Effectiveness of laboratory biofiltration systems in removal of pharmaceuticals and pesticides from stormwater

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Highlights

- Pharmaceuticals and pesticides detected in stormwater at concentrations from 10-1500 ng/L.
- Removal efficiency of these contaminants with lab-scale biofiltration systems up to 90%
- Multiple chemical and biological processes occur in the biofilter: absorption, and microbial, chemical and UV degradation.

Introduction

Pollutants are deposited into the urban environments that can be washed into receiving waters by stormwater. The polluted stormwater is then directly discharged into the receiving environment via surface or underground drainage networks, which is detrimental to the water quality of the receiving aquatic environment (Brown, Keath, & Wong, 2009). Recently, there has been growing concern about the level of emerging contaminants pharmaceuticals and pesticides into streams and bays from urban areas. These compounds are of concern because many of these pharmaceuticals and pesticides can persist and bioaccumulate over months to years in waterways (Monteiro & Boxall, 2009). Since pesticides and pharmaceuticals are created with an aim to restore, modify, inhibit or kill targeted processes and pathways in plants, humans and animals, they are designed to interfere with biological systems. Therefore, there is concern about the risks of pharmaceuticals and pesticides on aquatic ecosystems. Previous studies have shown that urban stormwater transports pharmaceuticals and pesticides into streams and bays. (Boyd, Palmeri, Zhang, & Grimm, 2004; Sidhu et al., 2013). Stormwater biofilters have been implemented throughout urban areas to mitigate the impact of urbanisation on water quality of urban streams and bays by removing pollutants from stormwater. Compared to conventional treatment, biofiltration offers numerous advantages, such as reduction of flow and pollutant loads (Winston, M. Davidson-Bennett, M. Buccier, & F. Hunt, 2016), and low set-up cost and maintenance, as they are passive treatment systems (Payne, McCarthy, Deletic, & Zhang, 2019). Whilst these biofilters have been shown to effectively remove metals, suspended sediments and nutrients from urban stormwater, we still do not know whether they can remove pharmaceuticals and pesticides from urban runoff. Therefore, the objective of this study is to determine the performance of urban stormwater biofilters in removing emerging contaminants from urban stormwater, using a laboratory-scale column study

Methodology

Biofilters

Lab-scaled biofiltration systems were designed using 150 mm diameter PVC columns. The columns contained three layers of filter media: triple washed sand, a transition layer of coarse sand and a drainage layer containing gravel. There are five replicate columns, all system were planted with sedges (*Carex appressa)* and sampling was commenced after six months of maturity. To avoid pollutant concentration variation, semi-synthetic stormwater was prepared during the entire experiment. The semi-synthetic stormwater was prepared by mixing deionised water and mixing with known concentrations of sediments (taken from bottom of a stormwater wetland), nutrients these concentrations were determined by Australian urban stormwater quality as detailed (Taylor, Fletcher, Wong, Breen, & Duncan, 2005). Pharmaceuticals and pesticides concentrations were determined through our own sampling of urban stormwater in Melbourne, Australia (Table 1).

Table 1 Synthetic stormwater targeted pollutant concentrations.

Pollutant	Concentration (mg/L)	Pollutant	Concentration (ng/L)	Pollutant	Concentration (ng/L)
TSS	150	Caffeine	150	DCMU	400
TN	2.18	Carbamazepine	15	MCPA	200
NOx	0.74	Diclofenac	150	Triclopyr	60
NH_3	0.34	Fluconazole	40	2,4-D	80
TP	0.35	Xylazine	15		
FRP	0.12	Atrazine	90		

TSS- total suspended solids, TN- total nitrogen, NOx- NO_2/NO_3, TP- total phosphate, FRP- filtered reactive phosphate

