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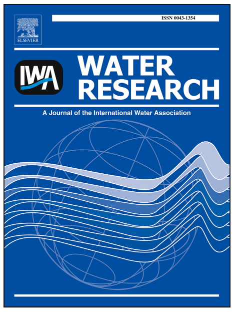

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Predicting long term removal of heavy metals from porous pavements for stormwater treatment

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Abstract

Porous pavements are commonly used stormwater management systems. However, the understanding of their long-term capacity to retain heavy metals is limited. This study aims to investigate the long-term removal of heavy metals in three different porous pavements – Porous Asphalt (PA), Hydrapave (HP) and Permapave (PP) over accelerated laboratory experiments representing 26 years with varying hydrological conditions (drying/wetting periods and flow rates). A treatment model that simulates adsorption and desorption processes was developed for the first time to predict the long-term heavy metal removal by porous pavements. Unsurprisingly, all tested porous pavements performed better in removing metals that tend to attach to solid particles (*e.g.* Pb, Al, Fe) than more soluble ones (*e.g.* Cu, Zn, and Mn). There was a general increase of heavy metal concentrations at the outlet of the pavements over time as a result of a decrease in adsorption capacity of the systems, especially after the occurrence of clogging; the soluble heavy metals removal decreased with a reduction in flow rates which was speculated to be due to more time being available for desorption of metals and breakdown of accumulated sediments. The proposed model simulated the trend, fluctuations and peaks of heavy metal concentrations reasonably well, achieving the Nash-Sutcliffe coefficient (NSE) values of 0.53-0.68 during model calibration. The model was most promising in predicting Al and Cu release from porous pavements (50%-91% of the observed data within the 90% uncertainty bands, NSE=0.44-0.74), followed by Fe and Pb (27-77% observations within the bands, NSE=0.20-0.69). Further improvements of the model are needed for it to be applicable for Zn and Mn.

Keywords: k-C* model; process-based model; clogging; adsorption; desorption

1. Introduction

Due to the increase in impervious areas alongside rapid urbanisation, urban stormwater runoff and pollution have increased significantly (Goonetilleke *et al.*, 2005;Zgheib *et al.*, 2012). This causes adverse impacts not only on downstream water quality (Jeng *et al.*, 2005), but also on stream health (Booth and Jackson, 1997). Meanwhile stormwater can also be an alternative resource if collected and treated properly. To manage stormwater issues in cities, a variety of techniques have been developed under the concept of Water Sensitive Urban Design (WSUD, also called Low Impact Development in USA, Sustainable Urban Drainage Systems in the UK, and Sponge City in China - Fletcher *et al.* (2015)). Porous pavements are one WSUD technology that can be easily retrofitted within dense urban areas, providing unique opportunities to infiltrate stormwater on site as source control measures without taking up space in urban landscape (Mullaney and Lucke, 2014).

Previous studies of the porous pavements have largely focused on their hydraulic performance (Bean *et al.*, 2007;Pezzaniti *et al.*, 2009). Indeed, the ability of porous pavement in reducing peak flow discharges and runoff volumes through filtration to the surrounding soils are the major reasons for their widespread adoption around the world (Scholz and Grabowiecki, 2007;Mullaney and Lucke, 2014). Clogging (*i.e.* the decrease of its infiltration capacity) is a problem that must be considered if permeable pavements are demanded to be used as an alternative to traditional drainage systems. For example, Brattebo and Booth (2003) tested the long term infiltration capacity of four permeable pavement systems in Pacific Northwest and found they were able to infiltrate virtually all precipitations, even during the most intense stormwater (121 mm rainfall over 72 hours). Yong *et al.* (2013) studied the clogging of three permeable pavements using accelerated laboratory experiments; results show that clogging of porous pavements varied not only by their design (Porous Asphalt clogged on surface layer while Hydrapave clogged at the geotextile layer), but also subject to the operational conditions (systems exposed to drying periods have longer lifespan).

