

Copper-zeolite integrated stormwater biofilter for nutrient removal – the impact of intermittent wetting and drying conditions

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Abstract

A large-scale column study was conducted to examine the sediment and nutrient removal performance of stormwater biofilters that contained layers of novel copper-zeolite filter media. The filters were exposed to stormwater under varied dosing frequency over 33 weeks and were assessed for their hydraulic performance and their efficiency in removing sediment and nutrients. The non-vegetated sand filters with layers of copper-zeolite media (SCu filters) achieved consistently good removal of total phosphorus (87%) despite the challenging dry-wet cycles, and the effluent concentration met a long-term irrigation guideline (0.05 mg/L). The same design achieved 51% removal of total nitrogen above the Australian runoff quality load reduction targets (45%). Incorporation of *Leptospermum continentale* into the copper-zeolite filters (LCCu-T) maintained the phosphorus removal (86%) and led to a slight increase in total nitrogen removal (57%). Both designs maintained good water permeability (200 mm/h at the end of the last wet period). Copper-zeolite played a mixed role in the system: enhancing nutrients removal through precipitation and ion exchange, maintaining high water permeability, limiting the advantages of vegetation on nutrient removal. Future studies should refine biofilter design and vegetation selection to augment the performance of copper-zeolite filters by integrating the advantages of vegetation on nutrient removal.

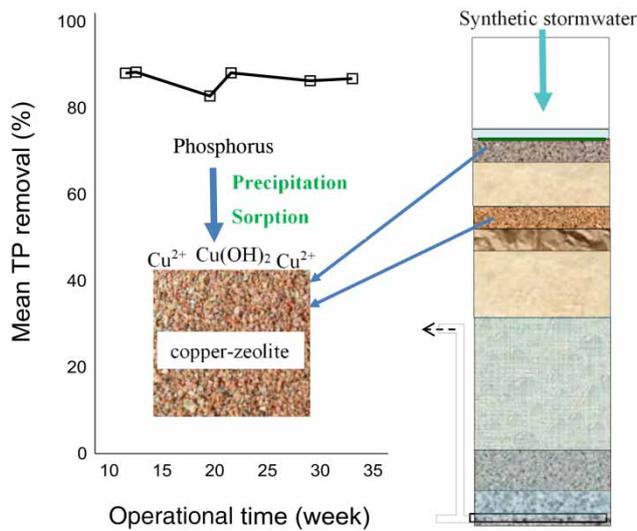
Key words: biofilter, copper-zeolite filter media, nutrients, stormwater harvesting

Highlights

- The first study investigating nutrient removal by copper-zeolite integrated stormwater biofilters.
- Consistently higher total phosphorus removal during 33-week operation with intermittent dry periods.
- Varied performance in the presence of different vegetation species.
- Adequate hydraulic performance of vegetated biofilters.

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Graphical Abstract



INTRODUCTION

Rapid urbanisation is creating a range of critical pressures related to climate change, including flooding and extreme drought, water shortages, degradation of streams and waterways. Stormwater harvesting has the potential to mitigate these issues, helping to reduce the degree of hydrologic disturbance to waterways, improve water quality and, at the same time, lower the stresses placed on precious water supplies (Wong *et al.* 2013). One concern with stormwater harvesting, however, is the presence of high nitrogen and phosphorus levels supporting algal growth in open storage, potentially increasing turbidity and possibly reaching bloom levels, and bioclogging irrigation equipment (NRMMC *et al.* 2009).

Stormwater biofilters are becoming popular for stormwater treatment. They are vegetated gravity-fed filter beds, which remove nutrients mainly by means of fine filtration, sorption, ionic exchange, precipitation, and plant/microbial uptake. Limited field and laboratory investigations (Hatt *et al.* 2009) indicate varied results for nutrient removal (ranging from good removal to net leaching), and the effluent phosphorus concentration can barely meet the long-term irrigation trigger value of 0.05 mg/L (NRMMC *et al.* 2009). Fletcher *et al.* (2007) found that vegetated soil-based biofilters were effective for reducing inflow suspended solids and phosphorus concentrations by approximately 98 and 80% respectively. Removal of at least 50% of nitrogen is also achievable but depends on vegetation selection. The removal effectiveness of nutrients by biofilters is influenced by filter media, vegetation, saturated zone, and operational conditions. Zhang *et al.* (2020) demonstrated that nutrient removal by biofilters varied to different degrees: 0.42–0.61 for phosphorus and 0.37–0.63 for nitrogen (a Nash-Sutcliffe Efficiency). The most important design characteristics influencing removal variation are filter media type (sand or sandy loam) and depth for phosphorus treatment, and vegetation and saturated zone for nitrogen treatment. In addition, operational conditions, for example extended drying, greatly influence outflow phosphorus and nitrogen concentrations (Payne *et al.* 2014). Extended drying periods can result in plant die-off, long-term damage to media microstructures and leaching of pollutants when stormwater inflows resume (Barron *et al.* 2020).