Analytical method

The effluent samples from each of the five biofilter columns were collected in 1 L bottles and were filtered through a 0.2 mm glass fibre filter paper and spiked with internal standard (state what this is) to give a final internal standard concentration of 100 ng/L prior to solid phase extraction (SPE). In addition, a 1 L sample of the influent semi-synthetic stormwater was taken during each sampling run. Each inflow and effluent sample, was extracted onto 6 cc 200 mg hydrophilic-lipophilic balance (HLB) cartridges (Waters, USA), which were conditioned with 5 mL of each water, methanol and methyl tert-butyl ether (MTBE). Samples were loaded onto the cartridge at 10 mL/min and following the extraction, the loaded cartridge was dried with nitrogen gas at 15 mL/min for 10 min. Next, the samples were eluted from the cartridge with 5 mL of methanol and 5 mL solution of 1:9 (v/v) methanol/MTBE. The samples were then evaporated to dryness using a gentle stream of nitrogen and reconstituted to 1 mL with 1:1 (v/v) methanol/water. These samples are stored in darkness at 4 °C in 2 mL LCMS vials until ready for ultra-trace analysis. The samples were analysed on an Agilent An 1290 Infinity II HPLC and Agilent 6470 triple quadrupole mass spectrometer as described in Moiyadi et al. (in preparation).

Results and discussion

In total, eight inflow and 40 outflow samples were analysed for pharmaceuticals and pesticides over 75 days. Figures 1 and 2 indicate the high efficiency of the biofiltration systems in removal or degrading the pharmaceuticals and pesticides from the stormwater. As none of the pharmaceuticals and pesticides have a removal efficiency >20%, it is proposed the systems have not yet been saturated and are capable of removing or degrading them. Figures 1 and 2 indicate that these systems are quite efficient at removing these pollutants from stormwater from 70-100% for some of the compounds (xylazine, carbamazepine, fluconazole, diclofenac, 2,4-D, MCPA and DCMU) over 75 days.

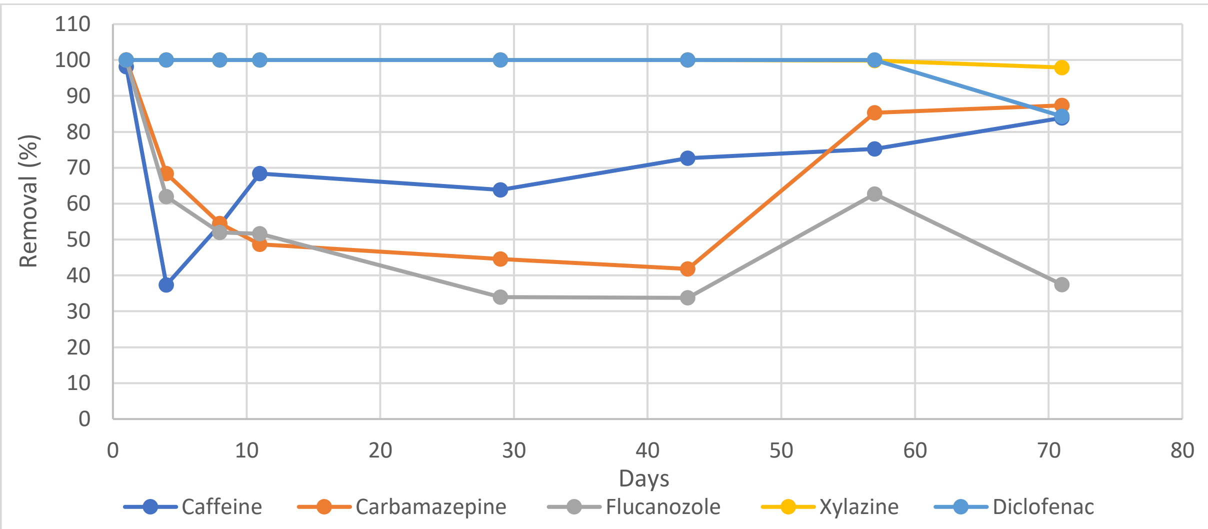

Figure 1 Lab-scaled biofiltration removal (%) of pharmaceuticals from semi-synthetic stormwater over 75 days.