Porous pavements are usually regarded as being successfully in removing pollutants by adsorption, filtering and biological decomposition (Beecham *et al.*, 2012;Imran *et al.*, 2013). Heavy metals are one of the major concerns due to their acute toxicity and long-term accumulation and persistence. Pagotto *et al.* (2000) tested a porous asphalt pavement at a French highway and found 74% Pb, 62% Cd, 59% Zn and 20% Cu were removed; the authors argued that higher particulate percentage of heavy metals got more removal. 38.9% Zn, 18.2% Ni and 9.4% Pb were removed on permeable pavement made of 20-mm grave sub-base (280 mm high) over several rain events in a car park of south Australia (Beecham *et al.*, 2012). Myers *et al.* (2011) assessed the impact of residence time on heavy metal retention on permeable pavement with quartzite and dolomite as base material during a large simulated event; they discovered that Zn, Cu and Pb removal was between 94 and 99% after 144 h of retention in the base layer, but the removal was lower (~61% Zn, 35% Pb and 30% Cu) during the initial stages where the residence time was only 1 hour. Dierkes *et al.* (2002) used accelerated experiments to test four different types of pavers at a rainfall intensity of 144 mm/hr as worst case scenario simulating 5 years of rain in Germany, results show that 89-98% Pb, 74-98% Cd, 89-96% and 72-97% Zn were removed, respectively; same study also suggested that basalt and gravel as subbase materials are better in removing heavy metals than limestone and sandstone materials. A recent study by Sounthararajah *et al.* (2017) found that using zeolite or basalt as bed material in porous pavements removed 41-72% Cd, 67-74% Cu, 38-43% Ni, 61-72% Pb and 63-73% Zn respectively during accelerated 80h period experiment that simulated 10 years of Sydney rainfall using uniform distribution of rainfall.

The methodologies used in the above studies were mostly simple short-term field or accelerated laboratory studies on relatively new systems, which failed to consider the impact of highly variable operational conditions (e.g. dry/wetting periods between events and varying flow rates) over life span of these systems. Brattebo and Booth (2003) conducted a rare long-term experiment (over six-year operation) on a heavily used porous pavement in a parking area, and found that both positive and negative changes of released heavy metal concentrations: Zn outflow concentration increased from 5 μg/L to 10 μg/L, while that of Cu decreased from 10 μg/L to < 3 μg/L during the six-year study period. In can be concluded that, although life span of porous pavements can go well over 25 years, the knowledge on how these systems perform in removing heavy metals over long time periods is still limited. Additionally, there is no specific study that investigates heavy metal removal processes within porous pavements which may help to understand the long-term removal performance.

There are models available to simulate the hydraulic behaviour of porous pavements; *e.g.* in the commercially available software SWMM by USEPA (Rossman, 2017), a porous pavement system is modelled as an infiltration system that combines three vertical lays (*i.e.* the surface, pavement and the storage layers). The method has also been tested by others to understand the hydraulic performance of permeable pavement systems (Zhang and Guo, 2015). To account for the clogging process that is often observed in porous pavements, Yong *et al.* (2013) proposed a simple four-parameter black-box regression model that for the first time predicts physical clogging as a function of cumulative volume and climatic conditions.

Unfortunately, there is a lack of algorithems that can simulate the pollution treatment processes within porous pavement systes. The first order kinetic decay model (also called k-C* model), serves the mostly widely used method that has also been adopted in software packages such as SWMM (Rossman, 2017) and MUSIC by eWater (eWater, 2014). However, the inadequacies of k-C* model are often mentioned due to its simplicity (*e.g.* assumption of constant k and C* value) (Kadlec and Knight, 1996;Newton, 2005). Newton (2005) successfully used a one-parameter first decay model adapted from filtration theory for wastewater treatment to predict particle removal efficiency from pavement with satisfactory, *e.g.* NSE=0.36-0.98 for low flow rates and from negative to 0.39 for high flow rates. Both empirical models and conceptual model (adapted from a sediment removal model for a sand filter) were developed by He *et al.* (2015) to predict suspend solids and phosphorus removal by a porous concrete pavement; the prediction errors were within 5.29% for two validation events. These models are however mainly for event-based predictions and do not account for specific treatment processes (*e.g.* adsorption & desorption); they are also developed for mainly sediments and nutrients, not suitable for heavy metals that undergo via different removal mechanisms. Hence development of a process-based water quality model that not only involves key treatment processes but also can simulate long-term treatment performance of heavy metal by porous pavements is required to assist in better designs of these systems.