Biofilters have been shown to clog over time, with hydraulic conductivity decreasing on average by a factor of 3.6 (Le Coustumer *et al.* 2012), defeating the function of stormwater harvesting. The processes contributing to reduced hydraulic capacity or clogging include compaction of the media, downward transport of fine particles, accumulation and development of microbial community on

the surface and in pore spaces, occupation of pore space by root development, swelling and shrinkage of organic matter (Hatt *et al.* 2008).

To minimise performance variation and sensitivity, recent advances in system design include media amendments for targeted pollutant removal (Payne *et al.* 2019). Amendments containing sorptive metals such as aluminium, iron, and calcium have been introduced in recent years to increase the phosphorus sorption capacities (Yan *et al.* 2018; Marvin *et al.* 2020). Al-rich amendments such as bottom ash, red mud, and zeolite seem to be the most promising materials for phosphorus sorption amendments in bioretention media. They perform well under a range of neutral to acidic pH levels and can act as a pH buffer. Li *et al.* (2014) have developed a copper-coated natural zeolite through ion-exchange and $\text{Cu}(\text{OH})_2$ coating, followed by heat treatment. Copper-coated natural zeolite can enhance the performance of microbial removal via improved adsorption and inactivation processes during wet weather periods and via accelerated inactivation of entrapped microbes during dry weather periods. A large-scale biofilter column study showed that the integration of copper-zeolite media into sand filters increased *E. coli* removal from 1.5 log to 2.3 log (Li *et al.* 2016).

This study aimed to examine the effect of copper-coated natural zeolite, as biofilter media amendment, on nutrient and sediment removal. Triple-washed sand was chosen as the base medium in this study, reflecting the important design shift towards low-nutrient media with a higher sand content (FAWB 2009) and reliably available media reproduced from inert material, giving greater control and precision over the final media characteristics. A column study was conducted over 33 weeks to investigate the nutrient removal performance evolution over time with and without the presence of two plant types (*Palmetto buffalo* and *Leptospermum continentale*) under typical Melbourne climate conditions, i.e. twice weekly wet events and intermittent dry periods. Hydraulic performance of the biofilters was also monitored. It is expected that the design integrated with copper-zeolite may lead to an alternative method of nutrient removal under harsh operational environments for stormwater harvesting.

MATERIALS AND METHODS

Filter media specifications

As per FAWB guideline/best practice for biofilters (FAWB 2009), triple-washed sand (0.1–0.6 mm) from Daisy Garden Supplies, Melbourne, was used as the main biofilter medium. Natural zeolite (0.1–0.6 mm), known as Escott Zeolite from Zeolite Australia, was used to prepare copper-zeolite ZCu400 and ZCuCuO180, as specified by Li *et al.* (2014). In brief, natural zeolite was first treated with a sodium chloride solution to achieve Na^+ -exchanged zeolite, followed by copper sulphate solution treatment to obtain Cu^{2+} -exchanged zeolite. This prepared Cu^{2+} -exchanged zeolite was then calcined at 400 °C to obtain ZCu400; or coated with $\text{Cu}(\text{OH})_2$ followed by heat treatment at 180 °C to obtain ZCuCuO180, which contained 10 mg Cu/g media and 13 mg Cu/g media respectively, as analysed using ICP-MS.

Experimental set-up

Twenty-one mesocosms were constructed from PVC pipes (diameter 240 mm, depth 860 mm, sand-blasted inner walls) joined with a transparent Perspex top (depth 280 mm) allowing plant growth and ponding of water (Figure 1). The construction was in accordance with industrial guidelines (FAWB 2009) and other studies in this field (Bratieres *et al.* 2008). In brief, each filter (from bottom to top) had 70 mm of coarse gravel, 70 mm of coarse sand, 300 mm of sand (mixed with 68 g sugarcane mulch and 202 g pine wood chips), and 400 mm of filter media layer. The gravel

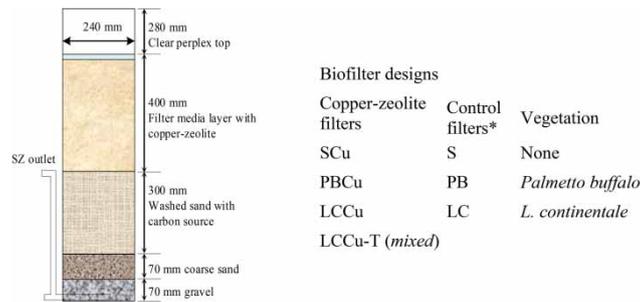


Figure 1 | Copper-zeolite biofilters: column construction (left) and biofilter designs (right: *the same designs as copper-zeolite filters but having copper-zeolite replaced by untreated natural zeolite serving as controls).

