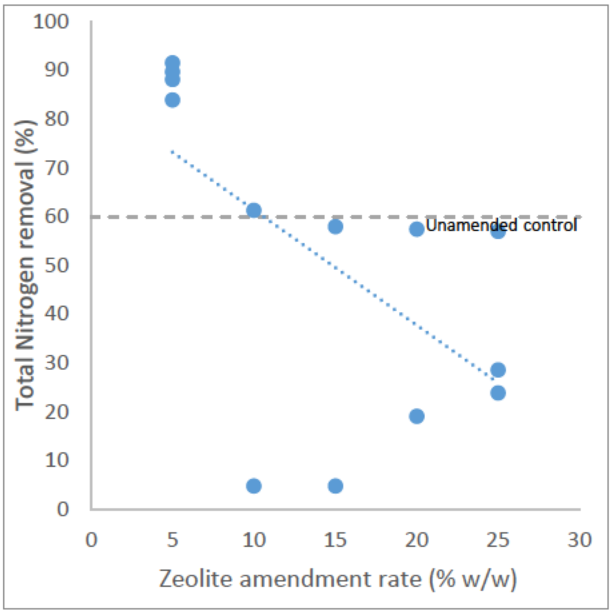


Figure 70: Total Nitrogen (TN) removal efficiency with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

Figure 70 shows that a 5% w/w zeolite amendment had enhanced TN removal in comparison to the unamended control, but as amendment rate increase TN removal performance decreased, as indicated by a high negative correlation ($r = -0.60$) between zeolite amendment and TN removal. The 5% w/w treatment had the highest removal performance with a median of 88.9% which surpassed the unamended control and the City's 45% reduction target. Amendment rates of >10% w/w had lower removal performance than the unamended control and had TN removal efficiencies that were below the DCP target. Overall, the pooled amended treatment had a median removal of the 57.4%, which was just below that of the unamended control, and was compliant with the City's reduction target.

5.3.4.1.4. Total Phosphorus

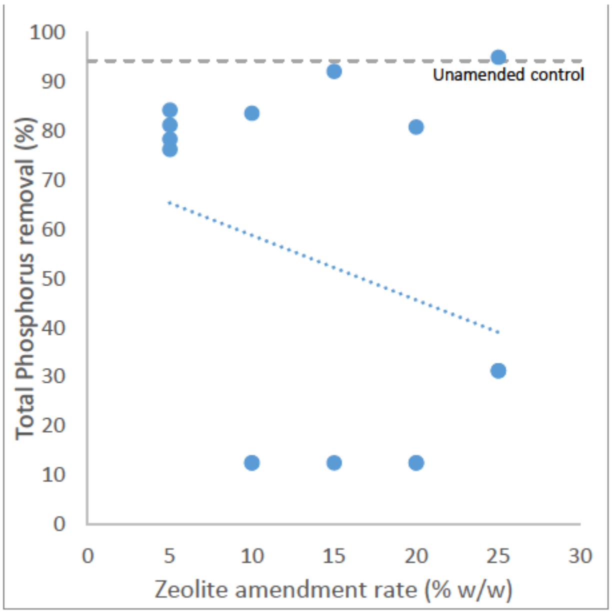


Figure 71: Total Phosphorus (TP) removal efficiency with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

There was a large degree of variation in TP removal, with amendment tending to lower removal performance in comparison to the unamended control. High amendment rates tended to lower removal, as indicated by a low negative correlation ($r = -0.29$) between the reduction results and amendment rate (Figure 71). There was a median decrease in removal from 94.2% for the unamended control to 76.2% for the pooled amendment treatment; however, the difference between the two groups was not significant ($p = 0.46$). Overall, median TP removal by the pooled zeolite treatments complied with the City's reduction targets, of which only the 5% w/w rate treatment had TP removal which was consistently greater than the 45% target.

Zeolite's dominate adsorption mechanism is cation exchange, as phosphorus is predominately found as an anion (PO_4^{3-}), zeolite has practically no phosphorus absorptive capacity, with a 1 g zeolite to 30 mL of a 1000 mg/L P solution only adsorbing 3.6% after 48 hours of contact (Lim et al., 2016a). Zeolite's limited phosphors sorption capacity explains the general negative impact on TP, with the zeolite replacing sandy loam fractions within the filter layer which would otherwise be removing phosphorus. Hence, the system has less removal capacity and TP removal performance decreases as a result.

5.3.4.2. Heavy metal removal: dissolved-phase heavy metal

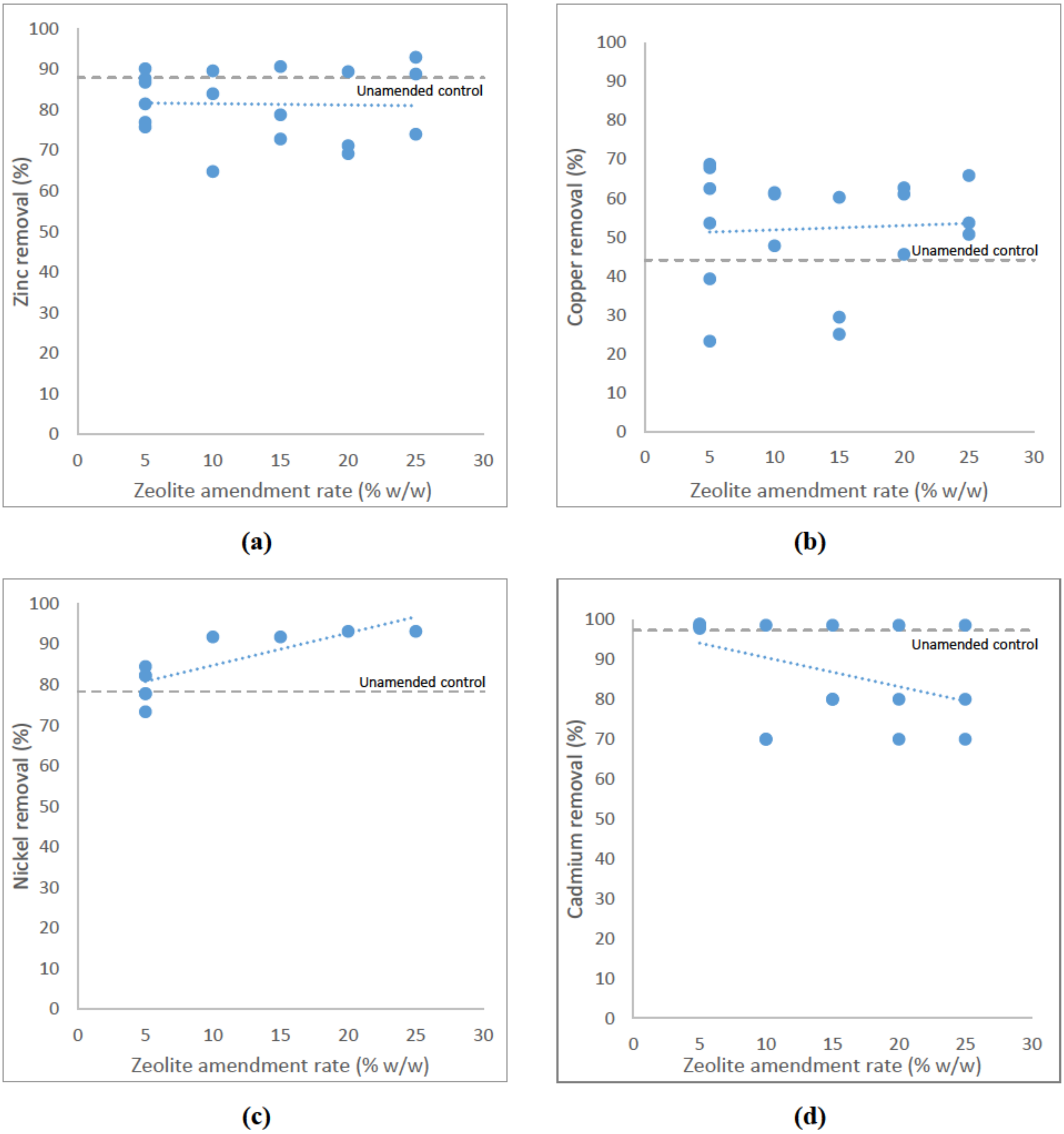


Figure 72: Dissolved-phase heavy metal removal efficiency: (a) zinc, (b) copper, (c) nickel and (d) cadmium with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

There were mixed results for the removal of dissolved-phase heavy metals by zeolite amended biofilters with the zeolite amendment enhancing the removal of some of the metals and not substantially affecting others with their removals being equivalent to the unamended control (Figure 72).

An improvement in copper and nickel removal performance was with zeolite amendment, with the amended columns increasing removal of these metal to above that of the unamended control. Median copper removal was enhanced from 44.1% for the unamended control to 57% for the pooled zeolite amended treatment, while median nickel removal increased to 83.3% from the 78.3% of the unamended control. Overall, higher amendment rates tended to promote greater removal, with Figure 72 showing a weak negative correlation for copper ($r = +0.06$) and a high positive correlation for nickel ($r = +0.81$).

The zeolite amended biofilters had statistically ($p = 0.61$ and 0.28 respectively) equivalent cadmium and zinc removal to that of the unamended control, with the median removal of 98.1 and 82.8% which were slightly lower than the median removal for the unamended control. Rate of zeolite amendment tended to have limited influence upon the removal of these metals, with zinc having a very weak negative correlation (-0.03). Cadmium showed a moderate negative correlation ($r = -0.45$), but this arose due to a consistently high removal by the 5% w/w rate treatment (Figure 72d), if 5% w/w treatment is excluded from analysis, then cadmium had a very low positive correlation ($r = +0.06$) alike that of copper (Figure 72).

Overall, the generally high removal performance by the zeolite amended simulation column meant that concentration of dissolved-phase metals discharged conformed to ANZG (2018) ecological protection limits, with the exception of copper. Nickel and cadmium levels discharged by the zeolite amended columns complied to the 95% guideline. Zinc concentrations discharged collectively conformed to the 90% guideline; however, the 5 and 20% w/w zeolite amendment treatments did not comply to 90% guideline, although the 20% w/w zeolite amendment treatment was only just above guideline value at 0.072 mg/L.

It was generally expected that the zeolite amendment should have a positive influence on dissolved-phase heavy metal removal, as the zeolites high CEC (19 cmol/kg) should have contributed to greater adsorption of the positively charged metal ions. Past research generally reports that clinoptilolite is an effective absorbent for metal ions, (Damian et al., 2013), showing a maximum absorbance of 39.7 mg/g for nickel, 24 mg/g for copper, and only 0.5

mg/g for zinc and cadmium at low solute concentrations similar to that used in the synthetic stormwater (Kyzioł-Komosińska et al., 2015, Irannajad et al., 2016, Hannachi et al., 2012).

There is a preferential selection in zeolite sorption in multi-metal solutions, with a reduced absorptive capacity of 87%, 38% and 53% for zinc, cadmium, and copper respectively, between a single and multiple metal species solutions (Li et al., 2019). Preferential sorption by the zeolite is most likely why nickel shows a positive correlation with the amendment, as the zeolite with its high capacity and preferential sorption effectively removes the nickel from the synthetic stormwater, while zinc and cadmium have a weak relationship with amendment, as the zeolite does not as readily adsorb these metal ions. These results suggest that zeolite amendment has potential to effectively capture dissolve phase metals from the stormwater, which could potentially enhance biofilter metal removal performance and extend service life of the system.

5.3.4.3. Heavy metal removal: suspended- or-settled-phase heavy metals

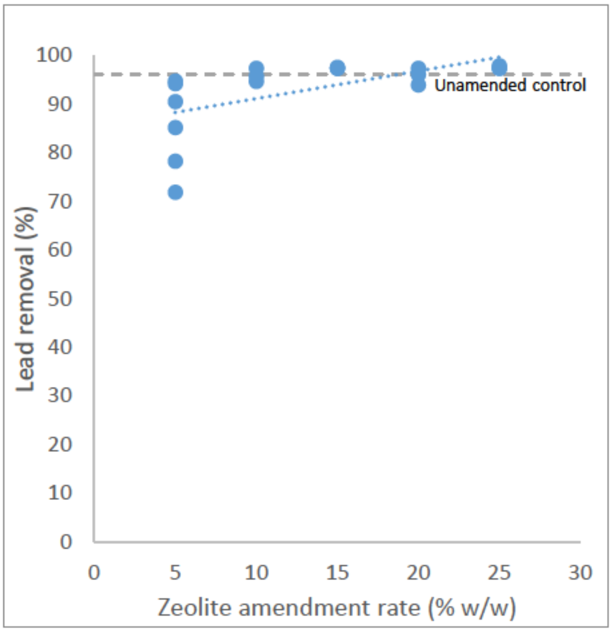


Figure 73: Lead removal efficiency with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

Zeolite amended tended to increase lead removal performance, with there being a significant ($p = 0.01$) difference and a moderate positive correlation ($r = +0.59$) for lead removal efficiency between zeolite amendment rates (Figure 73). The amended biofilter simulations had equivalent removal to that of the unamended control, with there being no significant ($p = 0.61$) difference between these two treatments.

The amended biofilter columns had a high median removal efficiency of 95.8% which reduced lead concentration to below the 95% ecological protection target, for all rate amendment except for the 5% w/w that had a median discharge concentration of 0.023 mg/L, which conformed to the 90% protection target.

A positive relationship between lead removal and zeolite amendment was expected, considering zeolite has a strong affinity for lead, as clinoptilolite has been shown to have a maximum absorbance of 78-92.5 mg/g from a 100-400 mg/L lead solution (Stojakovic et al., 2017, Li et al., 2019, Kragović et al., 2012). Also, unlike the dissolve-phase heavy metals, lead is effectively removed by zeolite regardless of the presence of competitive metal ion species with only a 2% reduction between the single and multi-species metal solutions, (Li et al., 2019).

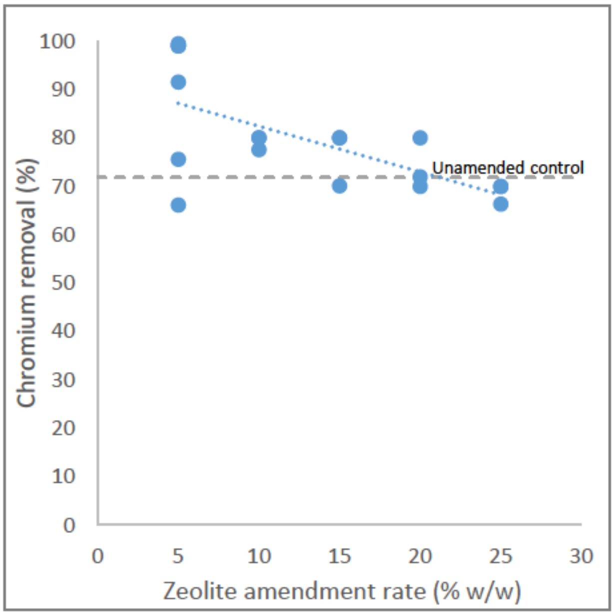


Figure 74: Chromium removal efficiency with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

Zeolite amended biofilter columns tended to have equivalent to greater chromium removal to that of the unamended control, with zeolite having a high negative correlation (r = -0.65) for chromium removal with amendment rate (Figure 74). Amendment rates of <25% w/w all had chromium removal efficiencies that were greater than the unamended control, which meant that median removal performance by the pooled zeolite treatment of 78.8 was greater than median 71.8% of the unamended control. Overall, the pooled zeolite amendment biofilters reduced chromium concentration to levels which conformed to the had chromium removal performance that complied with the 0.006 mg/L ANZG (2018) 90% protection target (Table 35 in appendix).

Zeolite primarily has a cation exchange mechanism for the sorption of metals; therefore, it has minimal affinity for the oxyanion chromate (CrO_4^{2-}). For instance, a natural zeolite was shown to be only capable of absorbing about 5% of Cr (VI) from a 1 mg/L dichromate solution (Kucic et al., 2018). Therefore, as amendment rate increases, the zeolite displaces filter fill (humic and clay materials) which were otherwise absorbing Cr (VI), and hence the decline in Cr (VI) removal with increased amendment (Figure 74).

5.3.4.4. Metalloid removal: arsenic

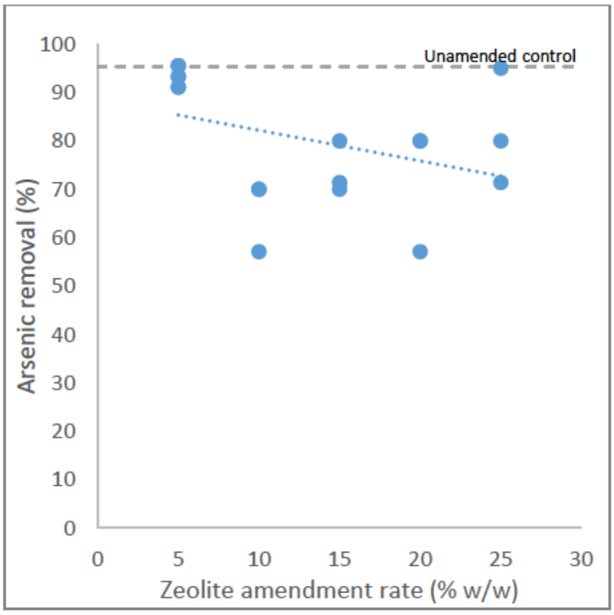


Figure 75: Metalloid arsenic removal efficiency with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

Zeolite amendment had a negative influence on arsenic removal showing a low negative correlation ($r = -0.38$) between zeolite amendment and As (III) removal efficiency (Figure 75). Furthermore, there was a significant ($p = 0.003$) decrease in As (III) removal efficiency between the pooled zeolite amendment and unamended control (Table 14 and table 35 and 37 in appendix). Regardless, all amended rate treatments still discharged arsenic to levels that complied to the 95% ecological protection guideline.

Due to the zeolite's negative structural charge, zeolites have a negligible affinity for exchange of arsenic oxyanions (Figueiredo and Quintelas, 2014), with clinoptilolite zeolite showing a maximum As (III) sorption capacity of 0.5 mmol/kg (Li et al., 2007). Similar to the other anion pollutants, zeolite had a negligible capacity for arsenic adsorption and so amendment likely reduces the overall biofilter systems removal capacity, as zeolite displaces biofilter media that would otherwise be actively absorbing arsenic.

5.3.4.5. Hydrological performance

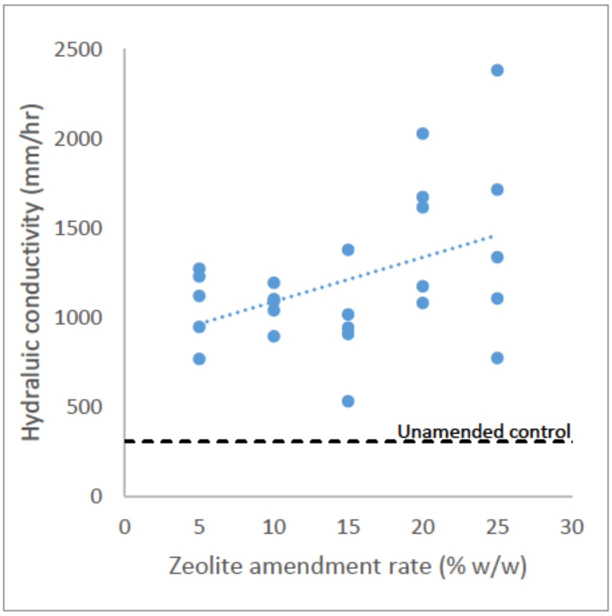


Figure 76: Hydraulic conductivity of a sand-based filter fill amended with zeolite at rates between 5 to 25% w/w. The dashed line represents the median removal for the unamended control

There was a moderate positive correlation (r = +0.44) between fill hydraulic conductivity and zeolite amendment rate. Regardless of amendment rate, there was a consistent and significant ($p < 0.001$) increase in hydraulic conductivity with zeolite amendment in comparison with the unamended control, with pooled zeolite amendment increasing median hydraulic conductivity to 1104.6 mm/hr, which is an increase of 264% upon the unamended control (Figure 76).

Changes in hydraulic conductivity through zeolite amendment has largely been contributed to zeolite modifying soil particles size distribution, bulk density and porosity (Nakhli et al., 2017, Xiubin and Zhanbin, 2001). For instance, a 30% w/w coarse zeolite (1-8mm grade) amendment significantly increased saturated hydraulic conductivity of an engineered biofilter media by 46% (Liu and Fassman-Beck, 2016).