This paper aims to fill in these knowledge gaps, firstly by understanding heavy metal removal performance of three different porous pavements (porous asphalt, hydrapave and permapave) over a long term under different conditions, and then developing for the first time a model that not only predicts long-term heavy metal removal but also explains the removal processes. The specific objectives of this study are to:

- test the treatment performance of the three porous pavements for different heavy metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) using accerlated laboratory experiments spanning over 1 year representing 26 years of operation under varying operational conditions;
- understand the impact of clogging, pavement type and flow rate on treatment performance; and
- develop, test and validate a treatment model accounting for main removal processes (e.g. adsorption and desorption) for prediction of long term removal of heavy metals;

We hypothesis that heavy metals will accumulate in the system and also get released over time from the systems, and the metal characteristics, pavement design, and hydrological conditions are the key influential factors. The proposed model accounting for heavy metal adsorption and desorption will be able to provide reasonable predictions for majority of the tested heavy metals but not good for some that have other removal processes.

2. Methods

2.1 Experimental set-up

Three porous pavement systems that are commercially available were used in this study:

- **monolithic porous asphalt (PA)** – a standard bituminous asphalt surface (40mm), underlaid by a layer of crushed aggregate (40 mm), and a highly permeable layer of open graded clean washed aggregate with >40% void space as reservoir bed (570 mm);

- **modular Hydrapave (HP)** – a thick paver made of Boral clay and concrete (80 mm), which is laid on Φ5 mm clean stone (50mm), a geotextile layer, and another two sublayers of Φ5-20 mm stone (100 mm) and Φ10-63 mm stone (250 mm);
- **Permapave (PP)** – a thick paver of Φ 10-12 mm crashed gravel (50 mm), underlaid by a sub-base layer of Φ 5-20 washed gravel (350 mm).

We used the same experimental rig (Figure 1) that has been employed in the parallel studies of the clogging and nutrient removal by the porous pavements, as reported in Yong *et al.* (2013). The rig had a 550 L tank with constant mixing, from which the inflow is evenly distributed via a distribution system (peristaltic pump + rotating sprinkler) into three separate vertical compartments representing three different pavements (each has a size of 0.9 × 0.45 × 1.95 m); three separate tipping bucket rain gauges (0.2 mm/tip resolution) were installed at the end of the system to monitor the outflow rates. Results from the clogging study (Yong *et al.*, 2013) have shown that PA and HP exhibited initial clogging (*i.e.* the ponding above the pavement surfaces overflows) after 11 years and 12 year respectively of accelerated operations under various drying and wetting conditions, while PP had no sign of clogging after 26 years. All the three systems had good performance in removing sediments, but had varying performance for nutrients removal depending on the flow rates (Yong *et al.*, 2011).

Figure 1 *The experimental set-up for testing Porous Asphalt, Hydrapave and Permapave (adapted from Yong et al. (2013))*

2.2 Experimental procedure

2.2.1 Inflow synthetic stormwater

Semi-synthetic stormwater was prepared in the 550 L tank according to the methods described previous in stormwater studies (Blecken *et al.*, 2009), with standard Australia stormwater quality (Duncan, 1999). The target concentrations of sediments, nutrients and heavy metals in semi-synthetic stormwater are presented in Table 1, together with the primary source of the pollutants.

Table 1 Semi-synthetic stormwater water quality

Pollutant	Target concentration	Primary source of pollutant added
Total suspend solids (TSS)	150 mg/L	Stormwater wetland sediment
Total Nitrogen (TN)	2.1 mg/L	KNO_3, NH_4CL, $C_6H_5O_2N$, wetland Sediment
Total Phosphorus (TP)	0.35 mg/L	KH_2PO_4
Aluminium (Al)	4.0 mg/L	standard solution
Cadmium (Cd)	0.0045 mg/L	standard solution
Chromium (Cr)	0.025 mg/L	$Cr(NO_3)_3$
Copper (Cu)	0.05 mg/L	$CuSO_4$
Iron (Fe)	3.0 mg/L	standard solution
Manganese (Mn)	0.25 mg/L	$Mn(NO_3)_2$
Nickel (Ni)	0.03 mg/L	$Ni(NO_3)_2$
Lead (Pb)	0.14 mg/L	$Pb(NO_3)_2$
Zinc (Zn)	0.25 mg/L	$ZnCl_2$

2.2.2 Dosing of the system under varying wetting/drying regimes

Over a course of one year, 26 years of operation in a typical sub-tropical Brisbane climate (average annual rainfall – 1200 mm) was simulated, under various wetting/drying conditions. Four inflow rates were simulated (Table 2), with flow A, B, C and D representing the average rainfall intensity of the 0-39, 40-59, 60-79 and 80-100 percentile groups, respectively; in addition, a 1 in 5-year design storm over 5 minutes was also chosen to simulate the typical design storm for small catchments where porous pavements are likely to be installed. These flows were estimated from the Brisbane runoff-frequency curve, which was generated using MUSIC model (eWater, 2014) and six-minute rainfall data collected between 1988 and 1997 in Brisbane.