layer included a slotted drainage pipe connected to a vertical riser pipe with an outlet at the end, creating a 440 mm deep saturated zone (SZ) in the system. The top 400 mm filter media layer consisted of sand, natural zeolite and copper-zeolite (ZCu400 and ZCuCuO180) in the following two types of configuration (listed from the top, Figure 1):

- *Layered* – 50 mm of ZCu400; 100 mm of sand (the top 50 mm was ameliorated with appropriate organic matter, fertiliser and trace elements as per Australian biofiltration design guidelines (Bratieres *et al.* 2009)); 50 mm of ZCuCuO180; 50 mm of untreated natural zeolite to adsorb any leached copper; and 150 mm of sand.
- *Mixed* – 100 mm of ZCu400/ZCuCuO180 mixture (1:1 ratio in volume); 50 mm of untreated natural zeolite; and 250 mm of sand.

The ‘layered’ design was investigated without vegetation (SCu), with *Palmetto buffalo* (PBCu, the entire filter top surface was covered with grass), and with *Leptospermum continentale* (LCCu, one plant per filter). The same designs but having copper-zeolite replaced by untreated natural zeolite served as controls (called S, PB, and LC). In addition, one ‘mixed’ design planted with *Leptospermum continentale* (LCCu-T) was constructed to assess the potential for retrofitting existing biofilters with copper-zeolite media. All configurations were tested using three replicates. The biofilters were tested in a greenhouse with a clear impermeable roof admitting full natural sunlight. After construction, all filters were subjected to twice-weekly watering (13 L/filter/watering) for 6 weeks using dechlorinated tap water, to establish the plants and to achieve hydraulic compaction.

Experimental procedure

Dosing

Semi-synthetic stormwater was used in the manner reported by many others in the field (Bratieres *et al.* 2008). Stormwater was prepared in a continuously stirred tank by mixing dechlorinated tap water with raw sewage (collected from Pakenham Treatment Plant and Eastern Treatment Plant), sediment (collected from the Huntingdale stormwater wetland and sieved through a 1,000 μm sieve) and other chemicals. Target pollutant concentrations were matched to ‘typical’ Australian urban stormwater quality characteristics (NRMCC *et al.* 2009). In particular, the mean targeted total suspended solids (TSS), total nitrogen (TN) and total phosphorus (TP) were 85 mg/L, 2.4 mg/L and 0.37 mg/L respectively.

The dosing frequency was varied to simulate a typical long-term climatic pattern for Melbourne, Australia and a biofilter sized to 2% of its impervious catchment area (Bratieres *et al.* 2008; FAWB 2009). The columns were exposed to periods of ‘wet’ and ‘dry’ operations. During wet periods, each filter received a twice-weekly dosing of 13 L – equivalent to loading of 6.5 mm per event as

typically seen in Melbourne, and none at all during dry periods. To achieve consistent input concentrations for each filter, the target volume was applied in ‘pulses’, i.e. during a ‘dosing event’, each filter received roughly three pulses of water from the tank. Four dry periods were planned over the span of 33 weeks experiment: 1-week dry period (weeks 11.5–12.5), 2-week dry period (weeks 19.5–21.5), 4-week dry period (weeks 23.5–27.5, eliminated from data analysis due to sampling error) and 4-week dry period (weeks 29–33). The experiment was designed to examine the performance of copper-zeolite amended biofilters under challenging conditions since dry weather has been repeatedly shown to diminish sediment and nutrient removal (Payne *et al.* 2014; Barron *et al.* 2020).

Sampling

Six sampling events were conducted: 3 wet sampling events (on the last day of twice-weekly dosing days during normal operation) and 3 dry sampling events (on the first dosing day after simulated dry weather periods). On sampling days, 20 L synthetic stormwater simulating inflow during a 10 mm rainfall event was applied to each filter using 4 pulses (5 L per pulse). During each sampling event, a composite inflow was collected from the four pulses, while the entire effluent from each filter was collected into 20 L barrel, thoroughly mixed and sub-sampled for laboratory analysis. All inflow and effluent samples were analysed for TSS, TN and TP concentrations in a NATA (National Association of Testing Authorities, Australia) accredited laboratory.

Infiltration rate measurement

The hydraulic performance change of the filters was monitored. During each sampling event, the drop in pond water level was continuously measured over 30 min. The recorded ponding depth was plotted against time, and the gradient of the graph was taken as the average infiltration rate through the filter (Chandrasena *et al.* 2014). The final infiltration rate was corrected for a temperature of 20 °C.

Data analysis

The reported analysis was undertaken on concentration removal data calculated as a percentage of the inflow concentration. Inflow and outflow concentration data are also presented as boxplots. TSS, TN, and TP removal data were checked for normality using the Shapiro-Wilk test. Univariate analysis of variance along with post-hoc tests (Tukey HSD) was performed to test the significance of biofilter design and operational conditions for removal of these pollutants. Both removal rate and outflow concentrations were compared with Australian stormwater harvesting guidelines (NRMCC *et al.* 2009).