Zeolite amendment altered the filter fills PSD, with a general decrease in the percent composition of the amended filter fill 425 to >75 µm fractions and a corresponding general increase in the course fractions greater than 425 µm (Table 36 in appendix).

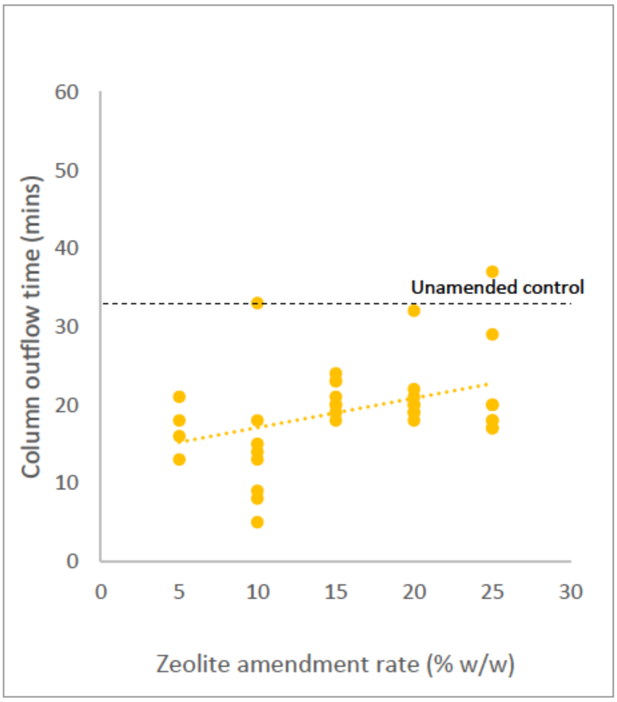


Figure 77: Column outflow time with zeolite amendment showing trend with zeolite dosage (dotted line) against unamended control (dashed line)

There was a significant (p = 0.002) decrease in outflow times by zeolite amendment biofilter columns compared to the unamended control, with the zeolite amendment reducing discharge times by 42% to a median of 19 minutes (Figure 77). Alike that of the hydraulic conductivity results, there was a moderate positive correlation (r = +0.48) between column outflow time and zeolite amendment rate.

Similar to the BFS results, column outflow time was a consequence of two competing variables, which include:

i. **Higher hydraulic conductivity of the zeolite** – The zeolite fill alone had a hydraulic conductivity of 828 mm/hr, which was greater than the unamended control, with the fast conductivity likely contributing to the decline column outflow observed.
ii. **Water holding capacity of the zeolite** – zeolite has been shown to have considerable water holding capabilities, related to their expansive internal surface areas (Nakhli et al., 2017). The retention of water within the zeolite molecular lattice causes the zeolite structure to slightly swell, which may decrease flow through the biofilter system (Bruch et al., 2014). These hydrological properties would have been most prominent in fills with a high rate zeolite amendment; hence, the slower discharge times in the higher zeolite amendments compared with the lower amendment rates.

5.3.5. Biochar

5.3.5.1. Nutrient removal: nitrogen and phosphorus

5.3.5.1.1. Total Kjeldahl Nitrogen

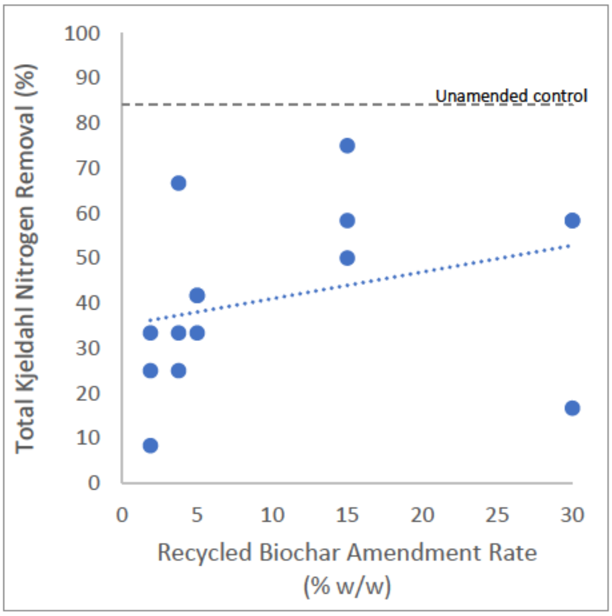


Figure 78: Total Kjeldahl Nitrogen (TKN) removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

Figure 78 shows that the amount of TKN removed generally increased with the amount of gypsum added, as indicated by a low positive correlation ($r = +0.33$), however, the biochar amended biofilters all had lower removal performance than the unamended control. Overall, pooled biochar amendment treatment significantly ($p = 0.001$) lowered TKN removal in comparison to the unamended control, with a median drop in removal from 84.1% to 41.7%.

Biochar has been demonstrated to have some capacity for ammonium removal through a cation exchange mechanism (Ding et al., 2010, Li et al., 2018b), but this capacity is dependent upon the biochar's feedstock properties and pyrolysis temperature (Li et al., 2018b).

Generally, biochar amended biofilter simulation columns (Figure 78) had removal performance that was comparable to past amendment studies that demonstrated similar 50-60% removal for rates of 15% and 30% w/w (Nabiul Afrooz and Boehm, 2017). Whereas, the median TKN removal of 47.2% for the 3.76 to 15% w/w biochar treatments was similar to the lower limits of the 50-90% NH_4^+ removal reported for a 4% and 10% w/w wood-derived biochar (500-550°C) amendment of a sand-based biofilter media (Tian et al., 2016, Tian and Liu, 2017).

The lower TKN removal performance than the literature most likely relates to the difference in biochar material employed. The literature studies tended to employ low-temperature biochars (500-550°C), whereas in this thesis a high-temperature (750°C) pyrolysed biochar was used. Higher temperature biochars tend to have lower CEC and NH_4^+ removal, due to the stripping of OH^- groups on the biochar surface during pyrolysis which reduces cation absorption sites (Cheng et al., 2018a, Li et al., 2018b).

5.3.5.1.2. Nitrate- and nitrite-nitrogen

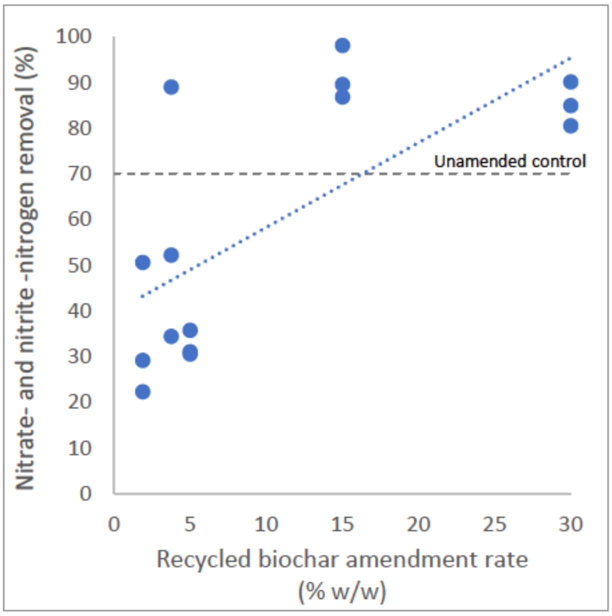


Figure 79: Nitrate- and nitrite-nitrogen (NOx) removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

There was a high positive correlation ($r = +0.71$) between NOx removal and biochar amendment (Figure 79), as there was a significant ($p = 0.03$) difference in removal performance between the rate treatments. Rates above 15% w/w significantly ($p = 0.03$) enhanced NOx removal in comparison to the unamended control, while the ≤5 % w/w rates had lower removal efficiencies than the control, but this difference was not statistically significant ($p = 0.27$). This is an important finding relevant to the City's field units where high rates of biochar could aid in removal of nitrogen oxides from stormwater flows which is desirable in the interests of receiving water quality.

Biochars' affinity for adsorption of NOx is dependent upon pyrolysis temperature; for example, biochar produced at 400°C had practically zero NO_3^- adsorption, while at 800°C adsorption was approximately 400 mg-NO_3^- kg^{-1} (Kameyama et al., 2012). Low-temperature biochars (<600°C) have an abundance of negatively charged and acidic functional groups on its surface of the biochar, which limits the capacity for sorption and retention of negatively charged inorganic nitrogenous compounds (Li et al., 2018b, Zhang et al., 2017a, Yang et al., 2017a, Zhao et al., 2017).

High pyrolysis temperatures tend to form base functional groups, which are most likely responsible for the improved NO_3^- adsorption by high temperature biochars (Kameyama et al., 2012, Yao et al., 2012, Zhao et al., 2017). The high temperature biochar used in the amendment of the column simulations provided optimal NOx sorption, as per the above scientific literature, and this may explain the high positive correlation observed between NOx removal efficiency and biochar amendment rate.

5.3.5.1.3. Total Nitrogen

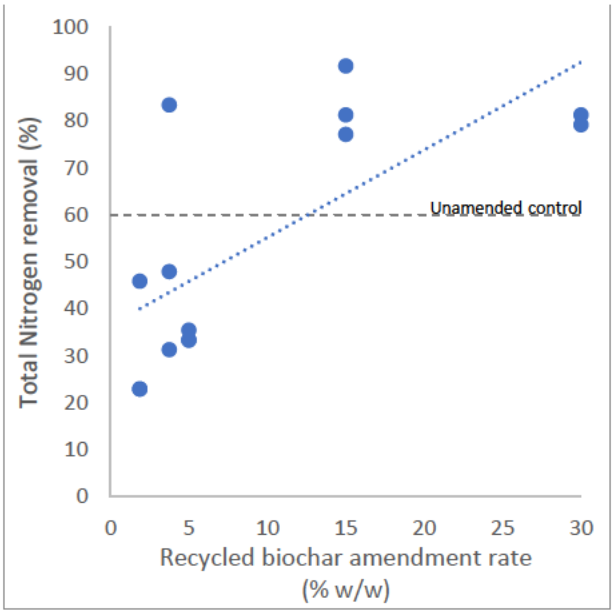


Figure 80: Total Nitrogen (TN) removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

The distribution of the TN removal (Figure 80) was similar to that of the NOx (Figure 79), which highlights that the dosing stormwater tended to be high in nitrates (as it was composed of nitrate-based chemicals). There was a high positive correlation ($r = +0.71$) between TN removal efficiency and amendment rate, with amendment rates above 15% w/w having an enhanced removal performance in comparison to the unamended control (Figure 80).

At the higher rates, the biochar amended biofilters removal performance of greater than 77% readily complied with the City's TN reduction target. In comparison, lower levels of <5% w/w had removal an efficiency that was less than 45% removal target, which was most likely due to the low removal performance seen for the both the TKN and NOx nutrient parameters. These results indicate that the application of biochar has some capacity to improve nitrogen removal from stormwater in the biofilter system especially at higher amendment rates.

5.3.5.1.4. Total Phosphorus

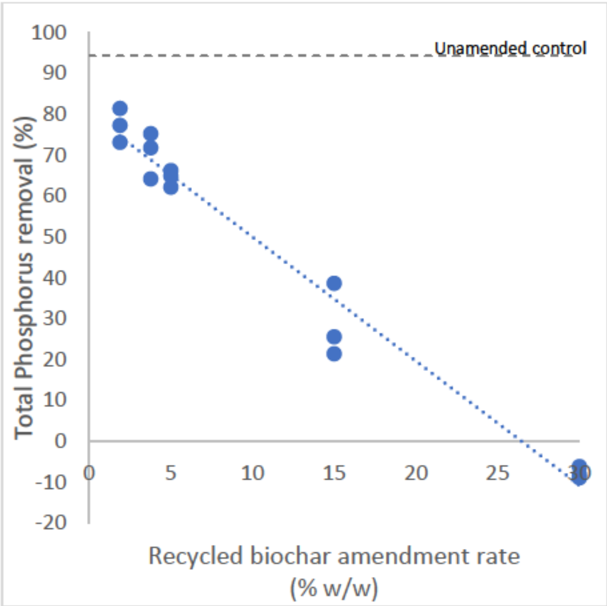


Figure 81: Total Phosphorus (TP) removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

Biochar amendment had a rate-dependent effect upon TP removal of the biofilter simulation columns, having a very high negative correlation (r = -0.99) between TP removal and amendment rate (Figure 81). At rates of <5% w/w, there was a high median removal of 72%, which complied with the City's DCP targets (Table 1), while the removal performance below ≥15% w/w all failed to meet the City's reduction target (Figure 81). As a result of the progressive decline in TP removal (Figure 81), the biochar amended biofilter columns collectively had significantly ($p < 0.001$) lower TP removal performance than the unamended control.

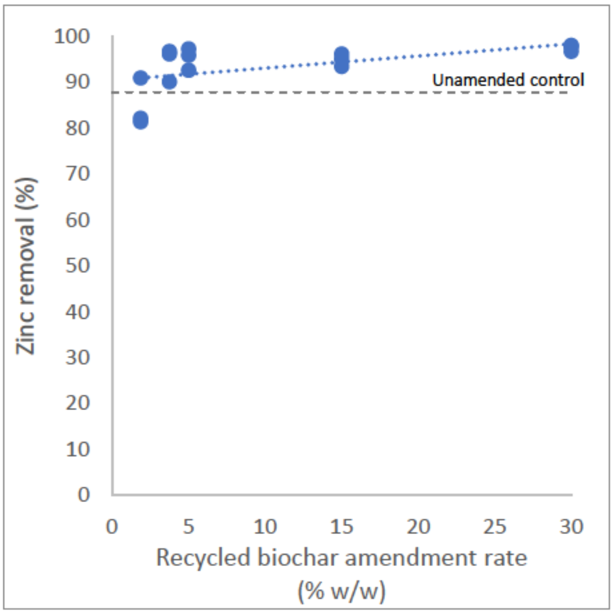
Biochar's poor TP retention properties have been linked to the concentration of phosphorus in the biochar. During pyrolysis, many chemical species such as C, N, S, O and H are volatilized from the biomass feedstock, but phosphorus is retained, as there are no gaseous pathways for phosphorus loss (Sun et al., 2018). In addition, higher pyrolysis temperatures also tend to lead to increased phosphorus levels, through the greater volatilization of the other chemical species (Zhao et al., 2017).

Chemical testing showed that the biochar used in this thesis research had an initial phosphorus concentration of 690 mg/kg (Table 11). However, this level was much lower than some plant-based biochars reported in the literature; for instance, a grape pomace derived biochar pyrolyzed at 500°C had upwards of 6930 mg P/kg (Manolikaki et al., 2016).

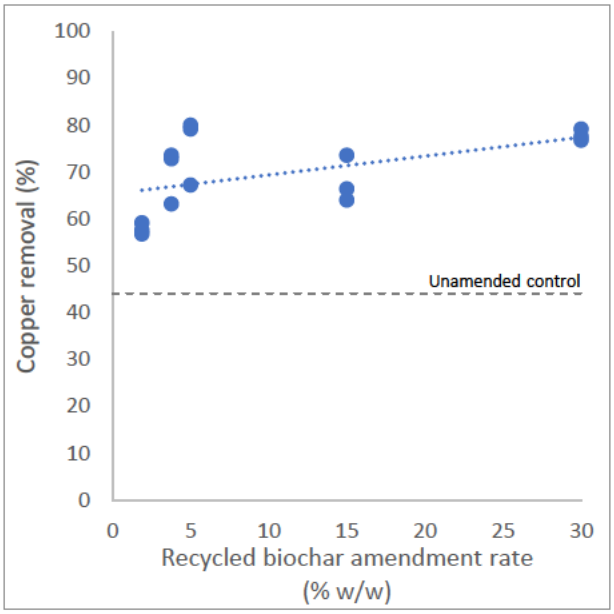
Biochar contains a variety of phosphorus species, with plant-based biochars produced at high temperatures of >500°C predominately contain the readily soluble and reactive pyrophosphate ($P_2O_7^{4-}$) and orthophosphate (PO_4^{2-}) species (Uchimiya and Hiradate, 2014). Higher temperature biochars tend to leach a considerable amount of TP, with upwards of 10% of the available phosphate being leachable (Manolikaki et al., 2016).

Biochar amendment, therefore, tended to increase the phosphorus concentration to above 16 mg/kg of the unamended sand-based filter fill, and the available phosphorus added was in a form which was readily leached, hence the progressive decline in phosphorus removal efficiency seen in Figure 81.

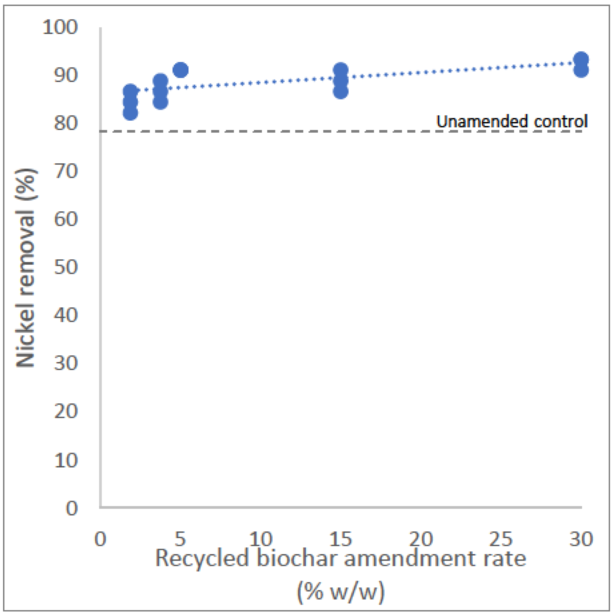
5.3.5.2. Heavy metal removal: dissolved-phase heavy metals



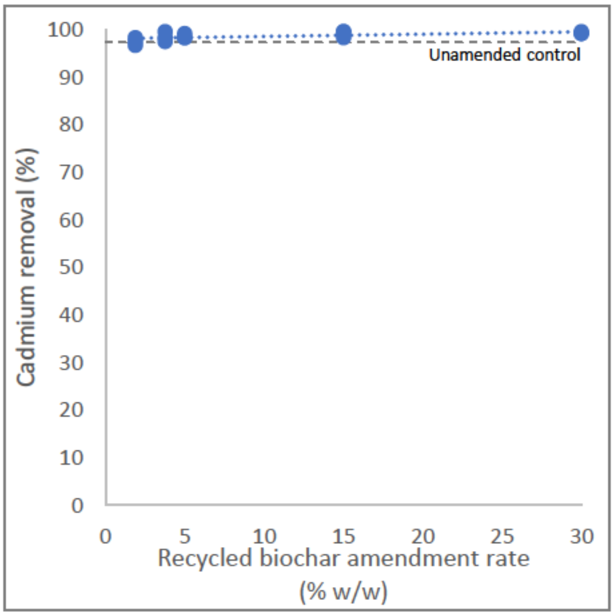
(a)



(b)



(c)



(d)

Figure 82: Dissolved-phase heavy metal removal efficiency: (a) zinc, (b) copper, (c) nickel and (d) cadmium removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

All dissolved-phase heavy metals had a positive relationship between biochar amendment rate and metal removal efficiency (Figure 82), with a high positive correlation for nickel ($r = +0.66$) and a moderate positive correlation for zinc, copper and cadmium ($r = +0.54$, $+0.53$ and $+0.58$ respectively). In all cases, biochar amendment enhanced metal removal to above that established by the unamended control, which meant that this efficient removal performance resulted in median discharge concentrations (Table 35 in appendix) conforming with the 95% ecological protection guideline, with the exception of copper which did not comply with the 90% ANZG (2018) default guideline value.

Biochar amendment significantly ($p = 0.03$) enhanced the biofilter's cadmium removal performance in comparison to the unamended control, with median removal increase to 97.3%. Biochar has been demonstrated to be an effective absorbent for cadmium (Cui et al., 2016, Wang et al., 2018b, Zhou et al., 2018); for instance, a 700°C bamboo biochar sorbed upwards of 74.39 mg/g of cadmium within two minutes of contact time through a π electrons coordination mechanism (Wang et al., 2018b).

Copper had the lowest removal of any of the dissolved-phase heavy metals (Figure 82), however biochar amendment still significantly ($p < 0.001$) enhanced copper removal performance, with median removal increasing to 72.8% for the pooled biochar amended treatment, in comparison to the 44.1% for the unamended control.