Table 2 System inflow rates used in the experiment

Flow	Frequency (percentile range)	Flow rate (L/h/ha)	Velocity (mm/h)	Number of times flow rate was simulated	Duration of inflow each time flow was simulated (h)
A	0-39	0.6	0.2	26	96
B	40-59	2.9	1.0	26	48
C	60-79	7.1	2.6	26	48
D	80-100	60.9	21.9	26	48
1 in 5-yr storm	-	530	191	6[a]	5

[a] Occurred in Year 5.9, 8.1, 11.8, 15.6 19.5 and 23.5.

Generally, each simulated year consisted of four flow types: A, B, C and D, which were applied for 96, 48, 48 and 48 h respectively (48 h represents approximately 52 simulated days, note each flow was not applied continuously but with many dry periods – see next paragraph for details); the total amount of applied annual inflow was 1243 mm (close to Brisbane annual rainfall). The order of the flow types was applied randomly, *e.g.* in year 1, the sequence of D, C, B, A may be applied, while in Year 2 it may become the sequence of C, A, B, D. The 1 in 5-year stormwater events were simulated in Year 5.9 (Storm 1), 8.1 (Storm 2), 11.8 (Storm 3), 15.6 (Storm 4), 19.5 (Storm 5) and 23.5 (Storm 6).

To account for the drying, the inflow was not applied continuously, but with dry periods in-between each event. According to the methods described in our previous work (Yong *et al.*, 2013), it was determined that an average of 21 dry weather periods occurred during any given year in Brisbane. As such, in each simulated year, 21 dry periods were mimicked by applying fan heaters at 25 ˚C for 3 h (which removed 80% of the moisture content in the pavements that is equivalent to 4 days of natural dry – this was determined through a preliminary experiment).

2.2.3 Sampling and analysis

For each flow rate, three time-weighted samples were collected at both inflow and outflow point over the entire duration of the event to form two composite samples (*i.e.* one inflow and one outflow). The collection of samples was accompanied by pH measurement to enable early predictions to be made about the behaviour of heavy metals in the systems. Once collected, the samples were acidified, stored in fridge and then delivered to a NATA accredited laboratory for analysis of nine heavy metals in accordance with the standard methods described in APHA-AWWA-WPCF (2005): Aluminium (Al), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn); the LOR (limit of report) was 0.01 mg/L for Al and Fe and 0.001 mg/L for the rest.

2.3 Long term treatment model development

2.3.1 Proposed model algorithms

In this study the simple first order decay model (k – C* model, Kadlec and Knight (1996)) is adapted with revisions to include adsorption and desorption processes for simulation of the long-term of heavy metals from porous pavements. The basic equation of the k – C* model is:

$$\frac{C_{out} - C^*}{C_{\text{in}} - C^*} = e^{-\frac{k}{q}} \qquad 1$$

where C_{in} - inflow concentration, mg/L; C_{out} – outflow concentration, mg/L; C^* - the background concentration, mg/L; k – the event decay parameter, day/L; and q is the hydraulic loading (in this case flow rate, L/day).

Equation 1 can be rearranged and written in time-step basis for estimating C_{out}, as:

$$C_{out}(t) = C^* + [C_{\text{in}}(t) - C^*\,]e^{-\frac{k}{q(t)}} \qquad 2$$

The background concentration C^* is often used as a constant parameter (*e.g.* in MUSIC, pre-calibrated C^* values are used for treatment performance modelling for all the treatment measures (eWater, 2014)). However, we hypothesised that C^* is not constant, and may (1) decrease due to adsorption process – depending on inflow (as bench marking concentration) and adsorption rate (k_{ad}), and (2) increase due to desorption process – depending on the total amount of pollutant accumulated in the previous time step (M(t-1), g) and desorption rate (k_{des},1/L). So we proposed that:

$$C^*(t) = [C_{\text{in}}(t) - k_{ad}\,C_{\text{in}}(t)] + k_{des}\,\mathrm{M(t-1)} \qquad 3$$