RESULTS AND DISCUSSION

Design factors: copper-zeolite filter media and vegetations

The removal of TSS, TN, TP was found to vary significantly with different designs ($p < 0.001$, univariate). All biofilter configurations were effective in removing TSS (around 90%), as shown in Figure 2. Exceptions, however, were PB and LC filters showing less TSS removal. This phenomenon might relate to the intensive plant activity (particularly root development) involved in plant growth and establishment over time. The root development may influence and complicate TSS removal by the filtration system in dynamic ways: temporal pore clogging due to root growth into pre-existing pores leading to improved retention of fine particles; crack formation and micro-fissuring by intermittent wetting-drying negatively impacting retention of fine particles; pore distribution change and particle

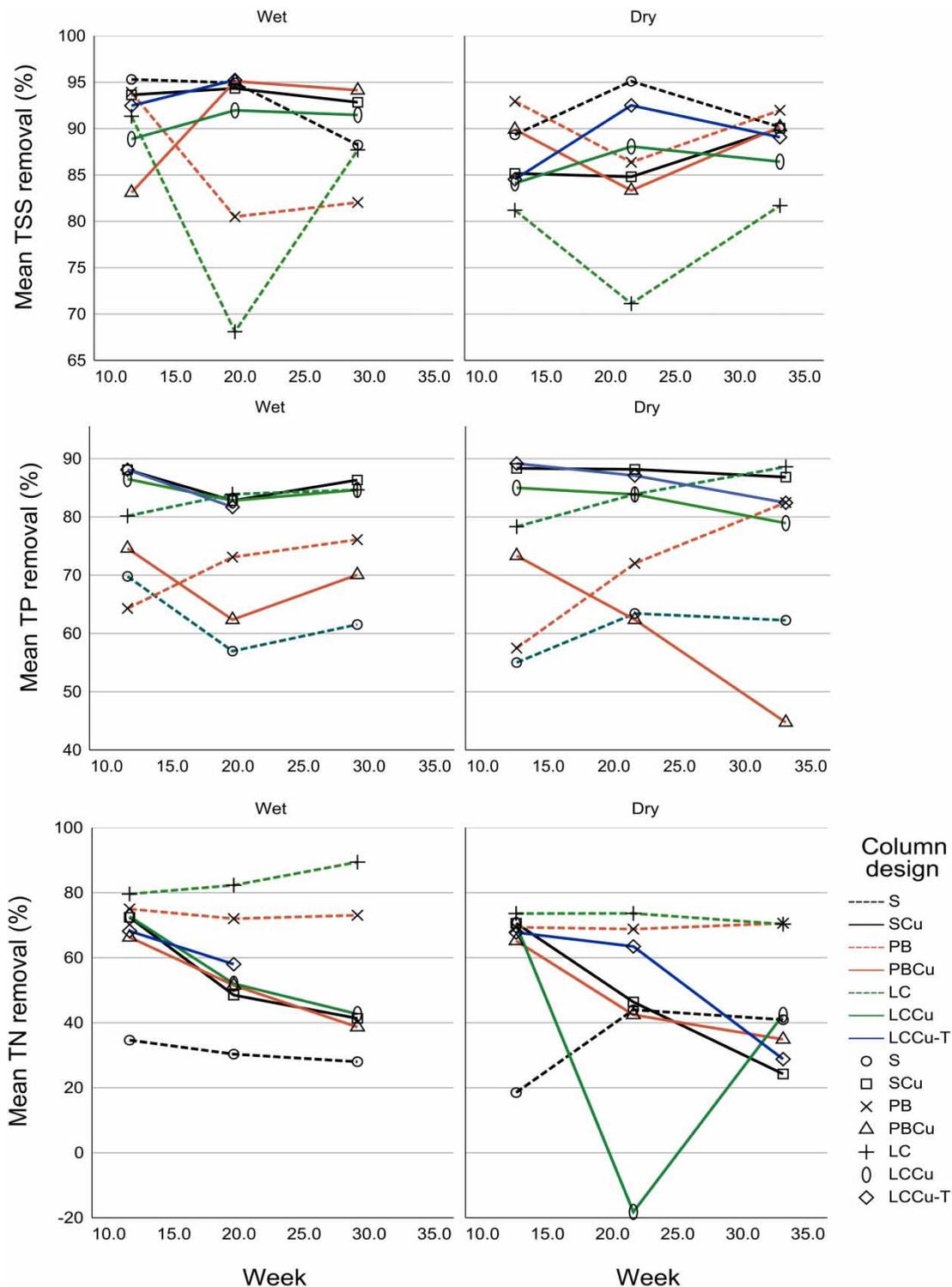


Figure 2 | TSS and nutrient removal rate for all seven designs over 3 wet sampling events and 3 dry sampling events.

movement due to mechanical effects during soil penetration, and change in interactions between soil particles in the presence of root organic matter and exudates add more complexity to the system (Bodner *et al.* 2014).