Increased carbon fraction within the filtration layer most likely explains the enhanced copper removal observed, as copper ions tend to effectively bind to organic structures on the surfaces of the biochar particulates (Chen et al., 2007, Alam et al., 2018). The biochar had the highest percentage of organic carbon (9.5%) of any of the amendment materials (Table 34 in appendix), so the application of the biochar increased the availability of organic carbon in the filtration layer to above that of the unamended filter fill.

Lower copper removal in comparison to the other heavy metals may be due to the effect that pyrolysis temperature has on biochar's copper sorption capacity. High pyrolysis temperatures tend to strip oxygen-containing functional groups on the surface of the biochar which is key for copper adsorption, and creates greater aromatic and carbonate functional groups that favour the retention of other metals like lead and cadmium (Zhou et al., 2018). Despite the unfavourable pyrolysis conditions, high-temperature biochar can still have some capacity for copper sorption; for instance, a 600°C straw derived biochar had a maximum adsorption capacity of 42.1 mg/g (Park et al., 2017). Latent copper sorption capacity by the high pyrolysis temperature biochar may be equivalent or marginally higher to that of the sand-based filter fill, which would explain the positive correlation and increased removal performance with biochar amendment when compared against the unamended control.

The biochar amended stormwater biofilter simulation columns had a significant ($p = 0.004$) increase in zinc removal in comparison with the unamended control; with median removal increasing from 87.9% for the unamended control to 95.9% for the pooled biochar amended treatment.

Biochar amendment has been shown to influence zinc sorption and immobilization; with a 3% w/w biochar amendment reducing the exchangeable zinc concentration in the amended soil matrix (Meng et al., 2018) and a 10% w/w amendment of a sugar cane (700°C) biochar increases sorption efficiency from 0.12 mg/g to 1 mg/g (Melo et al., 2013).

Biochar’s zinc sorption is strongly influenced by the pyrolysis temperature of the biochar, with the highest adsorption capacity being produced by higher pyrolysis temperatures; for instance, a 700°C sugar cane straw derived biochar had an approximately 6.4 mg/g sorption from a 2 mM zinc solution (Melo et al., 2013).

Additionally, the presence of competitive metals in the stormwater solution also reduces the biochars zinc removal capacity, with a 600°C straw biochar has a maximum adsorption capacity of 40.2 mg/g in a zinc solution, which is dropped to 7.9 mg/g in a zinc/copper solution (Park et al., 2017). Zinc actively competes with copper for sorption on proton-active carboxyl (−COOH) and hydroxyl (−OH) functional groups on the biochar surface (Alam et al., 2018). Increasing biochar amendment rates in the column experiment likely countered the competition influence for binding sites experienced by zinc resulting in the positive correlation in removal performance observed (Figure 82).

Biochar reportedly has the lowest absorbance efficiency for nickel of any of the dissolved-phase heavy metals, with pinewood (550°C) and peanut shell (600°C) biochar both showing low maximum absorbance for nickel of 3.1 and 4.9 mg/g respectively (Alam et al., 2018, Hu et al., 2018). The nickel removal by the biochar was most likely similar to that of the unamended filter fill, and that is why there was no significant difference in removal between the biochar amended and unamended simulation columns.

The improved removal of dissolved-phased metals by biochar amended biofilters are important results, as it indicates that amendment of field systems with recycled biochar could effectively enhance system metal removal performance, reducing discharge of these metals into receiving waterways and aquifer, thus promoting aquatic system quality improvement.

5.3.5.3. Heavy metal removal: suspended- or-settled-phase heavy metals

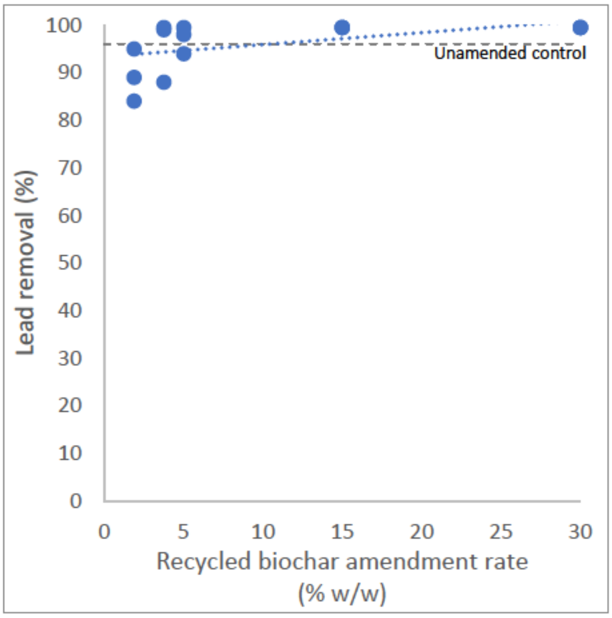


Figure 83: Lead removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

Lead was effectively removed by the biochar amended biofilters, which is an important finding as lead is ecotoxic to downstream aquatic biota and for human health considerations. There was a moderate positive correlation ($r = +0.53$) for lead removal with biochar amendment rates greater than 15% significantly ($p = 0.001$) enhancing removal performance in comparison to the unamended control, while the ≤ 5% w/w rate treatments had equivalent non-significant ($p = 0.53$) removal performance to that of the unamended control (Figure 83). Overall, biochar amendment significantly ($p = 0.04$) increased median removal from 96.1% for the unamended control to 99.5% for the pooled biochar amended treatments. As the biochar amended simulation columns effectively removed lead, the median concentrations discharged was reduced to below the 95% ecological protection guideline value for all biochar amendment rate treatments.

Biochar removes lead from aqueous solutions primarily through a precipitation mechanism with surface carbonate groups that are not decomposed at high biochar pyrolysis temperatures (Shen et al., 2017). Therefore it tends to be an effective sorbent for lead with maximum sorption of upwards of 3990 mg/g for a 700°C tobacco stem biochar (Zhou et al., 2018).

It has been shown that a 10% w/w amendment of an agricultural sand-based soil can substantially decrease the concentration of lead following 48 hours of equilibrium (Uchimiya et al., 2011). Biochar has a fast-initial adsorption pathway, with 40-70% of the total lead being adsorbed within the first hour of contact time (Mohan et al., 2007). When contact is limited, it has been shown that a 7.5% w/w biochar amendment of a tree pit soil did not substantially alter the sorption capacity of the media (Seguin et al., 2018), which supports the insignificant lead removal performance observed for the less than 5% w/w biochar treatments.

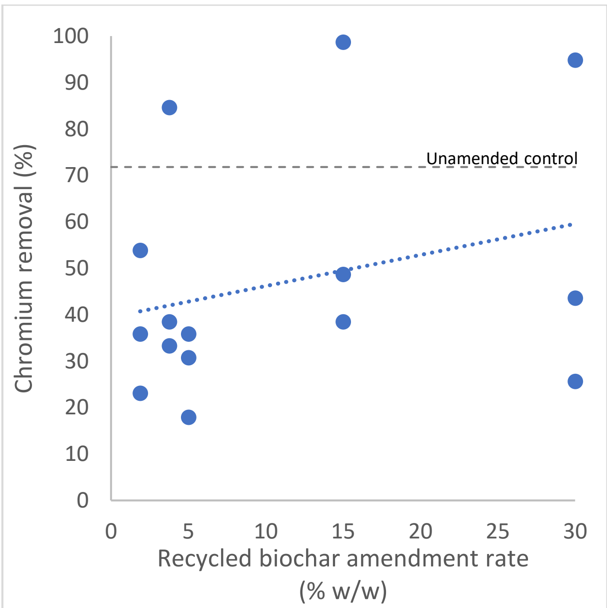


Figure 84: Chromium removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

There was practically no relationship between the biochar amendment and chromium removal efficiency (Figure 84) indicated by a very low positive correlation (r = +0.08). There was a significant ($p = 0.002$) reduction in median removal efficiency from 71.8% for the unamended control to 35.9% for the pooled biochar amended columns. The low removal efficiency resulted in the median Cr (VI) discharge from the biochar amended columns (Table 35 in appendix) to not comply with the 90% ecological protection target (Table 7).

Biochar may have some capacity for the adsorption of Cr (VI) with a *Eucalyptus globulus* bark biochar (500 °C) having been shown to have a maximum absorbance of 21.3 mg/g, and a corncob derived biochar (400-600°C) had a maximum sorption capacity of 25.69 mg/g (Gupta et al., 2018, Choudhary and Paul, 2018). Soil pH is the most influential factor controlling absorption capacity, with biochar having a maximum Cr (VI) removal at pH 2.01, which progressively falls as pH increases, with removal dropping to practically zero at pH 10 (Gupta et al., 2018).

The sand-based filter fill had a pH of 6.3 while the biochar's pH was 9.6, so under these soil conditions, the biochar would have had a limited absorptive capacity for Cr (VI), and did not actively contribute to the chromium removal by the biochar amended biofilter columns. Thus, with less removal capacity, the chromium removal performance was suppressed in comparison to the unamended control.

5.3.5.4. Metalloid removal: arsenic

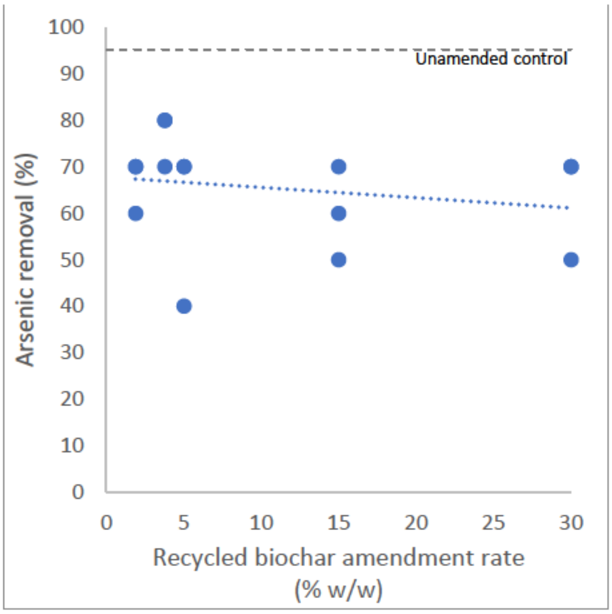


Figure 85: Metalloid arsenic removal efficiency with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

The influence of biochar amendment on arsenic removal was not rate-specific, with removal showing a low negative correlation ($r = -0.21$) with the increase in biochar amendment and no significant ($p = 0.22$) difference in removal between the rate treatments (Figure 85). Biochar amendment generally decreased arsenic removal, with a significant ($p < 0.001$) reduction in median removal between the unamended control and the amended treatments being observed (Table 14 and Table 35 and 37 in appendix). Despite the negative impact of the biochar amendment on the simulation biofilter columns performance, the arsenic concentration discharged still complied to the 95% ANZG (2018) default guideline value.

The scientific literature suggests that biochar may be a promising sorbent for arsenic removal in soil and water remediation, with upwards of 89% arsenic removal having been previously reported (Vithanage et al., 2017, Van Vinh et al., 2015, Agrafioti et al., 2014). Despite this predicted positive impact of biochar on arsenic removal, the results of this experiment indicate that biochar reduces arsenic removal by the soil system.

The bulk of biochars that have analysed arsenic removal capacity have been low temperature derived biochars (300-500°C) which were derived from rice hull, pine/oak wood or sewage sludge feedstocks. In contrast, the biochar used in this experiment was a high temperature *Eucalyptus* wood-derived biochar (750°C). The literature suggests that low-temperature pyrolysis allows for the formation of more functional groups on the biochar surface which promote adsorption of arsenic than that of high temperature derived biochars (Vithanage et al., 2017).

Further, the physiochemical conditions that the biofilter experienced, particularly pH, was not conducive to effective arsenic removal by biochar, as biochar's arsenic removal is most effective at low pH (<4) and adsorption is practically non-existent at pH above 5 (Vithanage et al., 2017). All the active components in the biofilter had pH levels far above the biochar's optimal sorption range for arsenic.

The combination of high biochar pyrolysis temperature and unfavourable physiochemical fill conditions meant that biochar amendment did not remove arsenic from the synthetic stormwater; thus, the low negative correlation and reduced arsenic performance observed.

5.3.5.5. Total suspended solids

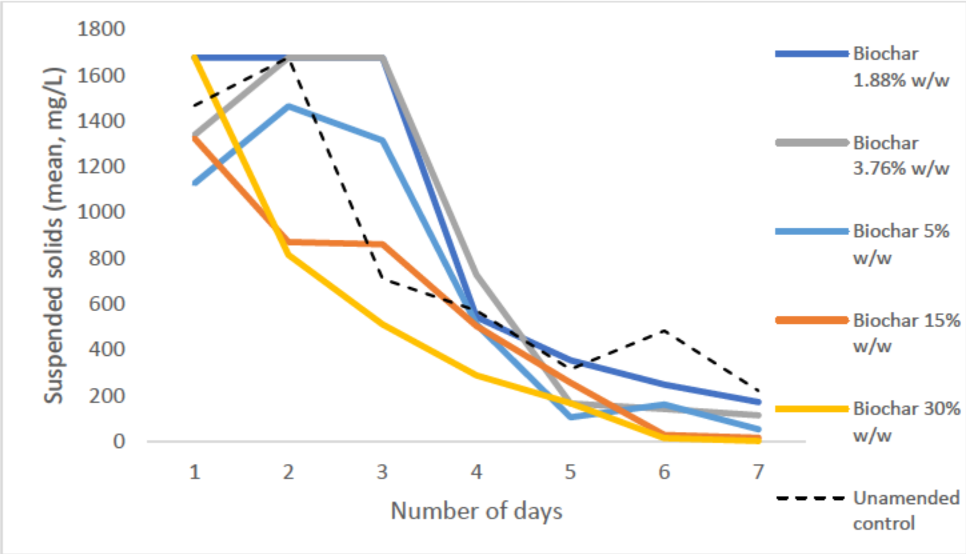


Figure 86: Mean total suspended solids discharged with biochar amendment in comparison to the unamended control (dotted line)

All biochar amended column simulations followed a similar declining trend in the discharge of suspended solids after day three of purging, with the exception of the 30% w/w treatment which had a continuous decline in TSS discharge throughout the entire purge period of seven days (Figure 86).

All biochar amended simulations had significantly ($p = 0.005$) lower TSS concentration in column discharge than the unamended control following seven days of purging. The 30% w/w rate treatment had the greatest reduction in TSS, with only 1.5 mg/L being released by day seven, which was an over 99% reduction in comparison to the unamended control.

The increased TSS retention performance by the biofilter columns seen with increased biochar amendment rates was similar to previously reported results where TSS removal from wastewater tended to increase with elevated amendment rates in the constructed wetland sand-based media (de Rozari et al., 2015).

Like the gypsum and crushed concrete, the biochar amendment may increase the Ca^{2+} ion concentration in the biofilter's soil matrix, as the biochar contains 6.8 cmol/kg of calcium, which was 5.6 times more than in the sand-based filter fill. The calcium concentration in the biochar was 8% and 19% of the available calcium to that of the gypsum and crushed concrete (Table 34 in appendix), and so the biochar amendment altering Ca^{2+} ion concentration within the fill matrix was probably only a minor contributing factor.

5.3.5.6. Hydrological performance

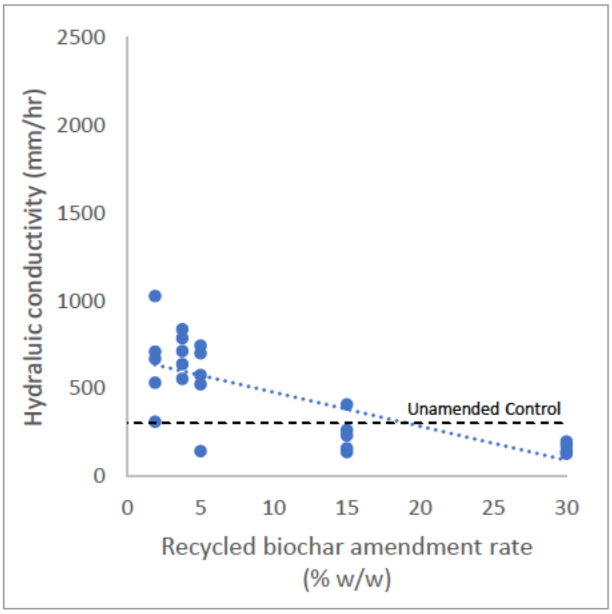


Figure 87: Hydraulic conductivity with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

There was a significant ($p = 0.006$) difference in hydraulic conductivity between the biochar amended rate treatments, with a high negative correlation ($r = -0.75$) between fill conductivity and the amount of biochar added (Figure 87). At rates of ≤5% w/w there was a significant ($p = 0.02$) increase, while at 30% w/w there was a significant decrease ($p = 0.003$) and at 15% w/w there was no statistical ($p = 0.06$) difference in hydrological performance between the biochar amended and the unamended control. Figure 87 clearly shows that amendment rates of greater than approximately 19% w/w should have hydraulic conductivities which are compliant with the less than 300 mm/hr limit established for optimal hydrological performance for biofilters operated in temperate climatic conditions.

The hydraulic conductivity of the amended biofilter fill is dependent upon the receiving soils and biochars physiochemical properties and amendment rate (Barnes et al., 2014, Lim et al., 2016b). The literature reports similar trends to that observed, for instance, a 2% w/w amendment of non-calcareous loamy sand with 620°C wood-chip derived biochar significantly increased soil infiltration rate by 1.7 times that of the unamended control (Abrol et al., 2016). Increased infiltration with biochar amendment was attributed to a reduction in soil bulk density (Abrol et al., 2016).

The progressive decrease in hydraulic conductivity with increased biochar amendment (Figure 87), was also observed in the scientific literature, with hydraulic conductivity being shown to drop from 848 mm/hr for the unamended a calcareous sand to 66 mm/hrs for a 25% w/w amendment with a 500°C fast pyrolysis switchgrass biochar (Brockhoff et al., 2010).

The reduced hydraulic conductivity with biochar amendment has often been attributed to biochar hydrophobicity, which impedes hydrological flow (Githinji, 2014, Jeffery et al., 2015, Wiersma et al., 2020). However, this is at odds with observations that hydrophobicity decreases with increased pyrolysis temperature, with three different plant-based biochar's exhibiting minimal hydrophobic properties at pyrolysis temperatures above 500°C (Kinney et al., 2012). Given the greater than 500°C pyrolysis temperature of the plant-based biochar used in the current study, it is most likely that the amendment biochar had minimal hydrophobic properties. Thus, hydrophobicity was not likely the major mechanism for the reduction in hydraulic conductivity with increased biochar amendment.

Decreased hydraulic conductivity by the biochar amendment may instead relate to soil porosity and tortuosity (Liu et al., 2016). The addition of fine biochar particles filled spaces between the sand grains, resulting in greater fill compaction and bulk density which reduces porosity and increased tortuosity. In contrast, the addition of coarse biochar fragments resulted in these particulates being surrounded by the fine sand which increases bulk density and decreases pore throat size between particles and increase tortuosity (Liu et al., 2016).

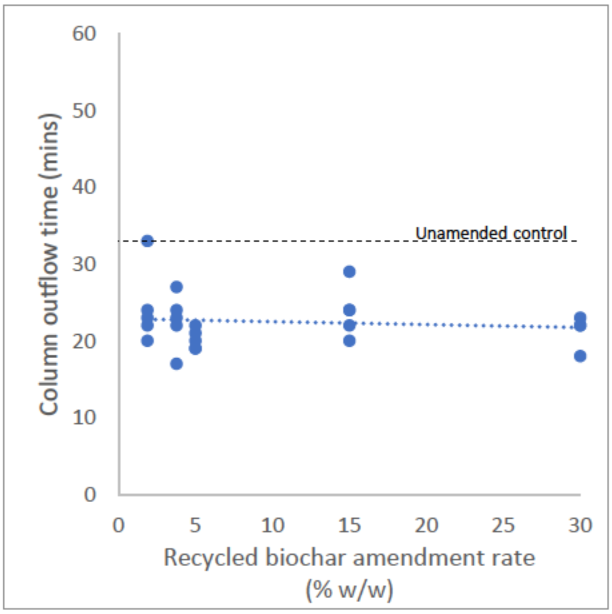


Figure 88: Column outflow time with biochar amendment showing trend with biochar dosage (dotted line) against unamended control (dashed line)

Unlike the hydraulic conductivity results, the biochar amendment significantly (p = 0.003) lowered the outflow time of the biofilter columns in comparison to the unamended control (Figure 88). Discharge time was not dependent upon amendment rate, as there was a very low positive correlation (r = +0.03) and no significant (p = 0.29) in outflow times between the amendment rates.