Hence, the outflow concentration (C_{out}) can be estimated using Equation 4 and 5:

$$C_{out}(t) = C_{\text{in}}(t) - k_{ad}\,C_{\text{in}}(t) + k_{des}\,\mathrm{M(t-1)} + [k_{ad}\,C_{\text{in}}(t) - k_{des}\,\mathrm{M(t-1)}]e^{-\frac{k}{q(t)}} \qquad 4$$

$$\mathrm{M(t)} = \mathrm{M(t-1)} + [q_{in}(t)C_{\text{in}}(t) - q_{out}(t)C_{\text{out}}(t)]d_t \qquad 5$$

The model has three parameters: the event decay rate (k), the adsorption rate (k_{ad}) and desorption rate (k_{des}). The initial condition is $M|_{t=0} = 0$.

2.3.2 Data preparation, model calibration and validation

The model was tested only for Hydrapave (HP) and Porous Asphalt (PA); Permapave was excluded for model testing as its outflow rates were not measured properly due to the failure of the rain gauge.

During the experiment, inflow rates were controlled (Table 2) while the outflow rates were measured using tipping-bucket rain gauge (0.2 mm/tip), the flow rates were then prepared in hourly time-steps (equivalent to 1.08 simulated day, *i.e.* approximately daily time-step). However, water quality samples were not collected on hourly time-steps, but as 48 hours (52 simulated days) composite samples (see Section 2.2.3). It was therefore assumed that the concentrations within each 48 hours period did not change; *i.e.* concentrations at any hour within the period were assumed to be the same as the measured composite concentration for the 48 hour period. In this way, inflow and outflow rate, as well as heavy metal concentrations were prepared on an hourly time-step (*i.e.* simulated daily time-step) for the proposed model testing.

The model was run in a simulated daily time-step for the first half of the experiment (*i.e.* simulated Year 1-13 for HP and Year 1-10 for PA) for model calibration. At the middle of the time-step when a composite sample was collected, the simulated concentration was extracted; *i.e.* if the composite sample was taken from Hour 1- Hour 48 (excluding the drying period), the simulated concentration is extracted at Hour 24. All the extracted concentrations from simulation were compared to the concentrations at that time-step (as observed) for model testing using the Nash-Sutcliffe coefficient – NSE (Nash and Sutcliffe, 1970). 10,000 model runs were conducted for parameter calibration, with parameters values randomly sampled from uniform distributions (the ranges were informed by preliminary model runs practices – refer to Table S1 of Supplementary Material for the detail information); the use of uniform distributions was recommended by previous studies by Freni and Mannina (2010) when there is lack of parameter information.

Validation of the proposed model was performed using the second half of the experiment (which is independent of the data for model calibration). Top 1% of the parameter sets (*i.e.* 100) from calibration were chosen to generate the parameter distributions, which were then used to estimate the model prediction uncertainty (90 % probability bands) using GLUE method (Beven and Binley, 1992). It should be acknowledged that selection of 100 behavioural runs was quite arbitrary; it however still satisfied the minimum runs required by GLUE, and selecting the top 1% simulations resulted in much higher acceptability thresholds (*e.g.* in this paper NSE > 0.45 for Al, Cu, Fe, Pb and Zn) comparing to traditional urban drainage models (*i.e.* 0.0); Freni *et al.* (2008) also suggested that higher thresholds not only allow for obtaining more relevant information of parameters responsibility in modelling uncertainty propagation but also allow for a stricter verification of the model. The thresholds for Mn were however only NSE of 0.10 for HA and <0.0 for PA, the uncertainty analysis was anyway proceeded using the top 1% parameter sets for Mn.