The observed TN removal by S filters (33%) in this study was the lowest among the designs, but was higher than the reported value in similar sand-based biofilters (Bratieres *et al.* 2009). In comparison to the previous study (Bratieres *et al.* 2009), the presence of a saturated zone at the bottom of the current

S filters was an important contributing factor. In addition, the incorporation of layers of natural zeolite, an excellent cation exchanger, in the current S filters was expected to improve NH_4^+ removal performance, thus contributing to TN removal.

The incorporation of copper-zeolite into S filters (i.e. SCu) significantly improved the mean TN removal to 51% meeting Australian stormwater treatment targets (45%) (ARQ 2006). This level of TN removal performance is even comparable to that achieved by the vegetated sand filters (Bratieres *et al.* 2009). Zeolite can selectively adsorb cations in series $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Cu}^{2+}$ (Langella *et al.* 2000). The Cu^{2+} -exchanged zeolite used in this study (i.e. ZCu400 and ZCuCuO180) would be expected to retain NH_4^+ more efficiently (through replacement of Cu^{2+} with NH_4^+) than raw zeolite, which could explain the superior performance of SCu (72%) over that of S filters (18–34%) in the first 12 weeks (Figure 2).

Though the presence of plant species in non-copper-zeolite filters (LC and PB) improved TN removal significantly, their presence in copper-zeolite filters (LCCu and PBCu) led to no improvement in TN removal in comparison with SCu filters. The reason could be that although the plants survived well in copper-zeolite filters, their growth was so stressed that the plants contributed limited function of taking up nitrogen. In LCCu filters, 50 mm ZCuCuO180 was layered below 100 mm washed sand topped by 50 mm ZCu400. This design, although it may protect the surface-sensitive ZCuCuO180 media from gross pollutants in stormwater and achieve deep treatment of the infiltrated water, may present a barrier for root growth due to the high concentration of active copper ion in that layer. A subsequent decommissioning study revealed that the roots of *L. continentale* plants in LCCu filters were extended only as far as the ZCuCuO180 layer, whereas the heavy mass of roots in LC extended to the bottom of the column.

With results similar to those for nitrogen, S filters showed the lowest TP removal (62%). Using copper-zeolite media instead of raw zeolite in S filters (SCu) resulted in a significant improvement in TP removal, achieving 87% ($p < 0.001$). Raw zeolite is unsuitable for the removal of dissolved phosphate due to its negligible affinity for anions. Zeolite modified with metal ion or metal oxide/hydroxide, in contrast, has shown effective removal of phosphate (Boujelben *et al.* 2008; Stojakovic *et al.* 2011; Yan *et al.* 2018) through precipitation at the solid-liquid interface. Similar processes were expected in SCu filters, i.e. trapping dissolved phosphate at the solid-liquid interface by reacting with $\text{Cu}(\text{OH})_2$ or Cu^{2+} forming slightly soluble or insoluble copper (II) phosphate. As with TN removal, the advantages of vegetation were not prominent in the copper-zeolite filters (PBCu and LCCu). TP removal performance by LCCu-T filters remained constant over the 33 weeks of operation, with negligible impact by intermittent dry periods (Figures 2 and 3). The mean TP removal rate 86% is the same as that by SCu filters.

Operational time

Operational time was found to affect TSS, TN and TP removal significantly ($p < 0.001$, univariate) though not equally for all designs. Whereas all other designs showed relatively steady TSS removal over time, LC filters and PB filters showed an initial reduction in TSS removal followed by a recovery in the subsequent sampling campaigns (Figures 2 and 3). This time-related transition phenomenon could be due to plant establishment leading to soil structure and chemistry changes, thus affecting the movement of fine particles (Bodner *et al.* 2014). Nonetheless, improved longer-term TSS removal by vegetated filters is expected due to the occurrence of surface clogging (Le Coustumer *et al.* 2012) and with pore sizes reduced by growing roots causing limited transport of fine particles (Bratieres *et al.* 2008).