Biochar amendment of the sand-based filter fill increased the concentration of coarse and fine (<75 µm) particulate fractions within the fill matrix, with there being an increase in the percentage composition of particles in the size range of >850 µm and the >75 µm particulates, a decrease in the 75-425 µm range and no change in the 425-850 µm (Table 36 in appendix). The shift in the PSD was most profound in higher biochar amendment rates, with elevated concentrations of coarser particulates within the fill matrix promoting faster subsurface flow rates; therefore, the biochar amended columns discharged the treated stormwater much faster than the unamended control.

5.3.6. Performance between amendments

Thus far, the effects of fill amendment on biofilter pollutant removal performance have been individually assessed for each of the five fill amendment treatments. This section compares pollutant removal performance between amendment treatments in order to assess the merit of each fill amendment in relation to that of the other treatments.

For comparison of pollution removal performance between the amendment treatment, two amendment rates were selected; a low (5% w/w) and high (25% or 30% w/w), as these rate treatments were essentially equivalent across all amendment treatments.

5.3.6.1. Nutrient removal: nitrogen and phosphorus

5.3.6.1.1. Total Kjeldahl Nitrogen

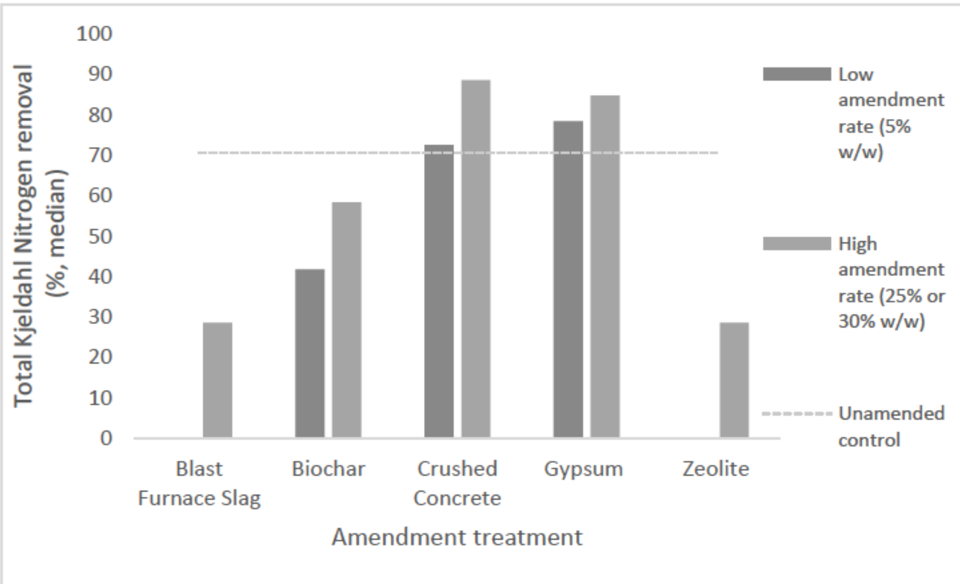


Figure 89: Median Total Kjeldahl Nitrogen removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

There was a significant difference in TKN removal efficiency by the simulation columns between the amendment treatments (including the unamended control) at both the low ($p = 0.01$) and high ($p = 0.02$) amendment rates (Figure 89).

Table 15: Statistical difference (p-values) in TKN removal efficiency between amendment treatments at a low amendment rate of 5% w/w

	Biochar	Control	Crushed Concrete
Control	0.48		
Crushed concrete	0.11	0.30	
Gypsum	0.01	0.02	0.16

At the low amendment rate, the gypsum amendment treatment had a significant (Table 15) increase in TKN removal in relation to biochar and the unamended control (Figure 89). This indicated that the 5% w/w gypsum amendment treatment had the greatest removal performance of any of the amendment treatments trialled. Based on these results, the TKN removal performance of the amendment treatments are roughly ranked from highest to lowest removal performance:

gypsum = crushed concrete ≥ control > biochar

Table 16: Statistical difference (p-values) in TKN removal efficiency between amendment treatments at a high amendment rate of >25% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.61				
Control	0.91	0.64			
Crushed Concrete	0.01	0.05	0.01		
Gypsum	0.04	0.13	0.03	0.67	
Zeolite	0.70	0.90	0.74	0.04	0.10

At high amendment rates, a significant difference in TKN removal between amendment treatments was observed with crushed concrete having significantly higher TKN removal than biochar, BFS, zeolite and the unamended control, and gypsum having significantly higher TKN removal than the biochar and control treatments (Figure 89 and Table 16). These results indicate at a high amendment rate, crushed concrete and gypsum were the best performing amendment materials for TKN removal, and both had significantly higher TKN removal than the control. Therefore, for TKN removal performance at high amendment rates, the amendment treatment could be roughly ranked in the order of

crushed concrete = gypsum > control ≥ biochar > zeolite = BFS

5.3.6.1.2. Nitrate and nitrite-nitrogen

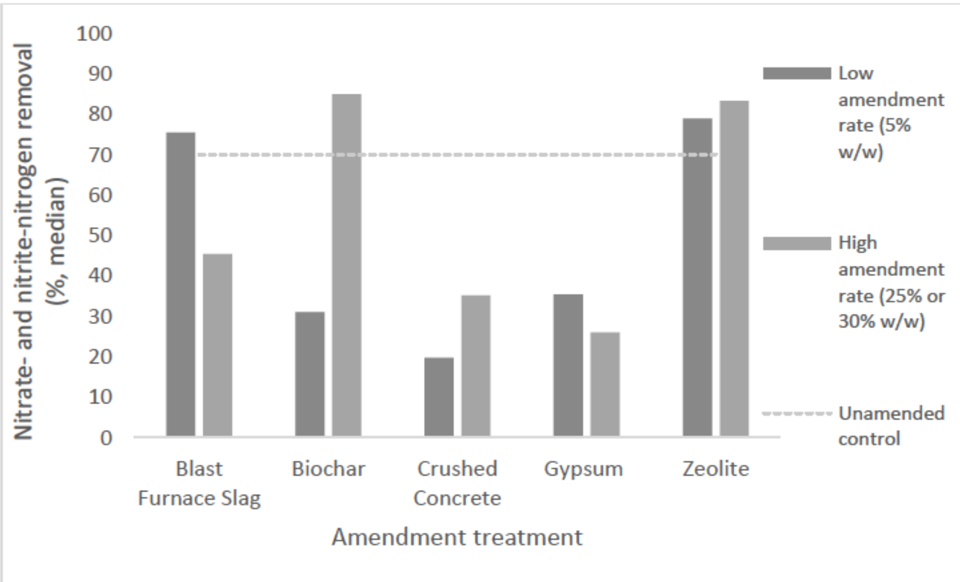


Figure 90: Median nitrate- and nitrite-nitrogen removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

There was no significant difference in NOx removal efficiency by the simulation columns between the amendment treatments (including the unamended control) at both the low ($p = 0.23$) and high ($p = 0.46$) amendment rates (Figure 90). Despite, the lack of significance between the amendment treatments, there was some variation in median NOx removal efficiency between the amendment treatments and based on these median removal efficiencies, performance from highest to lowest of the amendment treatments could be loosely ranked. At a low amendment rate NOx performance was in the order of

$$\text{zeolite} \geq \text{BFS} \geq \text{control} \geq \text{biochar} \geq \text{gypsum} \geq \text{crushed concrete}$$

while at high amendment rates,

$$\text{biochar} \geq \text{zeolite} \geq \text{BFS} \geq \text{control} \geq \text{crushed concrete} \geq \text{gypsum}$$

5.3.6.1.3. Total Nitrogen

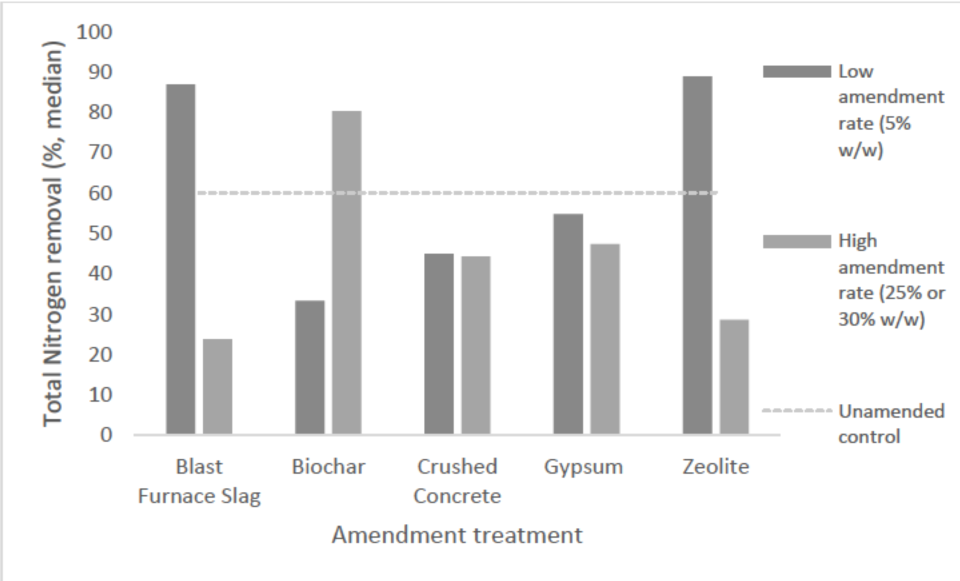


Figure 91: Median Total Nitrogen (TN) removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

TN removal efficiency varied between the amendment treatments (Figure 91). There was no significant difference in TN removal efficiency between the amended biofilter simulation columns (including the unamended control) at both the low ($p = 0.06$) and high ($p = 0.63$) amendment rates. There was some variation median removal efficiencies (Figure 91), and based on these performance results could be loosely ranked from highest to lowest of the amendment treatments. At a low amendment rate:

zeolite ≥ BFS ≥ control ≥ gypsum ≥ crushed concrete ≥ biochar

while at high amendment rates:

biochar ≥ control ≥ gypsum ≥ crushed concrete ≥ zeolite ≥ BFS

5.3.6.1.4. Total Phosphorus

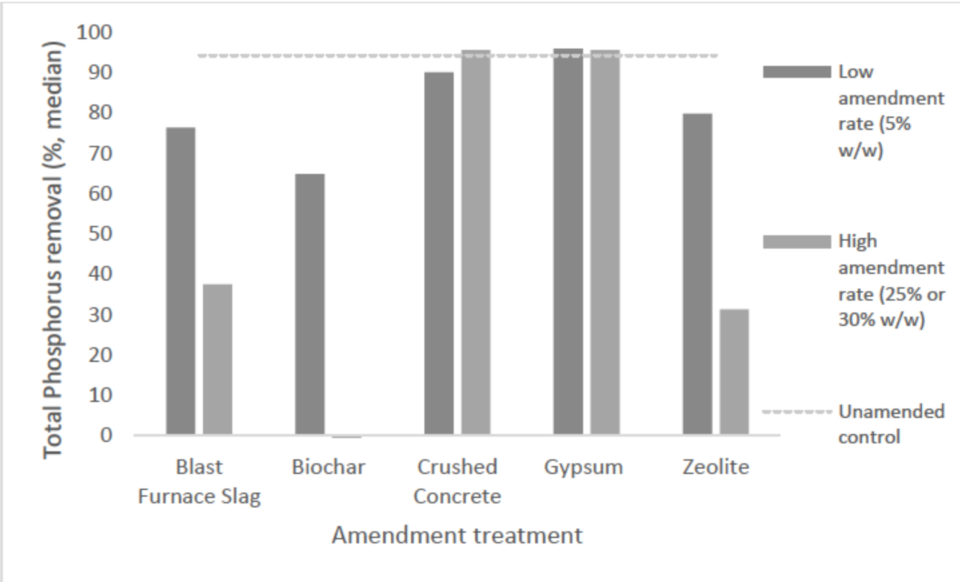


Figure 92: Median Total Phosphorus (TP) removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

There was a significant difference in TP removal efficiency between the amended stormwater biofilter columns at both the low ($p = 0.01$) and high ($p = 0.01$) amendment rate treatments. As discussed in the previous sections, the amendment agents all showed different levels of absorptive capacity for phosphorus; hence the variation observed in the median TP removal by the amended biofilter columns (Figure 92).

Table 17: Statistical difference (p-values) in TP removal efficiency between amendment treatments at a low amendment rate of 5% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.39				
Control	0.002	0.01			
Crushed Concrete	0.02	0.11	0.40		
Gypsum	<0.001	0.002	0.36	0.10	
Zeolite	0.30	0.85	0.02	0.16	0.004

At a 5% w/w amendment rate, there was a significant difference in TP removal between many of the amendment groups (Table 17). Biochar, BFS and zeolite tended to significantly reduce TP removal in comparison to the unamended control, while crushed concrete and gypsum were statistically equivalent to the unamended control. These results indicate that at low amendment rates, TP removal performance of the amended biofilter columns was in the order of:

gypsum ≥ control ≥ crushed > zeolite ≥ BFS ≥ biochar

Table 18: Statistical difference (p-values) in TP removal efficiency between amendment treatments at a high amendment rate of ≥ 25% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.39				
Control	0.02	0.18			
Crushed Concrete	0.002	0.03	0.28		
Gypsum	0.002	0.03	0.29	0.97	
Zeolite	0.26	0.79	0.30	0.06	0.06

At high amendment rates, gypsum and crushed concrete both showed a high affinity for phosphorus, which were again statistically equivalent to the unamended control, while BFS and zeolite had a limited removal capacity, and biochar tended to be a source of phosphorus leaching from the biochar matrix (Figure 92). Given there was a significant difference between treatments (Table 18) and the removal performance of the amendment agents shown in this thesis (Figure 92), performance from highest to lowest of the amendment treatments could be ranked as:

crushed concrete = gypsum = control > BFS > zeolite > biochar

5.3.6.2. Heavy metal removal: dissolved-phase heavy metal

5.3.6.2.1. Cadmium

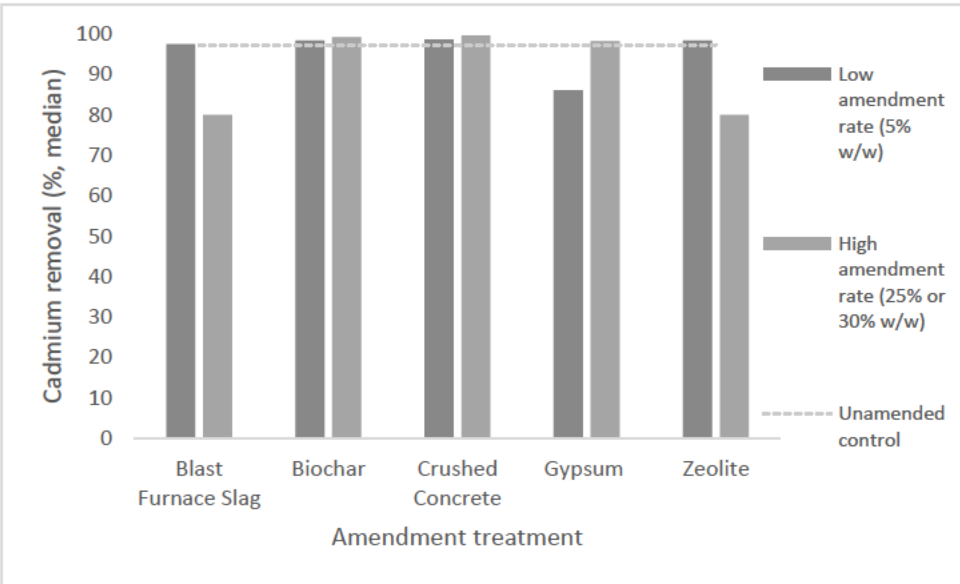


Figure 93: Median cadmium removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

At low amendment rates, all treatments had median cadmium removal efficiency of greater than 97%, with the exception of gypsum, which had a median cadmium removal of 86% (Figure 93). There was no significant ($p = 0.13$) difference in cadmium removal performance

(Figure 93) cadmium removal between treatments can be loosely ranked as:

crushed concrete = biochar = zeolite = BFS = control ≥ gypsum

Table 19: Statistical difference (p-values) in cadmium removal efficiency between amendment treatments at a high amendment rate of ≥25% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.05				
Control	0.08	0.50			
Crushed Concrete	0.42	<0.001	<0.001		
Gypsum	0.38	0.21	0.42	0.06	
Zeolite	0.05	1.00	0.50	<0.001	0.21

At higher amendment rates, there was a significant ($p = 0.01$) difference between the amendment treatments. Zeolite and BFS both had lower cadmium removal performance than the other amendment treatments, with a median cadmium removal of 80%, this was a significant decline to that of biochar and crushed concrete amendment (Table 19). Crushed concrete had the highest median cadmium removal of any of the amendment treatments of 99.6%, which was significantly ($p < 0.001$) different from the unamended control (Figure 93).

Given there was a significant difference between treatments (Table 19) and the removal performance of the amendment agents shown in this thesis, performance from highest to lowest could be ranked as:

crushed concrete > control = gypsum = biochar > BFS = zeolite

5.3.6.2.2. Copper

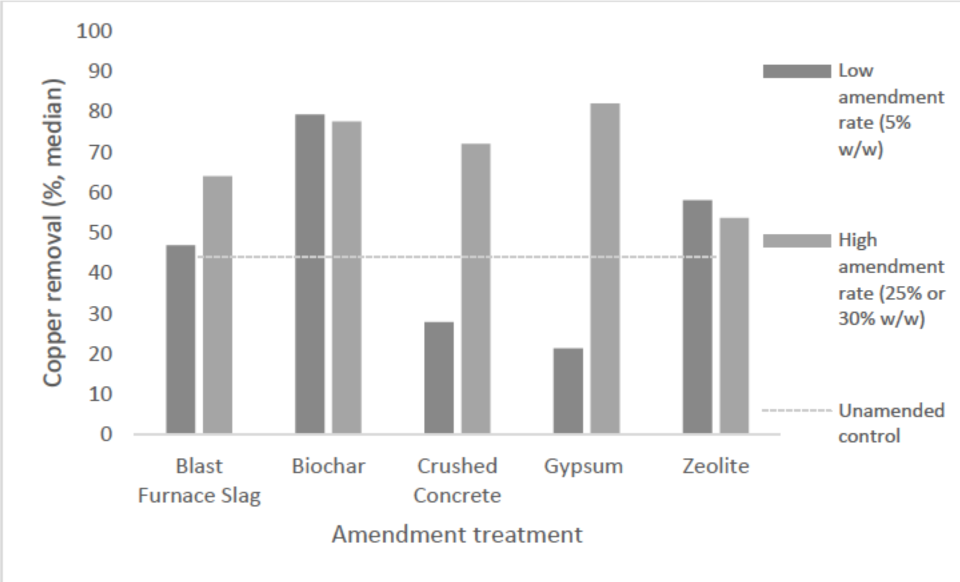


Figure 94: Median copper removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

At a 5% w/w amendment rate, there was no significant ($p = 0.57$) difference in copper removal performance between the amendment treatments. Despite, the lack of significance between the amendment treatments, there was some variation in copper removal efficiency between the amendment treatments, and based on these median removal efficiencies (Figure 94), performance from could be loosely ranked as

biochar ≥ zeolite ≥ BFS ≥ control ≥ crushed concrete ≥ gypsum

Table 20: Statistical difference (p-values) in copper removal efficiency between amendment treatments at a high amendment rate of ≥25% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.14				
Control	0.002	0.21			
Crushed Concrete	0.30	0.52	0.02		
Gypsum	0.62	0.04	<0.001	0.09	
Zeolite	0.09	0.83	0.32	0.38	0.02

At amendment rates of ≥ 25% w/w, there was a significant ($p = 0.01$) difference in copper removal between the amended simulation biofilter columns treatments, which was primarily due to the significant difference between biochar and the control, and gypsum with BFS, control and zeolite (Table 20). These results (Figure 94) indicate that at high amendment rates, copper removal performance of the amended biofilter columns was in the order of:

gypsum ≥ biochar ≥ crushed concrete > BFS ≥ zeolite ≥ control

5.3.6.2.3. Nickel

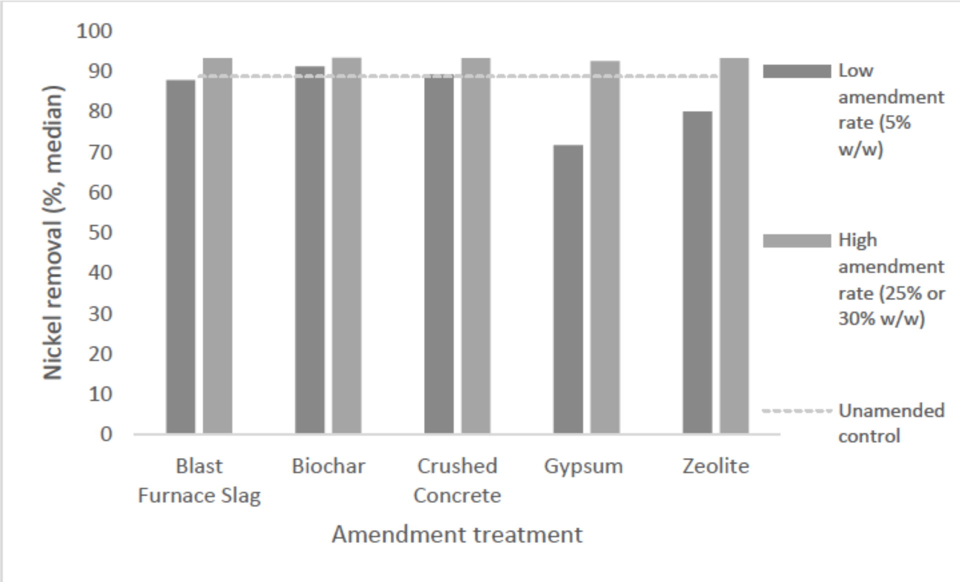


Figure 95: Median nickel removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

There was no significant difference in nickel removal efficiency by the simulation columns between the amendment treatments (including the unamended control) at both the low ($p = 0.4$) and high ($p = 0.18$) amendment rates (Figure 95). Despite, the lack of significance between the amendment treatments, there was some variation in nickel removal efficiency between the amendment treatments at a low amendment rate (Figure 95) and based on these median removal efficiencies, performance from highest to lowest of the amendment treatments could be loosely ranked:

biochar ≥ crushed concrete ≥ control ≥ BFS ≥ zeolite ≥ gypsum

At a high amendment rate, the difference between the amendment treatments was less than 1%, and therefore, there was insufficient variation to distinguish between the treatments; therefore, all treatments had equivalent nickel removal performance.