3. Results and discussion

3.1 Treatment performance

3.1.1 Overall performance

The metal treatment performance of the three porous pavements over 26 simulated years are summarized in Table 3. All three pavements had cumulative heavy metals removal rates of over 50%; they were the most effective for Pb (84±14%), Al (79±13%), Fe (77±13%), and less for Cu (68±19%) and Zn (66±20%). Lower but highly variable removal was found for Mn (35±35%), while for Ni, net productions were observed in most of the cases which could be entirely due to uncertainty in measurements of very low inflow concentration (often of <0.005 mg/L). Cd and Cr also had very low inflow concentrations (<0.01 mg/L) and were mostly non-detected in outflow samples; as such, Cd, Cr and Ni were then excluded from future discussions. These findings have good agreement with previous studies (Pagotto *et al.*, 2000;Sounthararajah *et al.*, 2017). The different performance between heavy metals can be explained by their affinity to particulates; *e.g.* Pb, Al and Fe are easily attached to sediments in stormwater (Makepeace *et al.*, 1995) and hence can be readily retained when filtering through porous pavements; these retained metals can form stable complexes via surface complexation reactions (Bradl, 2004). Cu and Zn are largely presented in dissolved form (Makepeace *et al.*, 1995) and their retention by porous pavements usually undergo via rather weak processes such as ion exchange. Mn also has good attachment with sediments/organic matter in stormwater, and in general the removal process of Mn can be very complex in the form of Mn oxides (Bradl, 2004); the low and variable removal observed in this study was probably due to the very low inflow concentrations (*i.e.* 0.0228 ± 0.006 mg/L for Mn and 0.0032 ±0.001 mg/L for Ni).

When considering reusing treated stormwater or discharging to protect eco-system health, the degrees of heavy removal by porous pavements were insufficient since the effluent heavy metal mostly exceed Australia Drinking Water Guidelines (NHMRC-NRMMC, 2011) and trigger values for aquatic health protect and irrigation, except for Mn (Table 3). Hence it is suggested further treatment through Water Sensitive Urban Design systems (*e.g.* stormwater biofilters) (Payne *et al.*, 2015) or some advanced technologies such as using nano-fibrous material filtrations shall be used (Southararajah *et al.*, 2017).

Table 3 *Performance of three different porous pavements over 26 simulated years: average inflow and outflow concentrations before clogging (BS) and after clogging (AC)*