Carbamazepine, diclofenac and xylazine all have a relatively higher log Kow value (octanol-water coefficient) than caffeine and fluconazole. This suggests that they are more likely to absorb onto the biofilter media and roots of the vegetation than caffeine or fluconazole. This may be why we are seeing higher removal rate. Even though caffeine has a low log Kow, meaning it is water-soluble and not readily absorbed to organic matter, from Figure 1 the graph indicates the biofiltration system can effectively remove caffeine up to 78%. This suggests that there are multiple processes likely to occur in these biofiltration systems such as microbial, chemical or UV degradation. Ubiquitous compounds such as ibuprofen and caffeine, which are commonly detected in wastewater effluent, are however of limited use as groundwater tracers, given their susceptibility to microbial degradation (Nakada et al., 2008; Tran et al., 2014).

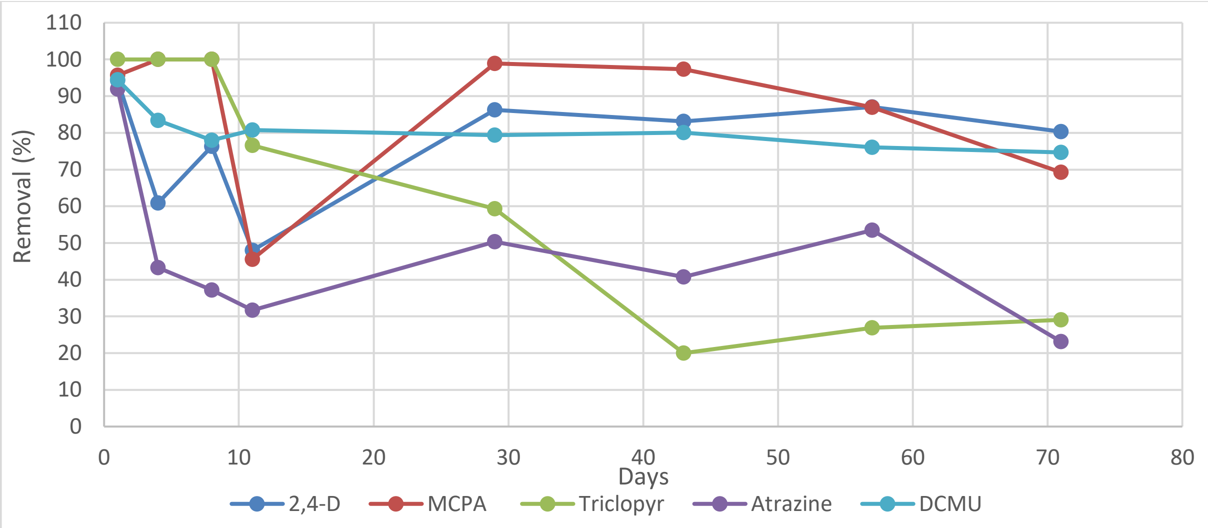

Figure 2 Lab-scaled biofiltration removal (%) of pesticides from semi-synthetic stormwater over 75 days

From Figure 2 it is determined that 2,4-D, MCPA and DCMU undergo similar chemical or physical processing in the stormwater biofiltration systems. There is not a great variation between the compounds removal efficiency over 75 days. All three compounds as well as triclopyr have similar pKa and log Kow values, with log Kow being higher than that of atrazine. This explains the lower removal % of atrazine observed over the 75 days, however not for triclopyr. As the removal of atrazine increases over the experiment duration indicates that there may be little to no absorption/degradation occurring. The results have only determined the lab scale biofiltration system's performance efficiency but further experiments need to be conducted to understand what physical and chemical process are occurring if any.

Conclusions and future work

The laboratory-scale biofiltration systems indicate promising removal rates of pharmaceuticals and pesticides with up to 95% of pharmaceuticals and 90% of pesticides being removed from urban stormwater. We plan to now conduct further analysis and experiments to identify the key removal degradation processes that these emerging compounds may undergo. This understanding will enable us to model the removal of emerging contaminants in urban biofiltration systems.

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