5.3.6.2.4. Zinc

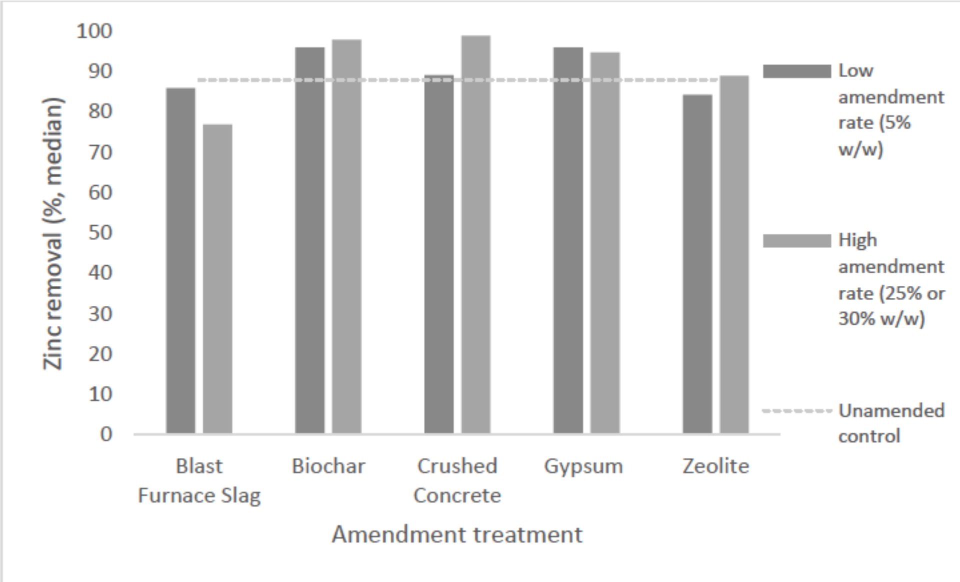


Figure 96: Median zinc removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

Table 21: Statistical difference (p-values) in zinc removal efficiency between amendment treatments at a low amendment rate of 5% w/w

	Biochar	**BFS**	**Control**	**Crushed Concrete**	**Gypsum**
BFS	0.01				
Control	0.03	0.54			
Crushed Concrete	0.20	0.17	0.38		
Gypsum	0.97	0.11	0.19	0.41	
Zeolite	0.01	0.76	0.35	0.10	0.08

At a 5% w/w amendment, there was a significant (p = 0.04) difference in zinc removal efficiency between the amendment treatments (including the unamended control), with biochar having a significantly increased performance in comparison to BFS, zeolite and the unamended control (Figure 96 and Table 21). Biochar, crushed concrete and gypsum all had statistically equivalent median zinc removal efficiency and this removal performance was greater than the median zinc removal of the unamended control. The amendment treatments were roughly ranked in terms of their zinc removal performance in the order of:

biochar ≥ gypsum ≥ crushed concrete ≥ control ≥ BFS ≥ zeolite

Table 22: Statistical difference (p-values) in zinc removal efficiency between amendment treatments at a high amendment rate of ≥25% w/w

	Biochar	BFS	Control	Crushed	Gypsum
BFS	0.03				
Control	0.03	0.65			
Crushed concrete	0.38	0.001	<0.001		
Gypsum	0.72	0.05	0.06	0.17	
Zeolite	0.10	0.63	0.90	0.01	0.16

At high amendment rates, there was a significant (p = 0.01) difference in zinc removal efficiency by simulation biofilter columns between the amendment treatments. The difference between biochar, crushed concrete and gypsum were all significant with some of the other amendment treatments (Table 22). Given then differences between treatments (Table 18) and the median removal performance (Figure 96) of the amendment, performance from highest to lowest of the amendment treatments could be ranked as:

crushed concrete ≥ biochar ≥ gypsum ≥ control ≥ zeolite ≥ BFS

5.3.6.3. Heavy metal removal: suspended -or-settled heavy metals

5.3.6.3.1. Lead

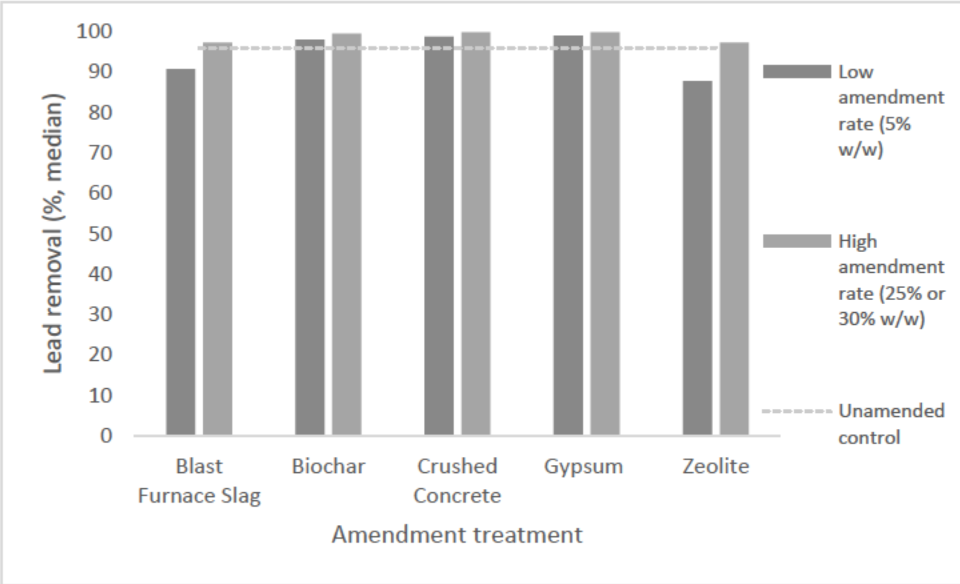


Figure 97: Median lead removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

Table 23: Statistical difference (p-values) in lead removal efficiency between amendment treatments at a low amendment rate of 5% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.05				
Control	0.25	0.28			
Crushed Concrete	0.94	0.02	0.14		
Gypsum	0.42	0.002	0.02	0.40	
Zeolite	0.03	0.71	0.14	0.01	<0.001

At a 5% w/w amendment, there was a significant (p = 0.03) difference in lead removal efficiency between the amendment treatments, only gypsum having a significant increase in comparison to the unamended control (Figure 97). Biochar, crushed concrete and gypsum were all statistically equivalent lead removal efficiency and all had statistically higher lead removal to that of the BFS and zeolite treatments (Table 23). Given these results, the amendment treatments were roughly ranked in terms of their lead removal performance in the order of:

gypsum ≥ crushed concrete ≥ biochar ≥ control ≥ BFS ≥ zeolite

Table 24: Statistical difference (p-values) in lead removal efficiency between amendment treatments at a high amendment rate of >25% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.30				
Control	0.02	0.27			
Crushed Concrete	0.32	0.03	<0.001		
Gypsum	0.53	0.08	<0.001	0.71	
Zeolite	0.33	0.96	0.24	0.04	0.09

At high amendment rates, there was a significant (p = 0.01) difference in lead removal efficiency by simulation biofilter columns between the amendment treatments. Biochar, crushed concrete and gypsum all showed significant difference with some of the other amendment treatments (Table 24). Given the difference between treatments (Table 24) and the median removal performance (Figure 97) of the amendment, performance from highest to lowest of the amendment treatments could be ranked as:

crushed concrete ≥ biochar ≥ gypsum ≥ control ≥ zeolite ≥ BFS.

5.3.6.3.2. Chromium

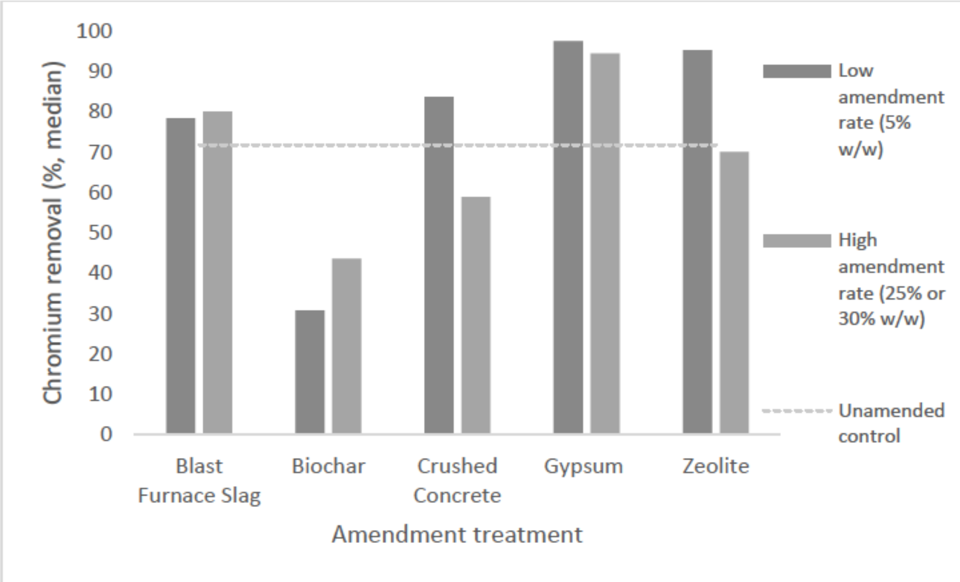


Figure 98: Median chromium removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

There was no significant difference in chromium removal efficiency by the simulation columns between the amendment treatments (including the unamended control) at both the low ($p = 0.07$) and high ($p = 0.68$) amendment rates (Figure 98). Despite, the lack of significance between the amendment treatments, there was some variation in median chromium removal efficiency between the amendment treatments and based on these median removal efficiencies, performance from highest to lowest of the amendment treatments could be loosely ranked. At a low amendment, rate ranked performance was:

gypsum ≥ zeolite ≥ crushed concrete ≥ BFS ≥ control ≥ biochar

while at a high amendment rate:

gypsum ≥ BFS ≥ control ≥ zeolite ≥ crushed concrete ≥ biochar

5.3.6.4. Metalloid removal: arsenic

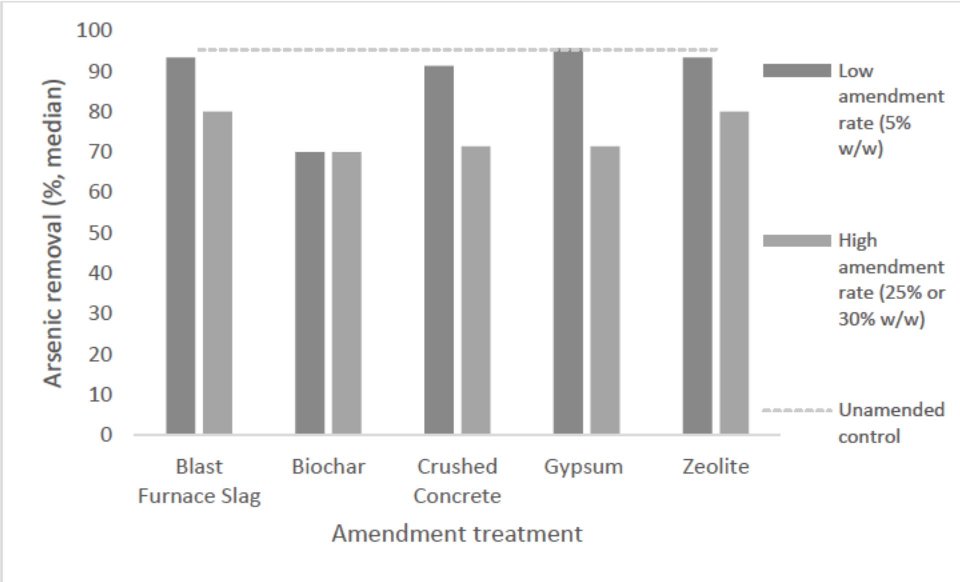


Figure 99: Median arsenic removal efficiency with fill amendment at low (5% w/w) and high (≥25% w/w) rates

Table 25: Statistical difference (p-values) in arsenic removal efficiency between amendment treatments at a high amendment rate of >25% w/w

	Biochar	BFS	Control	Crushed Concrete	Gypsum
BFS	0.06				
Control	<0.001	0.16			
Crushed Concrete	0.50	0.16	<0.001		
Gypsum	0.24	0.41	0.01	0.55	
Zeolite	0.04	0.85	0.24	0.11	0.31

At a 5% w/w amendment rate, there was no significant ($p = 0.1$) difference in arsenic removal performance between the amendment treatments, with all treatments having median arsenic removal of between 91-95% (Figure 99).

At a high amendment rate, there was a significant ($p = 0.01$) difference in arsenic removal performance between the amendment treatments, with arsenic removal by the biochar, crushed concrete, and gypsum amended columns all being significantly lower to that of the unamended control, and biochar and zeolite were significantly different to each other (Table 25). Based on these results, arsenic removal performance by the amended biofilter columns could be loosely ranked as:

$$\text{control} > \text{zeolite} = \text{BFS} \geq \text{crushed concrete} = \text{gypsum} \geq \text{biochar}$$

5.3.6.5. Hydrological performance

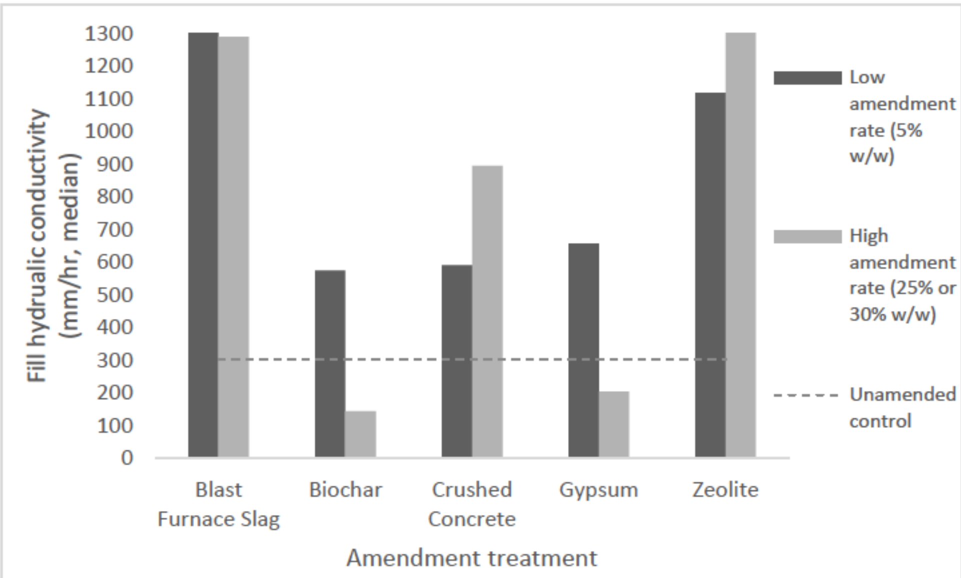


Figure 100: Median hydraulic conductivity with fill amendment at low (5% w/w) and high (≥25% w/w) rates

There was a significant ($p < 0.001$) difference in hydraulic conductivity between the amendment treatments for both the low and high amendment rates (Figure 100). At a low amendment, fill amendment consistently and significantly increased hydraulic conductivity to above the unamended control, to levels that exceed the 300 mm/hr optimal limit set by the City's fill specifications and the CRC (2015) guidelines, so all amendments are ranked below the control on hydrological performance:

Control > Biochar > Crushed Concrete > Gypsum > Zeolite > BFS

At a high amendment rate, fill amendment significantly increased hydraulic conductivity in comparison to the unamended control, with the exception of the biochar and gypsum treatments which had hydrological performance within the 100-300 mm/hr optimal range. Therefore, the biochar and gypsum can be considered to have equivalent optimal performance to that of the control, and ranked accordingly as:

Biochar ≥ Gypsum ≥ Control > Crushed Concrete > BFS > Zeolite

Fill amendment overall tended to significantly increase the hydraulic conductivity to above the optimal range (100-300 mm/hr), which is potentially detrimental to system performance in terms of plant establishment and pollutant removal.

Well-draining filter fill could result in less available water within the plant root zone, with the low water availability potentially detrimental to the wetland plant survival and establishment. Dieback and stunted plant growth would add additional economic cost in establishing and maintaining adequate plant cover and reduce the overall pollution removal performance of the system.

An above optimal (>300 mm/hr) hydraulic conductivity may be less effective in the removal of pollutants. Analysis of correlation between the biofilter pollution removal performance and fill hydraulic conductivity generally indicated that high hydraulic conductivities had a negative impact upon biofilter pollutant removal performance (Table 26), except for chromium and arsenic, which had a positive correlation (Table 26).

Table 26: Pearson's R correlation between biofilter pollution removal performance (% reduction) and biofilter fill hydraulic conductivity (mm/hr)

Pollutants	Pearson's R correlation	
Arsenic	0.19	Very low
Cadmium	-0.44	Moderate
Chromium	0.10	Very Low
Copper	-0.06	Very Low
Lead	-0.46	Moderate
Nickel	0.27	Low
Zinc	-0.12	Very Low
Nitrate-Nitrite	-0.32	Low
Total Kjeldahl nitrogen	-0.27	Low
Total nitrogen	-0.25	Low
Total phosphorus	-0.23	Low

There has been limited research performed on establishing the relationship between hydraulic conductivity and pollution removal performance in biofilter systems. There are a few papers which discuss the relationship between hydraulic load and biofilter system pollution removal (Wang et al., 2017a). For instance, biofilter media with high hydraulic conductivity (~800 mm/hr) had lower metal removal than media with low (~160 mm/hr) hydraulic conductivity (Good et al., 2012). However, this observation was not an objective of the study, and differences in fill media was the major contributing factor for the differences in pollution removal. Further research into the effects of hydraulic conductivity on pollution removal is recommended.

Alternatively, an elevated initial fill hydraulic conductivity may aid in maintain system hydrology over the long term. Studies have shown that hydraulic conductivity can be substantially reduced over time, as the fill settle and compact and pores clog with fine sediments from the stormwater. For instance, an sand-based biofilter fill which with an initial hydraulic conductivity of 186 mm/hr, after 72 weeks of hydraulic loading (twice weekly dosing that conformed to a Melbourne's climatic condition), was reduced to a median of 51 mm/hr (Le Coustumer et al., 2012).