Without copper-zeolite, an improvement in treatment performance of nitrogen over time was observed for LC biofilters. This temporal evolution was most likely due to the growth of the root system enhancing direct plant uptake and the development of microbial activity. However, a decrease

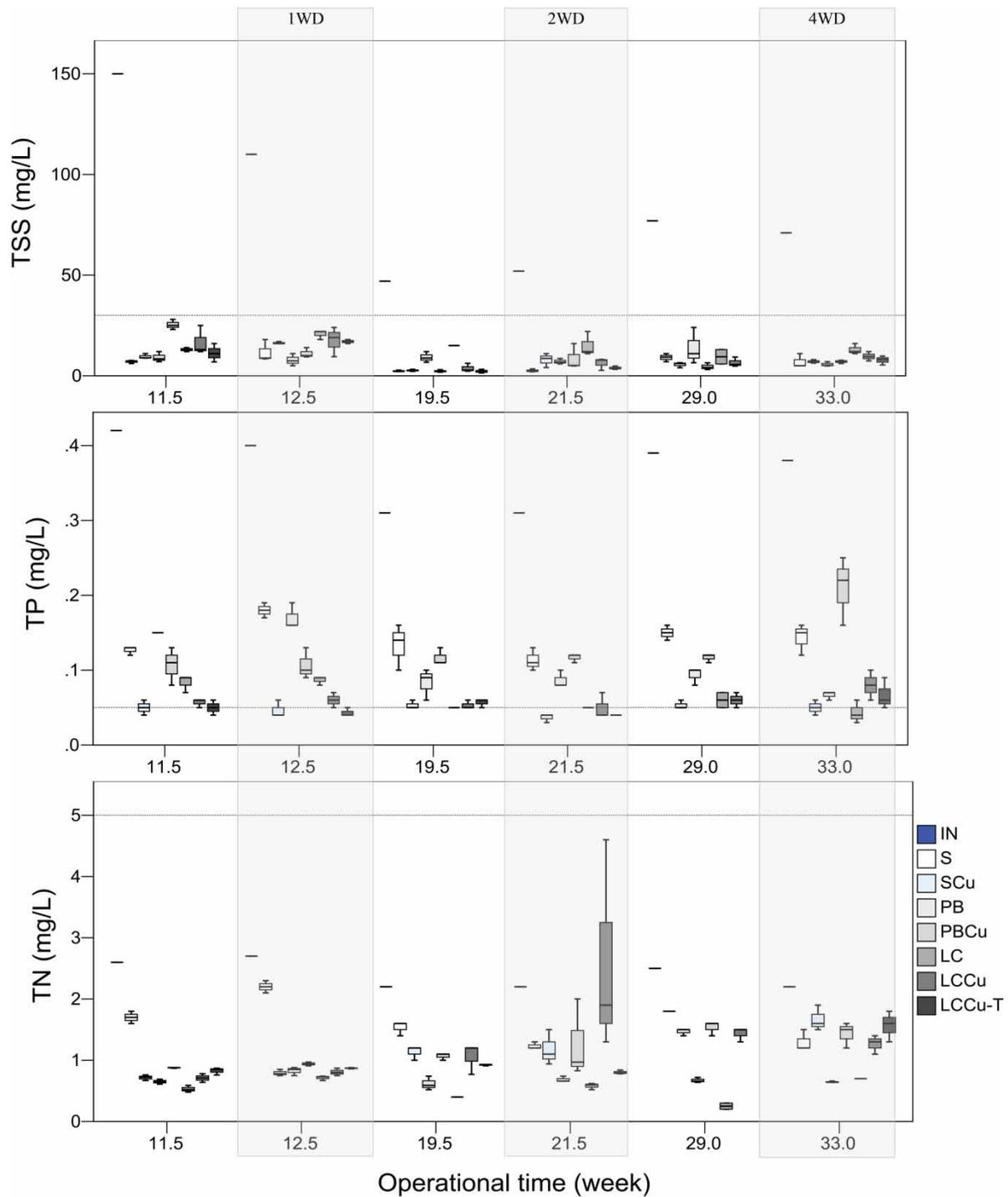


Figure 3 | Boxplots of TSS, TN and TP inflow and outflow concentrations by all designs during 3 wet sampling events (open area) and 3 dry sampling events (shaded area); WD: weeks of drying (dashed line indicates long-term trigger value guideline for agricultural irrigation water (NRMCC *et al.* 2009)).

in TN removal was observed in SCu over time (Figure 2). That decreased performance was possibly due to the accumulation and saturation of NH_4^+ and particulate organic nitrogen in the filters, with lack of adequate nitrification and denitrification due to the possible toxic environment for microbial communities. The mitigation effect through plant activity was not prominent in PBCu and LCCu filters.

TP removal by PB and LC filters showed a slight trend of increase, possibly due to plant establishment and system maturity. The TP removal by copper-zeolite filters (SCu, LCCu) remained stable and high, further demonstrating the advantages of the copper-zeolite medium for phosphorus removal.

Intermittent dry periods

Intermittent drying induced a significant reduction in TSS removal by SCu filters (from 94% during wet periods to 87% after dry periods) ($p < 0.05$) but not by S filters. Natural zeolite, known for its porous structure and high cation exchange capacity, can adsorb nutrients (K^+ , NH_4^+ etc.) and hold moisture well. Unlike S filters (the top 50 mm is raw zeolite), the top 50 mm of SCu filters is ZCu400 (Cu^{2+} -exchanged zeolite calcined at 400 °C), which may have relatively reduced moisture retention capacity due to chemical treatment. In fact, after 2 weeks or longer dry periods, all SCu filters (but no S filters) showed patches of dried surface (Figure 4), which could provide preferential flow paths for fine particles, thus reducing TSS removal efficiency. Reduced TSS removal after drying periods was also observed in vegetated copper-zeolite filters but to a less prominent extent, which could be due to the presence of root systems in these filters.