Under this progressively declining hydraulic conductivity scenario, an elevated initial hydraulic conductivity, that initially exceeds the maximum recommended hydraulic guidelines, may be advantageous in maintaining a long-term optimal hydrological performance. As the initially high infiltration would eventually decline to within the optimal guideline range. This premise requires further research to monitor amended fills hydrology over time, under hydraulic conditions that simulate expected field conditions, in order to determine the rate of decline and the expected time it takes to conform to guideline recommendations.

5.4. Conclusions

In this chapter, gypsum, crushed concrete, blast furnace slag, zeolite and biochar amendments were explored for their capacity to improve upon the baseline pollutant removal performance of the City's field biofilters. There were significant differences in removal efficiency between these amendment treatments, with gypsum and crushed concrete tending to have greater removal than the other amendments trialled. Overall, the results clearly showed that fill amendment could enhance the removal performance in comparison to the unamended control. This is an important finding for the biofilter designers and operators, as it means the application of fill amendment will aid pollutant capture by the field systems which will better support local pollutant reduction targets and improve catchment water quality.

Fill amendment significantly improved baseline removal metals from the synthetic stormwater, with gypsum and biochar increasing the removal of copper, zinc and lead, while crushed concrete had higher cadmium and lead removal than the unamended control.

The effectiveness of fill amendment on biofilter performance was rate dependent, with most of the pollutants examined showing a positive correlation with fill amendment, indicating that higher application rates tended to have a greater influence on the biofilter's pollution removal efficiency. For instance, rates of ≥18% w/w gypsum increased TP removal to above that achieved by the unamended control.

Gypsum and crushed concrete significantly reduced the quantity of TSS discharged from the biofilter columns, in comparison to the unamended control. Gypsum amendment had a median reduction of 97.1%, while crushed concrete was slightly less effective with a median reduction of 84.0%. Fill amendment, especially with gypsum, could therefore be an effective solution for minimising sediment release during biofilter establishment, which is a recognised problem for street biofilters City’s and could be an important factor in meeting local TSS reduction targets of 85% reduction as established under the City’s DCP targets.

Amendment significantly impacted fill and biofilter system hydrological performance, with low rates of amendment tending to increase hydraulic conductivity in comparison to the unamended control. Increased conductivity was primarily attributed to the addition of course particulates by the amendment fills, which reduced bulk density and increased soil porosity. Careful matching of the particle size distribution of the fill amendment with that of the base filter fill should overcome the issue of increasing fill conductivity. A 30% w/w gypsum and biochar amendment decreased median hydraulic conductivity to below the baseline of the unamended control and were, therefore, the only amendment treatments that were compliant with the CRC (2015) conductivity guidelines. These hydrological results are valuable findings for understanding the action of fill amendment on overall system performance, as amendment does not act on pollution removal in isolation and elevates hydrological flows to above optimal levels.

Overall, gypsum amendment at rates of ≥ 20% w/w are recommended for application in field biofilters as it mitigates against TSS release and promoted enhanced nutrient and metal removal, without adverse consequences on fill hydraulic conductivity. High rates (~30% w/w) of crushed concrete could also be applied, as it had a similar influence to that of gypsum; however, further research is needed to mitigate against crushed concrete increasing fill conductivity above optimal levels.

Chapter 6: Pollution removal efficiency with amendment layer thickness

6.1. Introduction

Experiments were carried out using columns filled only with amendment material with a typical unamended column as the control in order to assess the impact of amendment layer thickness and therefore quantity on pollutant removal. This was achieved by having a series of take-off points for sequential sample removal from each level, as shown in Figure 101 and Figure 102. The multi-port column design allowed for the pollution removal pathway of the biofilter to be established, highlighting areas with the highest and lowest removal potential. These results had the potential to be extrapolated back to the ideal concentration of amendment material to be used in field units.

6.2. Method

6.2.1. Column apparatus

A series of six multi-port biofilter column simulation units were established; made of 1400 mm length black PVC plastic with an internal diameter of 67 mm (Figure 101). Along the length of each column were six valved sample ports, spaced 200 mm apart, except for the second port from the bottom, which was 300 mm from the base outlet (Figure 102) (Ak and Gunduz, 2013).

Figure 101: 1200 mm length multi-port biofilter simulation column apparatus with a valve regulated outflow ports

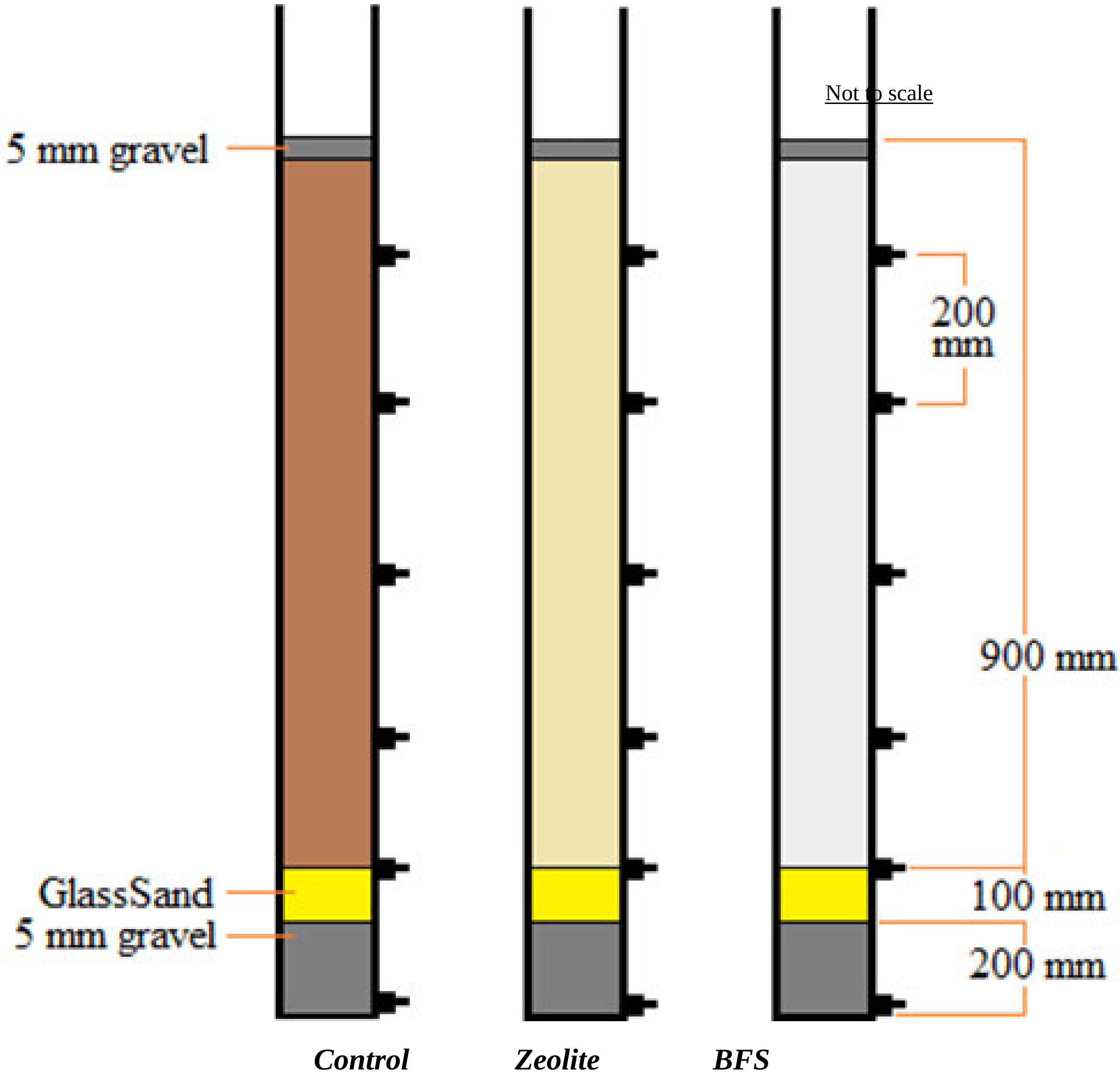


Figure 102: Sectional schematic of multi-port biofilter simulation showing arrangement and layering

6.2.2. Fill

The columns were filled as per the standard method established in chapter 2. All column treatments had identical drainage, transitional and mulch layers and differed in terms of the 900 mm filter layer (Figure 102), which was filled with either:

i. **Control** – unamended filter layer as used in chapters 4 and 5
ii. **Granular blast furnace slag** filter layer, as used in chapter 5
iii. **Zeolite** filter layer, 2-3 mm grade was used, which was coarser than the zeolite employed in chapter 5, in order to enhance water flow through the homogeneous filter layer.

Only BFS and zeolite fill amendments were examined, as the biochar, crushed concrete and gypsum were demonstrated to have hydrological properties that interfered with the experiment. 100% crushed concrete fill showed very high infiltration and flow rate through the column, prohibiting extraction from the upper sample ports of a sample of sufficient volume for analysis. The gypsum and biochar columns showed the opposite property with impractically slow drainage times in comparison to the control experiment.

6.2.3. Dosing

Synthetic stormwater was added into the column to create and sustain a 100 mm hydraulic head (ponding depth) in order to maintain the simultaneous abstraction of samples from all ports. Approximately 1.8 L of water in total was applied to each column and allowed to filter through the substrate medium. This volume was equal to the theoretical runoff volume for a biofilter with a surface area of 67 mm as per Equation 1 in chapter 2, with an additional 0.4 L volume in order to maintain the constant hydraulic head.

Previous research has identified ponding depth of biofilters to be an influential factor in determining biofilter performance (Guo, 2013, Davis et al., 2009), with depths ranging from no ponding to 450 mm (Table 27). The hydraulic head selected simulated the City’s street biofilter designs, where a 100 mm depth is not generally exceeded for safety reasons.

Table 27: Ponding depths of field and laboratory scale stormwater biofilter systems reported in the scientific literature

Ponding depth (mm)	Reference
24	(Hunt, 2003)
100	(Ak and Gunduz, 2013)
200	(Guo, 2013)
300	(Brown et al., 2009)
150-450	(Davis et al., 2009)

The biofilter column simulations were all monophasic, allowing for sample extraction from the simple hydraulic pathway. Column saturation mitigated against the influence of edge effect in these narrow diameter columns (Lewis and Sjöstrom, 2010).

6.2.4. Sample collection

A 60 mL water sample was collected from each of the lateral ports as the hydrological front entered them. The upper ports were only opened for sampling, while the base outlet remained open throughout the experiment, as per a general test design by Davis et al. (2003).

The samples were pre-treated in a Sigma 2-7 centrifuge at 4000 rpm for 15 minutes in order to separate any sediment dislodged by the extraction process. The supernatant was decanted into transport bottles and sent for analysis at ALS laboratories as per standard procedures.

Samples were analysed for heavy metals and metalloid arsenic concentrations. Nitrogen and phosphorus analyses were omitted, as results in the previous chapters indicated that design variations primarily influence the nutrient parameters.

Following collection, the columns were re-dosed, to continue the experiment while the fill was uniformly saturated. There was a total of two dosing events, one day apart.

6.2.5. Statistical analysis

Data analysis was performed as per standard methods described in chapter 2, with the inclusion of line graphs which depicted the changes in pollutant concentration as the stormwater passed through the columns. Percentage reductions were also calculated between port depths, for example; in calculating the removal performance at 500 mm depth, the pollutant concentrations of the 300 mm depth was used as the initial concentrations, as per Equation 5

Equation 5 $$retention\ (\%) = \frac{effluent_{300} - effluent_{500}}{effluent_{300}} \times 100$$

The metal removal performance between the 100- and 900-mm port depths were pooled for statistical analysis, to allow for the comparison between the fill treatments via Kruskal-Wallis test. Depths below 900 mm were excluded due to the difference in fill as depicted in Figure 102.

6.2.6. Leaching potential

Biofilters are designed to capture and contain stormwater pollutants, however, under some circumstances pollutants can leach from the biofilter system. Although, the ultimate fate of the pollutants in the column simulation was outside the scope this study, leaching, where higher concentrations were discharge than were initial dosed were observed on several occasions (particularly for copper), and warranted investigation to understand the cause of these leaching events. The leaching potential of the fills was analysed to provide insight into the sources of elevated metal ion concentrations found in some samples, and was explored through two experimental approaches:

i. **Fill sampling**, where a representative sample, in terms of material composition, was collected to fill a 150 mL glass sample jar. These samples were analysed for total metals by the ALS Environmental Laboratories.
ii. **Leachate sampling** followed the field leach test method developed by the United States Geological Survey, which involved suspending and vigorously mixing a soil sample in water to extract/leach ions from the test fill (Hageman, 2007). A 25 g air-dried sample of each fill was suspended in 500 mL of deionised water contained within a 1 L plastic bottle (Figure 103). The bottle was vigorously hand-shaken for 5 minutes, then allow to rest for 10 minutes to settle the soil suspension

Figure 103: Experimental equipment used in the USGS field leach test method

A 100 mL subsample of the settled leachate was extracted with a 100 mL pipette and decanted into a plastic funnel lined with a grade 1 Whitman laboratory filter paper (Figure 104). A 60 mL subsample of the filtrate was collected and prepared transport and analysis as per the standard method outlined in chapter 2. Leachate samples were analysed for dissolved heavy metals and metalloid arsenic concentrations, by the ALS Environmental Laboratories, in order to understand the potential concentrations of water-extractable dissolved metals in the fills.

Figure 104: Filtration of leachate solution from reaction capped shaking jar. Biochar filtration was essential as it did not settle like the other solutions

6.3. Results and discussion

6.3.1. Leaching potential

Table 28: Concentration (mg/kg) of heavy metals and metalloid arsenic in biofilter and amendment fill samples

Fill material	Metal and metalloid arsenic concentration (mg/kg)						
	As	**Cd**	**Cr**	**Cu**	**Pb**	**Ni**	**Zn**
Detection limit	5	1	2	5	5	2	5
Filter fill (control)	<5	<1	3	<5	<5	<2	9
BFS	<5	<1	8	<5	<5	<2	<5
Biochar	<5	<1	18	11	<5	12	36
Crushed concrete	<5	<1	12	20	37	10	62
Gypsum	<5	<1	4	<5	<5	8	8
Zeolite	<5	<1	<2	<5	14	<2	23
Transitional fill (Glass Sand)	<5	<1	10	17	28	3	70

Table 29: Concentration (mg/L) of heavy metals and metalloid arsenic leached from the fills and amendment agent samples

	Metal and metalloid arsenic leachate concentration (mg/L)						
	As	**Cd**	**Cr**	**Cu**	**Pb**	**Ni**	**Zn**
Detection limit	0.001	0.0001	0.001	0.001	0.001	0.001	0.005
Filter fill	<0.001	0.0014	<0.001	0.077	<0.001	0.008	0.018
BFS	<0.001	0.0008	<0.001	0.014	<0.001	<0.001	<0.005
Biochar	0.002	0.0013	<0.001	0.028	0.006	0.002	0.015
Crushed concrete	0.001	0.0007	0.002	0.028	<0.001	0.005	0.01
Gypsum	0.001	0.0008	<0.001	0.013	0.002	<0.001	<0.005
Zeolite	<0.001	0.0013	<0.001	0.042	<0.001	0.006	0.009
Transitional fill	<0.001	0.0036	0.001	0.078	0.002	0.025	0.04
Gravel	<0.001	0.0021	<0.001	0.023	<0.001	<0.001	0.005

The biofilter fills had relatively low levels of metals within their matrices, as they tended to be equal to or less than the detection limit. The glass sand transitional and amendment fills all tended to have equal or greater availability of metals in comparison to that of the unamended filter fill control, with crushed concrete and biochar tending to have the highest initial concentration of metal ions (Table 28).

Despite the elevated initial concentration of metals in some of the fills, leachability was relatively low, with maximum leachate concentration being less than 0.08 mg/L and leachate concentrations typically being equivalent to the detection limits. There were a few exceptions, most notable the transitional sand which tended to have higher leachability relative to the unamended filter fill control, for instance, zinc was more than twice the concentration than the filter fill (Table 29). Also, copper tended to be highly leachable across all materials tested.

6.3.2. Pollution removal performance

Table 30: Final pollutant concentration and removal efficiency by the BFS, zeolite and unamended control multi-port biofilter simulations

Pollutant parameter	Pollutant conc. synthetic stormwater	Pollutant conc. (median) after biofiltration (mg/L)			Removal efficiency (median) for biofilter simulation (%)		
		Control	BFS	Zeolite	Control	BFS	Zeolite
Arsenic	0.03	0.012	0.006	0.0075	60	80	75
Cadmium	0.013	0.0043	0.0017	0.00085	67	87	93
Chromium	0.05	0.0025	0.059	0.05	95	-17	1
Copper	0.14	0.25	0.19	0.14	-78	-35	0.71
Lead	0.3	0.004	0.013	0.031	99	96	90
Nickel	0.07	0.046	0.025	0.029	35	64	59
Zinc	0.69	0.51	0.17	0.044	26	75	94

6.3.2.1. Dissolved-phase heavy metal removal

6.3.2.1.1. Cadmium

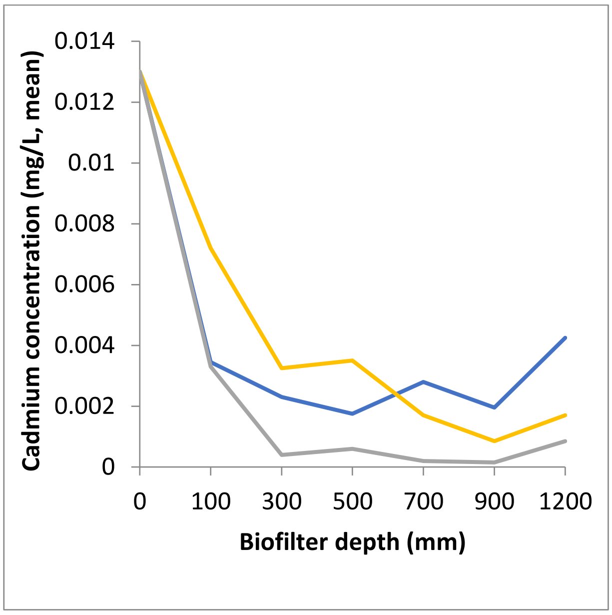


Figure 105: Outflow cadmium concentration with depth from unamended control (blue line), BFS (orange line) and zeolite (grey line) biofilters

There was a general decline in cadmium concentrations in column outflows with filter fill thickness, with 67%, 87% and 93% reductions occurring by the 1200 mm discharge depth, for the control, BFS and zeolite treatments respectively. The greatest removal efficiency occurred within the first 100 mm, with percentage reductions of 73.5%, 74.6% and 44.6% occurring respectively (Figure 105). This is an important finding as it highlights the most active area for cadmium capture, with the application of fill amendment should be applied to this region to promote enhanced pollution removal performance.

Between the 100-900 mm sampling ports, there was a general decline in cadmium concentration, for all the treatments, with the highest removal of 93% and 99% at the 900 mm port for BFS and zeolite respectively. The control had the greatest removal efficiency at the 500 mm depth, with a mean removal of 87% (Figure 105).

There was an increase in discharge concentration below the 900 mm depth, which was associated with the leaching of cadmium from the Glass Sand, as it had a higher leaching potential than the other fills tested (Table 29).

Overall, cadmium concentrations in the outflow stormwater conformed to the 95% protection ecological level for the zeolite and BFS treatments at the 900 mm port, which dropped to compliance with the 90% level at the 1200 m discharge point. The control biofilter was able to achieve the 90% protection level at the 900 mm port level, but leaching from the glass sand resulted in non-conformity at the final discharge point.

There was a statistically significant ($p = 0.02$) difference between the column fill treatments, with zeolite having consistently lower cadmium concentration than the other fill treatments (Figure 105). The difference in the absorptive capacity between the fill treatment likely accounts for this variance, with zeolite having a maximum cadmium absorptive capacity of between 3-33 mg/g (Li et al., 2019, Wang and Peng, 2010, Singh et al., 2000), while BFS had maximum cadmium sorption of 5 mg/g (Nguyen et al., 2018).