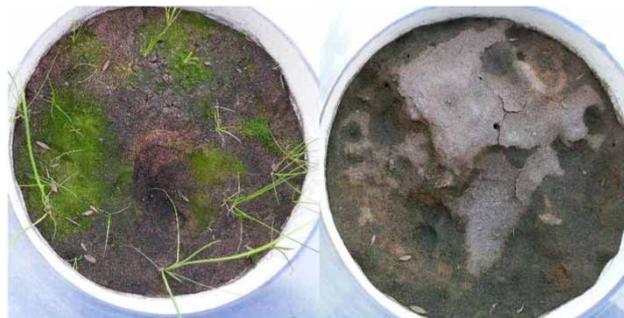


Figure 4 | Top soil surface of S (left) and SCu (right) (photos taken in week 33 after a 4-week dry period).

Intermittent drying induced significant changes in TN removal by S filters (a mean increase in 4%) and by LC filters (a reduction in 10%) ($p < 0.05$) but not for other designs. The integration of layers of raw zeolite and the presence of a saturated zone would maintain higher soil moisture and support microbial processing between inflow events. Growth of moss and weeds in S filters during a dry period (Figure 4) may have also increased nitrogen processing. The observed reduction in TN removal by LC filters after long dry periods could be due to severe moisture loss during dry periods (for example, about 5.6 L water loss after a 4-week dry period but only 1.5 L during wet periods) stressing plant activity and microbial activity. Seasonality can also play an important role in the observed lack of significantly negative effect on nutrient removal exerted by drying weather in this study: the 2-week and 4-week dry periods were simulated in a cold season (experimental temperature around 10–15 °C) when soil moisture loss would be less pronounced. Abnormally lower TN removal by LCCu filters was observed after a 2-week dry period (Figures 2 and 3): one LCCu filter was measured to have leaked TN, but the same filter performed consistently better than the two replicates during 7 out of 8 samplings.

The mean TN removal by LCCu-T after dry periods (53%) is slightly higher than that of SCu (47%), which may indicate the presence of beneficial plant activity contributing to nitrogen removal and deserves further investigation. Unlike the LCCu design, the LCCu-T filters with 100 mm ZCu400/ZCuCuO180 mixture (1:1 ratio) above 50 mm raw zeolite (capturing any leached copper ion) at the top of the biofilters may allow the roots of *L. continentale* to develop and extend into the sand

layer below, and contribute to nutrient removal. The active role of vegetation in this design could be amplified by the observed typical hydraulic behaviour of a vegetated system: reduced infiltration rate over time during wet weather but significantly recovered infiltration rate after intermittent dry periods (Figure 5). Excellent hydraulic performance is a key desired characteristic of a stormwater harvesting system offering low footprint fit-for-purpose water solutions in scenarios of limited land space.

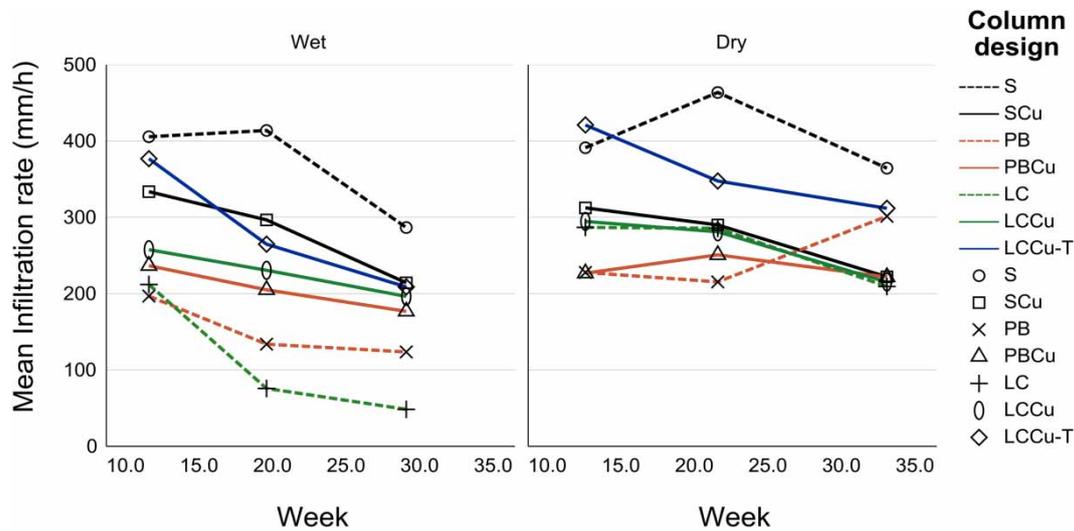


Figure 5 | Infiltration rate (corrected for a temperature of 20 °C) of seven biofilter designs over 3 wet sampling events and 3 dry sampling events.

Comparisons to several water quality targets of stormwater harvesting

Table 1 shows the mean treatment performance of seven filter designs for TSS, TN, and TP removal over 33 weeks' monitoring. The effluent TSS concentration of all designs always met the Australian stormwater harvesting guidelines for unrestricted irrigation (NRMCC *et al.* 2009). Effluent TN concentrations always met unrestricted irrigation and recreational use guidelines, which is logical since their inflow concentrations were below the same guidelines (NHMRC 2008; NRMCC *et al.* 2009). The average effluent quality regarding TP always met the Australian short-term irrigation guideline while that from SCu and LCCu-T filters met the long-term irrigation guideline (NRMCC *et al.* 2009). However, the guidelines for aquatic ecosystem protection were not met by any design, a finding which is typical for WSUD treatment devices (ANZECC/ARMCANZ 2000).

CONCLUSIONS

The performance of copper-zeolite amended biofilters with and without vegetation was monitored over 33 weeks. TSS was well removed, and effluent TSS concentration of all designs met the Australian stormwater harvesting guidelines for unrestricted irrigation. While maintaining sufficient hydraulic performance, two copper-zeolite biofilter designs (SCu and LCCu-T) exhibited constant TP removal despite challenging dry periods, and the effluent total phosphorus concentration met the long-term irrigation guideline. TN treatment performance by SCu design decreased rapidly over time, whereas the retrofitting design LCCu-T showed slightly less reduction in performance. Effluent TN concentrations of both designs met long-term irrigation and recreational use guidelines.

In a separate study, the copper-zeolite biofilters also showed consistently good microbial removal – *E. coli* removal met well the Australian unrestricted irrigation guideline and effluent *E. coli*

Table 1 | TSS, TN, TP removal performance of all biofilter designs over 33 weeks presented as mean value with one standard deviation in parentheses and compared to Australian stormwater harvesting guidelines

Biofilter design	Effluent water quality					
	TSS		TN		TP	
	Concentration, mg/L	Removal (%)	Concentration, mg/L	Removal (%)	concentration, mg/L	Removal (%)
S	6.6 (4.1)	92 (4.0)	1.63 (0.35)	32.7 (9.50)	0.14 (0.026)	61.5 (6.59)
SCu	8.2 (4.6)	90 (4.7)	1.16 (0.37)	50.6 (18.22)	0.05 (0.009)	86.8 (2.74)
PB	8.8 (4.4)	89 (7.2)	0.68 (0.09)	71.5 (3.13)	0.11 (0.040)	70.9 (8.90)
PBCu	9.8 (8.1)	89 (6.5)	1.19 (0.34)	49.8 (16.6)	0.13 (.0.042)	64.6 (11.61)
LC	14.6 (4.7)	81 (9.3)	0.56 (0.16)	76.8 (6.5)	0.06 (0.020)	83.1 (4.28)
LCCu	10.0 (6.7)	88 (5.0)	1.31 (0.89)	43.6 (41.7)	0.06 (0.015)	83.6 (3.88)
LCCu-T	8.4 (5.9)	91 (4.3)	1.00 (0.31)	57.3 (15.8)	0.05 (0.014)	85.7 (3.98)
Australian runoff quality (ARQ) ^a	17	80%	1.32	45%	0.20	45%
Short-term irrigation trigger value (STV) ^b	50		25–125		0.8	
Long-term irrigation trigger value (LTV) ^b	30		5		0.05	
Recreational water use ^c	NA		10 (nitrate-N)		NA	
Ecosystem protection – freshwater ^d			0.35		0.01	

^aAustralian runoff quality (ARQ) load reduction targets for TN, TP and TSS (45%, 45%, 80%) and equivalent effluent concentrations assuming: no inflow volume reduction, and mean inflow concentrations of 2.4 mg/L, 0.37 mg/L and 85 mg/L for TN, TP and TSS, respectively (ARQ 2006).

^bTrigger value guidelines for agricultural irrigation water (NRMHC *et al.* 2009). LTV: long-term trigger value, up to 100 years, STV: short-term trigger value, up to 20 years.

^cGuidelines for managing risks in recreational water (NHMRC 2008).

^dTrigger values for chemical stressors for south-east Australia freshwater lakes and reservoirs (ANZECC/ARMCANZ 2000).

concentrations met the primary contact recreation use (Li *et al.* 2016). This highlights the promising next generation biofilters using copper-zeolite filter media for stormwater harvesting. Future work could investigate alternative plant species along with optimal biofilter design to augment the level of pollutant removal thus achieving alternate water supplies and resilient cities of the future.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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