6.3.2.1.2. Nickel

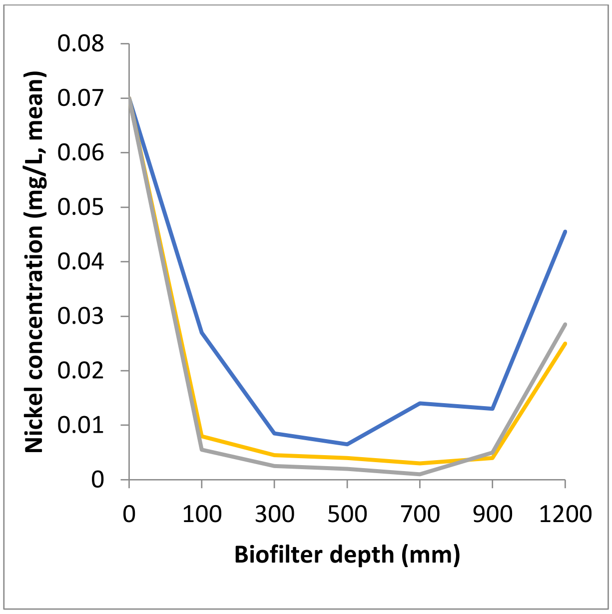


Figure 106: Outflow nickel concentration with depth from unamended control (blue line), BFS (orange line) and zeolite (grey line) biofilters

Nickel removal performance tended to increase with filter fill thickness to a point where leaching resulted in increases in discharge (Figure 106). All fill treatments had a very efficient removal within the first 100 mm, with 61.4% 88.6% and 92.1% removal respectively (Figure 106). The BFS and zeolite had greater removal than the unamended control with only 100 mm of fill. These results are important findings as they highlight the most active area for nickel capture, and the application of fill amendment in this region will promote enhanced pollution removal performance.

Nickel continued to be removed to the 700 mm depth for the BFS and zeolite treatments, achieving a maximum removal of 95.7% and 98.6%, while the unamended control had a maximum removal performance of 90.7% at the 500 mm depth. The stormwater biofilters had final nickel removal performance of 35%, 64%, and 59% for the control, BFS and zeolite filled biofilter columns.

There was a statistically significant (p = 0.006) difference between the fill treatments, which was most likely due to the greater absorptive capacity that BFS and zeolite had for nickel, with the literature showing that these fills are capable of upwards of 95% removal efficiency under similar physiochemical conditions (El-Dars et al., 2015, Rajic et al., 2010).

Again, there was a rise in nickel concentration from the transitional fill. The glass sand had relatively low levels of total nickel within the sand matrix (3 mg/kg), however, of the nickel available, it appears to be in a readily leachable with highest leaching rate (0.025 mg/L) of any of the fills tested (Table 28 and Table 29). Regardless of the increase, available calcium makes nickel less ecotoxic, and so all fill treatments at all depths were below the hardness-modified 95% ecological protection guideline value as per Table 7.

6.3.2.1.3. Zinc

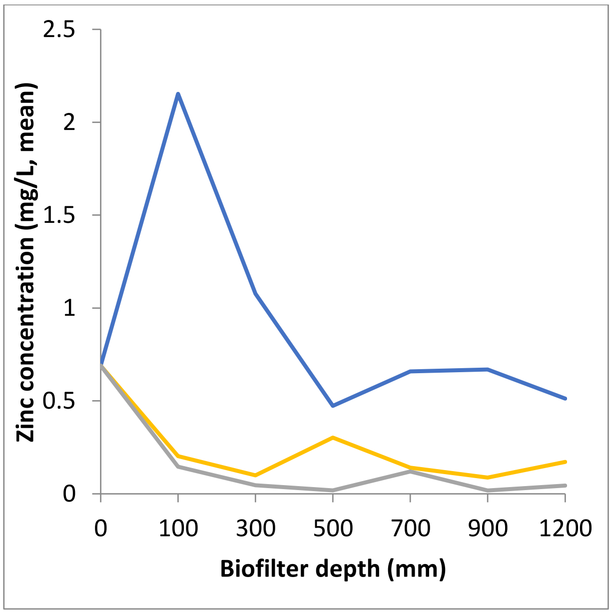


Figure 107: Outflow zinc concentration with depth from unamended control (blue line), BFS (orange line) and zeolite (grey line) biofilters

There was a 26%, 75% and 94% reduction in zinc concentration by the 1200 mm sampling depth for the control, BFS and zeolite filled biofilter columns. Only the zeolite treatment had a final discharge concentration that was below the hardness-modified 90% ecological protection level.

It is evident in Figure 107 that there is a significant ($p < 0.001$) difference between the three fill treatments, as the control had a consistently higher outflow concentration of zinc than that of the BFS and zeolite treatments and a substantial spike in zinc release at 100 mm port level. In contrast, the BFS and zeolite treatments had similar removal trends through the biofilter column (Figure 107).

The BFS and zeolite both effectively removed zinc, with the bulk of removal occurring in the first 100 mm, representing 70.5% and 78.8% removal respectively. There was over a 165% difference in zinc concentration released from the BFS and zeolite treatments in comparison to the unamended control. These results highlight that the 100 mm layer of fill amendment is more effective than the unamended control for pollution control.

The control biofilter column experienced a spike in zinc concentration at the 100 mm sampling port (Figure 107), with a maximum increase of 212%. The cause of the peak is unclear; however, it could be due to the heterogeneous nature of the biofilter fill, and that there was localised contamination of zinc in the original quarry fill where washing with river water is a standard procedure. Further, exploration of zinc removal by stormwater biofilters is warranted to understand the sources and sinks of zinc ions within the substrate matrix of the biofilter.

6.3.2.1.4. Copper

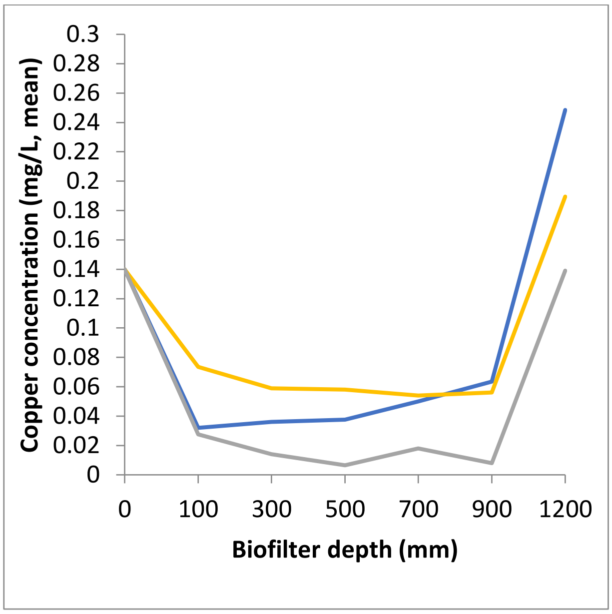


Figure 108: Outflow copper concentration with depth from unamended control (blue line), BFS (orange line) and zeolite (grey line) biofilters

Figure 108 shows that copper removal performance varied with fill type and filter thickness. All three treatments had effectively removed copper in the first 100 mm, with a mean reduction of 77.1%, 47.5% and 80.4% for the control, BFS and zeolite treatments respectively. There was a statistically significant difference ($p < 0.001$) in removal performance between the fill treatments. BFS and zeolite had a continual decrease in copper discharge, decreasing by a further 60 and 94.3%, while the unamended control progressively leached copper, increasing by 98.4% between the 100 mm and 900 mm depths. The leaching experiment showed that the unamended filter fill had one of the highest leachability of any of the fills tested (Table 29). Leaching of copper from the filter fill is a known issue with previous studies having reported meagre copper retention capacity of stormwater biofilters (Li and Davis, 2009, Macnamara and Derry, 2017).

All three treatments had an increase in discharge concentration through the transitional glass sand, which Table 29 indicates had the greatest copper leaching of any of the fills tested. As the glass sand and gravel fractions are largely inert, the source of copper must be from fines coating the particles, likely a residual from the processing of these materials. Leaching from the glass sand resulted in a net increase in copper concentrations from the columns overall, increasing by 35% and 78% for the BFS and control treatments respectively, while the zeolite treatment had a minuscule reduction of 0.71% by the 1200 mm column outlet (Table 30).

Differences in copper absorptive capacity and leachability were the most likely reasons for the variance in removal performance between the fill treatment. Both the BFS and zeolite fills have demonstrated capacity for copper removal, with zeolite's effective cation ion-exchange mechanism having a removal capacity of upwards of 24 mg/g from a mixed contaminant solution (Zhang et al., 2017b, Kyzioł-Komosińska et al., 2015), whereas, BFS has a much lower absorptive capacity of approximately 5 mg/g (Nguyen et al., 2018, Kyzioł-Komosińska et al., 2015). The sand-based filter fill likely worked through non-specific electrostatic adsorption of copper ions to negatively charged sites within the filter fill (Reddy et al., 2014), with copper binding to organic matter within the fill matrix, which was quite limited containing only 0.41% organic carbon.

6.3.2.2. Suspended- or settled-phase heavy metal removals

6.3.2.2.1. Lead

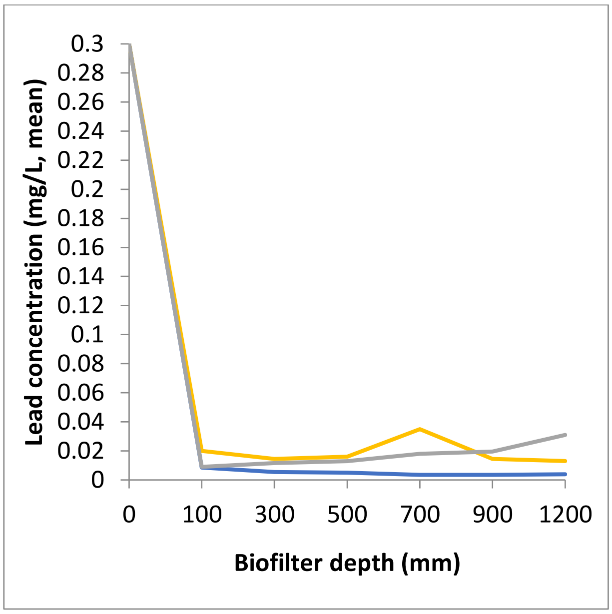


Figure 109: Outflow lead concentration with depth from unamended control (blue line), BFS (orange line) and zeolite (grey line) biofilters

Lead was effectively removed by the biofilter simulation, with 99%, 96% and 90% removal efficiency by the 1200 mm depth for the control, BFS and zeolite fill treatments. In all treatments, the bulk of this pollution removal occurred within the first 100 mm of fill thickness, where concentrations were decreased by 97.2%, 93.3% and 97% for the control, BFS and zeolite treatments respectively (Figure 109). Both the BFS and control fill treatments had final discharges that were below the hardness-modified ANZG 95% ecological protection limit of 0.015 mg/L. The zeolites progressive increase in lead concentration meant that the final discharge concentration was above the 90% ecological protection level.

There was a statistically significant ($p < 0.001$) difference in lead concentration between the three fill treatments, which is most likely attributed to differences in removal/leaching pathways experienced in the each of the treatments fill matrices.

The sand-based filter fill control had the most efficient lead removal performance, as it consistently had the lower lead discharge level than the other fill treatments with fill thickness. There was also a continual decline in lead concentration between the 100 mm to the 900 mm depths.

Below the 100 mm port, the zeolite fill had a progressive increase in lead concentration from 0.009 mg/L to 0.0195 mg/L by the 900 mm layer, which represents a 117% increase. Zeolite had the third-highest amount of lead (14 mg/kg) of any of the substrates used in the biofilter construction (Table 28), although had a low rate of leaching (0.001 mg/L), which was less than or equal to all of the other substrates used (Table 29), which may explain the progressive increase in lead concentration wit zeolite depth.

The lead concentration in the BFS treatment dropped to 0.0145 mg/L by the 300 mm sampling port, after which there was a gradually increased in lead concentration, peaking at the 700 mm sampling port with a concentration of 0.035 mg/L. Below the 700 mm port, lead concentration again decreased to 0.013 mg/L by the 1200 mm sampling port.

6.3.2.2.2. Chromium

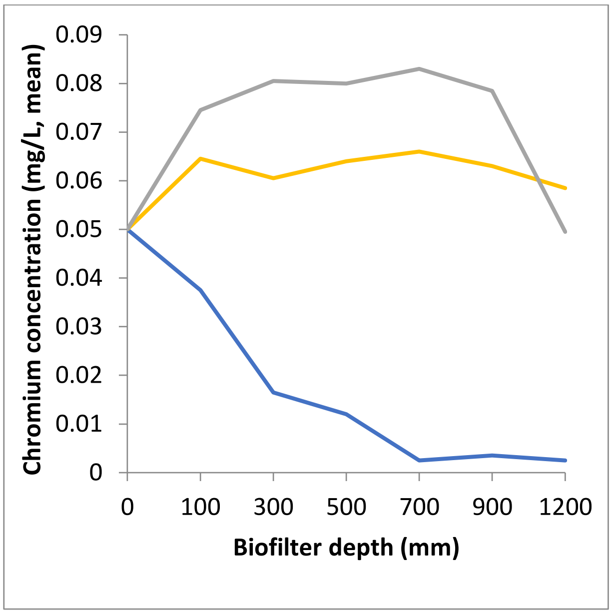


Figure 110: Outflow chromium concentration with depth from unamended control (blue line), BFS (orange line) and zeolite (grey line) biofilters

Chromium removal performance varied with fill thickness and type, with there being a statistically significant ($p < 0.001$) difference in chromium removal efficiency between the biofilter fill treatments (Figure 110). The control had a progressive decline in chromium concentrations, with a 95% removal performance by the final column outlet. Efficient removal, therefore, meant that final discharge concentration (0.0025 mg/L) were compliant with the 90% ecological protection guideline value of the ANZG (2018).

Chromium was not effectively removed by the BFS and zeolite columns, with both treatments discharging higher concentrations than were in the initial synthetic stormwater (Figure 110). The BFS and zeolite columns achieved a maximum discharge concentration of 0.066 and 0.083 mg/L at the 700 mm port depth (Figure 110), which corresponded to a 32% and 66% increase in chromium output from the biofilter at the 700 mm depth. Poor removal performance was a result of two factors:

i. **Leaching from the BFS and zeolite matrices** – BFS had an initial chromium concentration in its soil matrix of 8 mg/kg, with a leaching potential of <0.001 mg/L, while zeolite was cleaner with <2 mg/kg in its matrix and less than <0.001 mg/L being leached. These trace quantities may be left in the BFS and zeolite matrixes from the industrial processing and grading of these materials, derived from some types of stainless steel and chrome-plated machinery.
ii. **Limited sorption capacity** – BFS and zeolite both having ion removal mechanisms that favour cations, thus the anionic chromate molecules were not captured by the zeolite and BFS fills.

6.3.2.3. Metalloid arsenic

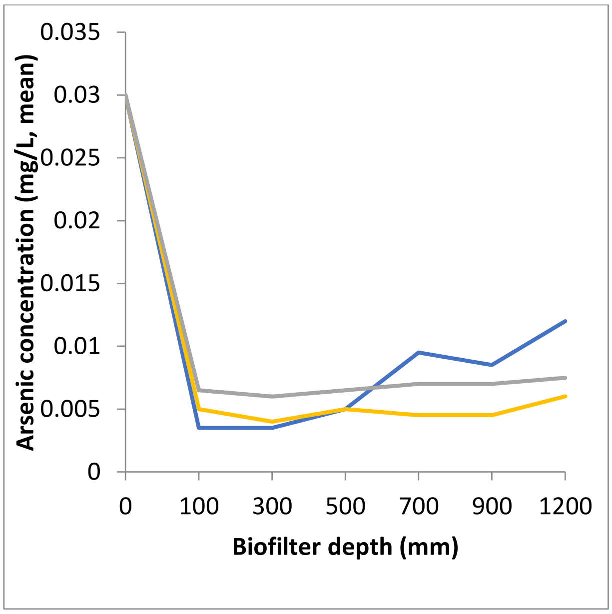


Figure 111: Outflow arsenic concentration with depth from unamended control (blue line), BFS (orange line) and zeolite (grey line) biofilters

Arsenic was effectively removed from the synthetic stormwater with a 60%, 80% and 75% removal performance for control, BFS and zeolite treatments respectively by the 1200 mm sampling port (Figure 111). Effective removal by the biofilter columns meant that for all three fill treatments, discharged concentrations below the 95% ecological protection level (0.024 mg/L) across all sampling depths.

All fill treatments showed similar removal trends, with an initial rapid decline in arsenic levels, followed by a progressive increase in discharge concentrations until the 1200 mm port (Figure 111). The first 100 mm of fill represented the greatest removal performance by the simulation columns, with 88.3%, 83.3% and 78.3% of arsenic being removed in the control, BFS and zeolite treatments respectively.

There was a statistically significant ($p = 0.006$) difference in discharge concentration between the three fill treatments for the 100 to 900 mm depths. Concentrations increased by 143% and 8% for the control and zeolite treatments, while the BFS had a 10% reduction by the 900 mm depth. A further 41%, 33% and 7% increase also occurred between the 900 and 1200 mm ports for the control, BFS and zeolite treatments, but this increase can be attributed to leaching of arsenic from the transitional glass sand.

The leaching experiment showed that only low levels of arsenic were present in the construction fills, with less than 5 mg/kg being contained within all the fills used (Table 28). As initial fill concentrations were low, so too was the rate of leaching which was at or below the detection limits (<0.001 mg/L). Still, as dosing concentrations (0.03 mg/L) were on such a trace scale, any variation in the fills arsenic concentration and leachate rate had a noticeable impact upon stormwater outflow quality.

6.4. Conclusions

At some stage in the column during sequential removal testing there was efficient removal of each of the metals, with some addition at lower levels believed, by comparison with the control, to be due to leaching from the commercial fill material provided by quarries where washing with river water was a standard procedure.

The biofilter columns, regardless of fill treatment, tended to have rapid removal of between 80-95% of metals within the first 100 mm. This is an important result as it highlights the area where the greatest pollutant removal performance occurs. It is recommended to that fill amendment is applied within this 100 mm depth to field biofilters in order to enhance the pollutant removal performance of the biofilter system.

There were statistically significant differences in the metal removal performance between the three fill treatments, with the BFS and zeolite tending to have better removal performance than the unamended filter fill control. This supports the notion that amendment can enhance pollutant removal performance, as established in chapter 5.

Leaching of metal ions from the transitional Glass Sand layer lowered the overall biofilters metal removal performance. The leaching results by the transitional glass sand fill indicate that it is most likely that if an alternative or pre-cleaned transitional fill was employed in the biofilter construction, then overall pollution removal performance for the biofilter system could have been higher than reported for this experiment and the experiments described in the previous chapter. Leaching from the transitional fill was an important result, as it highlights the issue of the impact of potentially unsatisfactory fill on overall biofilter performance. It is therefore recommended that laboratory modelling, using methods established in this thesis should be undertaken to determine initial fill pollutant removal performance before application on the field scale.

Chapter 7: Conclusions

7.1. Usefulness of laboratory column simulations

The results reported in this thesis show that column simulation experiments can play a valuable role in informing the design, operation and monitoring of street stormwater biofiltration units in warm temperate areas with the aim of optimising performance, potentially increasing service life by improving pollutant removal efficiency and retention through the addition of recycled amendment materials.

During performance efficiency experiments, local pollutant control targets as established by the City of Sydney were consistently met. The simulation biofilters had median removal efficiencies of >65% for TN and TP, which surpassed the 45% TN and 60% TP mandated reduction targets as set under the City's Development Control Plan (DCP). Heavy metal toxicants had >75% removal, with >90% removal for the potentially carcinogenic cadmium and lead pollutants, which meant that the metals generally conformed to the 90% ecological protection limits (ANZG 2018).

The laboratory research also investigated the issue of excessive and variable TSS release from biofilters during filter establishment. The study found that the TSS release can be limited in duration through the rigorous application of fill physical sizing specifications and the incorporation of recycled gypsum and crushed concrete fill amendment into the biofilter system.

The addition of largely recycled amendment substances resulted in increased biofilter pollution removal performance. Gypsum and biochar significantly increased copper, zinc and lead removal, while crushed concrete had higher cadmium and lead removal than the unamended control baseline. For example, gypsum amendment had an almost doubling of median copper removal, increasing to 80.7% compared to the 44.1% for the unamended standard biofilter simulations (control).

The laboratory experiments indicated the optimal concentration and placement of amendment that should be added to field biofilters to promote enhanced pollution removal performance. Higher amendment rates of ≥20% w/w tended to optimise pollution removal compared to the unamended control, and this material should be located within the surface 100 mm layer, as this region was demonstrated to perform the bulk of stormwater pollution capture. These are important findings for biofilter maintenance by the council, as underperforming or older field units nearing the end of their designed service life could be retrofitted with amended fill, which could rejuvenate and stem the need for replacing the entire system, thus achieving continued high-performance pollution removal and extending the system service life.

7.2. Column design innovations

A simple, compact and cost-effective laboratory-scale column simulation was developed to model the street biofilter systems as operated by the City of Sydney, in terms of the biofiltration designs and intended fill materials using a set of locally relevant monitoring parameters. The simulations were innovative in using readily available and cost-effective equipment, and designs that reduced problems such as edge effect while potentially facilitating the simulation technology transfer to the local government itself.

Standard 104 mm internal diameter PVC piping was successfully used in the column simulations, which was much smaller than that utilised in other laboratory experiments conducted in Australia; yet, removal performance results were similar to that obtained using more costly equipment elsewhere. For instance, the laboratory simulation achieved a median 84.0% and 89.0% TN removal for monophasic and biphasic design variations, which were remarkably similar to the TN removal efficiency (82%) of much larger rectangular (460 × 610 mm) soil columns (Ergas et al., 2010).

Being comprised of commercially available plumbing supplies, which have a wide range of standardised fittings, allowed the simulation units to be completely customisable and not requiring any specialised engineering skills to construct. In this thesis, the basic column structure established in chapter 2 was modified per experimental need to represent biofilter design configurations, including tandem linked units representing unsaturated monophasic and biphasic with saturated sump units which are commonly employed by the City. Furthermore, the simple columns were modified to include a series of valved extraction ports along the column's length, successfully allowing the study of pollution capture and release pathways with filter fill thickness. This showed that 60-90% removal efficiency occurred within the first 100 mm of fill, and lesser but important removal occurring throughout the filter fill layer. No other experiments in the literature attempted to identify the locus of optimal performance efficiency, which is important in siting amendment materials in the field units to optimise or prolong performance.

These design innovations allowed the simulation column technology to be readily transferable to the local council technicians, who could employ the technique to model performance of designs determined by local conditions such as ground texture and terrain or test a limited range of locally available fill material.

7.3. Column fill innovations – fill amendment

The column simulations demonstrated that the introduction of the local government fill specifications improved fill quality in terms of hydrological and pollutant removal performance. The post-specification filter fill complied with the recommended 300 mm/hr hydraulic conductivity limit for biofilters operated under temperate climatic conditions and had significantly higher median removal of lead and total phosphorus than the pre-specification fill. These findings are important as they validate the introduction by the local government of fill specifications. However, the thesis showed that while physical particulate sizing is a good starting point for identifying fill specifications, other properties such as the chemical nature of the fill and inclusion of amendment materials also need to be considered to optimise performance.

The amendment studies' findings highlighted that the recycling of largely unwanted materials, BFS, gypsum, crushed concrete, biochar and zeolite, could be used selectively to improve performance; however, the study identified several important constraints relating to concentration and placement of these materials in the biofilter.

Gypsum amendment had the best removal performance of all materials trialled, with median results significantly reducing the discharge of copper, zinc, and lead compared to the unamended control. Amendment rates greater than 20% w/w effectively reduced TKN, TN, TP, metals and TSS release and were compliant with optimal hydrological guidelines. Therefore, gypsum amendment at rates of $\geq$ 20% w/w is recommended for application to field systems within the first 100 mm of filter fill, where it will enhance ongoing pollution removal performance while reducing the initial discharge of TSS during filter establishment, which has been a frequently recorded problem, as discussed in the thesis. Although a mined gypsum was used for consistency in this research, it is suggested that recycled gypsum derived from building waste plasterboard could be used in the field amendment to better address triple-bottom-line recycling considerations.

Experiments in chapter 5 showed that further research into the influence of amendment on fill hydraulic conductivity is needed, as conductivity tended to be increased to above optimal levels with increased amendment rate of some materials, particularly BFS, zeolite and crushed concrete, which would limit their application as fill amendments in field systems. Further research to identify optimal particle size, dosage and placement is needed to overcome the elevated hydraulic conductivity associated with some amendment configurations.

Crushed concrete amendment at rates of up to 30% w/w showed promise for enhancing the biofilter system's pollutant removal performance; with improved removal for TKN, TP, and metals compared to the unamended control. Although, as discussed, the crushed concrete tended to elevate hydraulic conductivity to an undesirable level, which would limit its use in a field application. To overcome this hydrological issue and to further improve the crushed concrete amendment's performance it is hypothesised that it needs to be located in the biofilter system in a well-saturated setting, so the concrete can undergo partial dissolution, liberating Ca^{2+} ions that react to precipitate out orthophosphate. A coarser crushed concrete (5-20 mm) could also be used as a sustainable drainage gravel substitute where it could act as a final TP scrubber before discharge from the biofilter system.

These are valuable findings, as they extend the understanding of fill amendment in a stormwater biofilter context; with twenty-two amendment configurations over five materials being comparatively assessed to ascertain ideal amendment material and dosage rates, which was a more extensive study than any previously reported.

7.4. Adaptation of the column method for fill quality testing

The laboratory simulation approach developed in this study can be used by local government as a cheap and effective approach for testing performance characteristics of commercial fills and their suitability for field use, thus avoiding costly remediation in the post-construction stage. The thesis highlighted the need for prior fill testing as some of the commercial fills utilised were demonstrated to be a source of TSS and metal contaminates, and would not have otherwise been identified.

The column approach will be transferred to local government, which will be achieved through publication in peer-reviewed journals and the production of technical presentations and reports.

7.5. Recommendations for upgrading of the City’s water compliance targets

The City’s pollution reduction targets are primarily based on eutrophication alone as a limiter of biodiversity, and not toxicant levels (such as those for metals) which are just as important as the nutrient parameters for degrading downstream aquatic health. Therefore, it is recommended that an index of metal parameters be included in future council pollutant control targets.

Copper and zinc should be added as heavy metal indicators with relevance to road runoff. Copper is frequently found at high levels in association with smaller amounts of more toxic yet less detectable metals in urban environmental settings, acting as a good proxy for other toxic metals. Zinc is one of the most common automotive pollutants found in water from lubricants, tyre clutch plates, car bodies and extensive galvanising of crash barriers and gantries. Therefore, it is representative of a wide range of other organic and inorganic automotive pollutants, particularly where the road system is not well designed to minimise stop-start driving and collisions. While humans have a high zinc tolerance, it is toxic at relatively low levels to many plants and animals, including the wetland species themselves which are relied upon to secure biofilter toxin removal.

7.6. Recommendations for future research

The Research Partnership agreement between the City of Sydney and Western Sydney University provided a model for future linkages between the University, with its extensive laboratory research facilities, and Councils, with their field knowledge and expertise, and acted as a foundation for later project extension to the larger Southern Sydney area where extensive urban renewal was taking place. Therefore, there are continued opportunities to perform laboratory simulation research of the City's design modifications, in order to determine performance of proposed field systems, and to develop designs with optimised hydrological and pollution removal properties.

The research highlights the knowledge gap around recycling and reuse of industrial products. For instance, even though there is over 22 million tonnes of demolition waste concrete produced annually in Australia (Edge Environment Pty Ltd, 2011), there is surprisingly very little research into the reuse of this bulky waste material, other than application as an aggregate in creation of further concrete products. Therefore, this research opens another avenue of crushed concrete reuse as a soil amendment material, showing promise as to enhance removal of metals, and stabilise soil fines reducing TSS discharge during raingarden establishment. Further research into crushed concrete amendment could explore different types of concrete, sorption of different metal contaminates and longevity of concrete aided metal removal.

Although there has been some research on addressing soil amendment in biofilters for enhancing performance, there is still much to be explored. Fill amendment showed great potential for enhancing the pollution removal performance of the biofilter designs, with different amendments providing benefits such as reduced TSS, improved removal of nitrates, phosphates, or heavy metals. Therefore, further amendment research should be undertaken, exploring a combination of the amendment materials, in order to optimise fill compositions to provide the aforementioned benefits, whilst mitigating against negative hydrological consequences. For instance, a combination of gypsum and biochar could promote effective TN and metal removal, and the inclusion of gypsum may counter the leaching of TP as seen in the biochar-only amended columns. Amendment research should also be progressed beyond laboratory simulations and into a field scenario applying the learnings gained from the laboratory to a pilot system. The gypsum fill augmentation at an amendment rate of 30% w/w, which the simulation experiments demonstrated to have the greatest potential for enhanced pollution removal and TSS stabilisation, should be trialled in field.

7.7. Final considerations

The column simulation research provided important information for the design, construction, performance-enhancement and maintenance of field biofiltration units aimed at removing metal and nutrient pollution from urban stormwater flows entering Sydney rivers, bays and groundwater storages including the Cooks River, Botany Bay, Sydney Harbour (Port Jackson) and the Botany Sand Beds aquifer.

Carried out under controlled conditions, the research addressed several key problems relating to decentralised stormwater treatment and crystallised several problems and potential research approaches for addressing these.

An overarching research paper in an international journal has already been well received and a number of post-thesis publications and reports are planned to ensure further effective transmission of important technological approaches used and the relevant findings.

In a broad sense the outcome of the research reported in this thesis will be the improvement of the quality of urban stormwater runoff returned to important receiving surface- and groundwater reserves, in the ultimate interest of ecological and human health protection, within an economically-feasible research advisory framework.

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Appendix

Table 31: Statistical difference in pollution removal performance between the tandem and singular column designs

Pollutant	p-value
Arsenic	0.004
Cadmium	0.41
Chromium	0.01
Copper	0.48
Lead	0.48
Nickel	0.01
Zinc	0.16
NOx	0.15
TKN	0.60
TN	0.06
TP	0.01

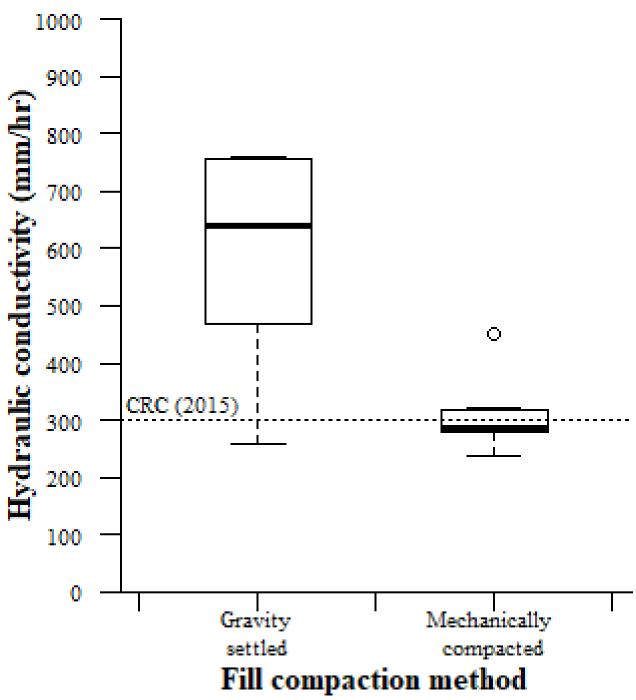

Figure 112: Influence of mechanical compaction upon the hydraulic conductivity of a sand-based filter fill. "○" indicates outlier

Table 32: Statistical difference in TSS released between monophasic and biphasic simulation biofilter columns

Purge event (day)	p-value
1	0.16
2	0.11
3	0.34
4	0.96
5	0.72
6	0.42
7	0.66
8	0.99
9	0.99
10	0.28
11	0.52
12	0.87
13	0.26
14	0.87
15	0.28
16	0.11
17	0.054
18	0.52
Overall	0.09

Table 33: Statistical difference in TSS released between the pre- and post- specification fill during the first 7 days of biofilter simulation column establishment

Days	p-value
1	0.003
2	0.003
3	0.79
4	<0.001
5	0.001
6	0.1
7	0.01

Table 34: Chemical makeup of amendment fills

Parameter	Gypsum	Crushed Concrete	Biochar	Zeolite	Blast Furnace Slag
Electrical conductivity (dS/cm)	3.6	0.6	6.4	0.007	0.05
pH (Water)	8	11	9.6	7.3	9.6
Phosphorus Colwell (mg/kg)	16	28	690	2.2	2
Phosphorus buffer index (L/kg)	66	4000	600	4	6
Organic carbon	0.17	0.47	9.5	<0.05	0.07
Total Nitrogen (mg/kg)	<200	<200	9500	260	730
Exchangeable cations (cmol(+)/kg)					
Aluminium	<0.1	<0.1	<0.1	<0.1	<0.1
Calcium	91	36	6.8	8	1.6
Potassium	0.25	0.65	44	0.6	0.03
Magnesium	2.2	0.23	8	1.4	13
Sodium	6.6	0.62	1.8	8.8	<0.03
Cation exchange capacity	100	38	60	19	1.8
Hardness Ca:Mg	41	160	0.85	5.6	12

Table 35: Final pollutant concentrations (mg/L, median) discharged from the amended biofilter columns

		Median final pollutant concentration (mg/L) in treated stormwater										
Amendment	Amendment Rate	As	Cd	Cr	Cu	Pb	Ni	Zn	NOx	TKN	TN	TP
Blast	5	0.0030	0.0005	0.0435	0.0595	0.0175	0.0055	0.0935	5.40		1.29	2.75
Furnace Slag	10	0.0020	0.0003	0.0020	0.0790	0.0030	0.0170	0.0760	1.81	1.90	2.70	0.14
	15	0.0010	0.0002	0.0020	0.0800	0.0020	0.0160	0.0520	1.74	1.60	2.70	0.11
	20	0.0010	0.0002	0.0020	0.0580	0.0020	0.0190	0.1340	0.14	1.40	1.60	0.10
	25	0.0020	0.0002	0.0020	0.0580	0.0020	0.0170	0.0580	0.11	1.50	1.60	0.12
Biochar	1.88	0.0030	0.0003	0.0250	0.0530	0.0110	0.0070	0.0650	2.58	0.90	3.70	0.33
	3.76	0.0020	0.0002	0.0240	0.0340	0.0010	0.0060	0.0140	1.74	0.80	2.50	0.41
	5	0.0030	0.0002	0.0270	0.0260	0.0020	0.0040	0.0150	2.51	0.70	3.20	0.51
	15	0.0040	0.0001	0.0200	0.0420	0.0005	0.0050	0.0180	0.38	0.50	0.90	1.08
	30	0.0030	0.0001	0.0220	0.0280	0.0005	0.0030	0.0080	0.55	0.50	1.00	1.57
Crushed	5	0.0020	0.0001	0.0080	0.0490	0.0030	0.0050	0.0260	4.88	1.50	6.30	0.16
Concrete	15	0.0030	0.0001	0.0220	0.0580	0.0020	0.0090	0.0220	4.48	1.30	5.80	0.15
	30	0.0020	0.0001	0.0220	0.0450	0.0005	0.0050	0.0060	8.46	0.90	9.40	0.08
Gypsum	0.38	0.0020	0.0003	0.0265	0.0715	0.0115	0.0140	0.0685	4.03	1.70	5.75	0.20
	5	0.0010	0.0010	0.0013	0.0535	0.0008	0.0130	0.3060	3.60	1.20	4.80	0.06
	15	0.0020	0.0002	0.0013	0.0360	0.0005	0.0065	0.0260	10.26	1.30	11.55	0.09
	30	0.0020	0.0003	0.0030	0.0290	0.0005	0.0055	0.0260	9.66	1.20	11.00	0.08
Zeolite	5	0.0030	0.0003	0.0095	0.0470	0.0230	0.0090	0.1045	4.65		1.10	2.36
	10	0.0030	0.0003	0.0020	0.0620	0.0040	0.0180	0.0500	0.01	2.00	2.30	0.14
	15	0.0020	0.0002	0.0020	0.0960	0.0020	0.0210	0.0530	0.18	2.00	2.50	0.14
	20	0.0020	0.0002	0.0030	0.0600	0.0030	0.0200	0.0720	2.54	1.70	4.60	0.14
	25	0.0020	0.0002	0.0030	0.0630	0.0020	0.0130	0.0340	0.01	1.50	1.60	0.11

Table 36: Percentage composition amended fills samples

Amendment	Rate (%w/w)	>2 mm	1-2 mm	850 µm-1mm	425 – 850 µm	75 – 425 µm	<75 µm
Unamended control	NA	4.0	0.9	0.3	21.8	71.3	1.8
Biochar	NA	14.1	18.2	2.3	21.6	30.2	13.5
	1.88	3.9	1.2	0.3	21.8	70.5	2.0
	3.76	4.4	1.5	0.4	21.8	69.7	2.2
	5	4.5	1.7	0.4	21.8	69.2	2.4
	15	5.5	3.5	0.6	21.8	65.1	3.6
	30	7.0	6.1	0.9	21.8	59.0	5.3
Blast furnace slag	NA	2.9	27.6	13.0	38.5	15.7	2.3
	5	3.9	2.2	0.9	22.6	68.5	1.8
	10	3.9	3.5	1.6	23.5	65.7	1.9
	15	3.8	4.9	2.2	24.3	62.9	1.9
	20	3.8	6.2	2.8	25.1	60.2	1.9
	25	3.7	7.5	3.5	26.0	57.4	1.9
Zeolite (fine grade)	NA	9.4	40.7	3.7	19.0	19.9	7.3
	5	4.3	4.8	0.6	21.5	66.1	2.4
	10	4.5	4.8	0.6	21.5	66.1	2.4
	15	4.8	6.8	0.8	21.4	63.6	2.6
	20	5.1	8.8	1.0	21.2	61.0	2.9
	25	5.3	10.8	1.1	21.1	58.4	3.2
Zeolite (coarse grade)	NA	17.5	76.0	4.0	0.1	2.4	0.0
	5	4.7	4.6	0.5	20.7	67.8	1.7
	10	5.3	8.4	0.7	19.6	64.4	1.6
	15	6.0	12.1	0.8	18.5	60.9	1.5
	20	6.7	15.9	1.0	17.5	57.5	1.5
	25	7.4	19.7	1.2	16.4	54.0	1.4
Gypsum	NA	11.0	8.9	2.3	10.7	51.0	16.1
	0.38	4.0	0.9	0.3	21.8	71.2	1.9
	5	4.3	1.3	0.4	21.3	70.2	2.5
	15	5.0	2.1	0.6	20.1	68.2	4.0
	30	6.1	3.3	0.9	18.5	65.2	6.1
Crushed concrete	NA	0.0	24.4	4.3	24.2	41.3	5.7
	5	3.8	2.0	0.5	21.9	69.8	2.0
	15	3.4	3.2	0.7	22.0	68.3	2.2
	30	2.8	7.9	1.5	22.5	62.3	3.0

Table 37: Pearson's correlation between biofilter pollution removal performance and amendment rate, with interpretation classes as per Devore (2015)

Treatment	As	Cd	Cr	Cu	Pb	Ni	Zn	NOx	TKN	TN	TP
Biochar	-0.21	0.58	0.28	0.52	0.52	0.65	0.54	0.7	0.33	0.71	-0.98
	Low	Moderate	Low	Moderate	Moderate	High	Moderate	High	Low	High	Very high
Blast Furnace Slag	0.01	-0.21	-0.58	-0.07	0.59	-0.36	-0.29	0.27	0.19	-0.55	0.36
	Very low	Low	Moderate	Very low	Moderate	Low	Low	Low	Low	Moderate	Low
Crushed Concrete	-0.09	0.42	-0.19	0.34	0.52	0.1	0.58	0.28	0.65	0.29	0.64
	Very low	Moderate	Very low	Low	Moderate	Very low	Moderate	Low	High	Low	High
Gypsum	-0.48	0.43	0.63	0.67	0.55	0.62	0.42	0.23	0.66	0.22	0.55
	Moderate	Moderate	High	High	Moderate	High	Moderate	Low	High	Low	Moderate
Zeolite	-0.04	-0.32	-0.83	-0.34	0.58	-0.29	0.07	-0.07	0.21	-0.07	0.29
	Very low	Low	Very high	Low	Moderate	Low	Very low	Very low	Low	Very low	Low

Table 38: Statistical difference in TSS released between crushed concrete and unamended control biofilter columns

Wash	p-values
1	<0.001
2	<0.001
3	0.02
4	0.003
5	0.005
6	0.001
7	0.001