	Flow		Al			Cd			Cr			Cu			Fe			Mn			Ni			Pb			Zn		
			In	Out	%	In	Out	%	In	Out	%	In	Out	%	In	Out	%	In	Out	%	In	Out	%	In	Out	%	In	Out	%
Porous pavement (PP)	A	BC	3.45	0.324	**91**	0.006	N.D.	-	0.005	N.D.	-	0.270	0.063	**77**	2.98	0.383	**87**	0.024	0.018	**25**	0.004	0.012	**-200**	0.110	0.002	**98**	0.391	0.113	**71**
		AC	1.19	0.453	**62**	0.003	N.D.	-	N.D.	N.D.	-	0.079	0.086	**-9**	1.02	0.505	**50**	0.008	0.017	**-113**	0.001	0.006	**-500**	0.023	0.003	**87**	0.238	0.217	**9**
	B	BC	4.34	0.492	**89**	0.006	N.D.	-	0.006	N.D.	-	0.29	0.068	**77**	3.75	0.505	**87**	0.025	0.018	**28**	0.005	0.010	**-100**	0.132	0.002	**98**	0.397	0.092	**77**
		AC	3.02	0.581	**81**	0.005	N.D.	-	0.004	N.D.	-	0.180	0.080	**56**	2.55	0.564	**78**	0.016	0.018	**-13**	0.002	0.005	**-150**	0.072	0.006	**92**	0.309	0.207	**33**
	C	BC	5.83	0.692	**88**	0.007	N.D.	-	0.009	N.D.	-	0.355	0.069	**81**	4.90	0.637	**87**	0.033	0.018	**45**	0.004	0.009	**-125**	0.148	0.002	**99**	0.466	0.101	**78**
		AC	6.38	0.574	**91**	0.006	N.D.	-	0.009	N.D.	-	0.309	0.087	**72**	5.44	0.582	**89**	0.029	0.021	**28**	0.003	0.006	**-100**	0.155	0.004	**97**	0.402	0.186	**54**
	D	BC	5.40	1.24	**77**	0.007	N.D.	-	0.008	N.D.	-	0.303	0.077	**75**	4.44	1.05	**76**	0.029	0.019	**34**	0.005	0.006	**-20**	0.134	0.013	**90**	0.430	0.163	**62**
		AC	4.92	1.21	**75**	0.006	N.D.	-	0.007	N.D.	-	0.267	0.089	**67**	4.07	1.02	**75**	0.022	0.016	**27**	0.002	0.005	**-150**	0.129	0.013	**90**	0.367	0.191	**48**
	5-yr	BC	5.73	2.78	**51**	0.007	N.D.	-	0.008	0.004	**50**	0.333	0.160	**52**	5.07	2.48	**51**	0.028	0.025	**11**	0.005	0.004	**20**	0.135	0.058	**57**	0.436	0.237	**46**
		AC	4.75	2.18	**54**	0.006	0.003	**50**	0.007	0.003	**57**	0.250	0.132	**47**	4.04	1.81	**55**	0.023	0.017	**26**	0.004	0.004	**0**	0.148	0.066	**55**	0.373	0.211	**43**
	Total	BC	4.80	0.778	**84**	0.007	N.D.	-	0.007	N.D.	-	0.305	0.073	**76**	4.06	0.723	**82**	0.028	0.019	**32**	0.004	0.009	**-125**	0.131	0.007	**95**	0.422	0.122	**71**
		AC	4.01	0.937	**77**	0.005	N.D.	-	0.005	N.D.	-	0.215	0.093	**57**	3.39	0.847	**75**	0.019	0.018	**5**	0.002	0.005	**-150**	0.103	0.016	**84**	0.336	0.202	**40**
Hydrapave (HP)	A	BC	2.89	0.097	**97**	0.005	N.D.	-	0.004	N.D.	-	0.218	0.046	**79**	2.35	0.206	**91**	0.020	0.017	**15**	0.002	0.011	**-450**	0.089	0.002	**98**	0.347	0.068	**80**
		AC	1.30	0.408	**69**	0.004	N.D.	-	0.003	N.D.	-	0.096	0.060	**38**	1.11	0.409	**63**	0.009	0.008	**11**	0.002	0.007	**-250**	0.041	0.007	**83**	0.249	0.118	**53**
	B	BC	4.53	0.124	**97**	0.006	N.D.	-	0.006	N.D.	-	0.288	0.039	**86**	3.85	0.201	**95**	0.026	0.017	**35**	0.003	0.011	**-267**	0.127	0.002	**98**	0.405	0.061	**85**
		AC	2.78	0.345	**88**	0.005	N.D.	-	0.003	N.D.	-	0.187	0.056	**70**	2.35	0.354	**85**	0.015	0.009	**40**	0.002	0.008	**-300**	0.080	0.005	**94**	0.308	0.136	**56**
	C	BC	4.87	0.205	**96**	0.006	N.D.	-	0.007	N.D.	-	0.302	0.037	**88**	4.10	0.284	**93**	0.027	0.017	**37**	0.003	0.008	**-167**	0.133	0.002	**98**	0.406	0.052	**87**
		AC	4.73	0.547	**88**	0.006	N.D.	-	0.006	N.D.	-	0.244	0.054	**78**	3.99	0.498	**88**	0.023	0.008	**65**	0.004	0.006	**-50**	0.124	0.012	**90**	0.380	0.116	**69**
	D	BC	5.18	1.053	**80**	0.006	N.D.	-	0.007	N.D.	-	0.292	0.062	**79**	4.36	0.892	**80**	0.027	0.013	**52**	0.003	0.004	**-33**	0.137	0.011	**92**	0.411	0.106	**74**
		AC	4.07	0.997	**76**	0.006	N.D.	-	0.006	N.D.	-	0.246	0.062	**75**	3.42	0.813	**76**	0.020	0.008	**60**	0.004	0.004	**0**	0.127	0.022	**83**	0.363	0.128	**65**
	5-yr	BC	5.63	2.17	**62**	0.007	N.D.	-	0.009	0.006	**33**	0.333	0.122	**63**	5.04	1.98	**61**	0.028	0.015	**46**	0.005	0.007	**-40**	0.136	0.039	**71**	0.429	0.160	**63**
		AC	4.65	2.11	**55**	0.006	N.D.	-	0.008	N.D.	-	0.270	0.120	**56**	3.93	1.69	**57**	0.023	0.012	**48**	0.003	0.003	**0**	0.159	0.072	**55**	0.379	0.157	**59**
	Total	BC	4.43	0.448	**90**	0.006	N.D.	-	0.006	0.002	**67**	0.277	0.049	**82**	3.73	0.464	**88**	0.025	0.016	**36**	0.003	0.008	**-167**	0.122	0.005	**96**	0.394	0.076	**81**
		AC	3.40	0.766	**77**	0.005	N.D.	-	0.005	0.002	**60**	0.203	0.066	**67**	2.87	0.665	**77**	0.018	0.009	**50**	0.003	0.006	**-100**	0.101	0.019	**81**	0.332	0.129	**61**
Permapave (PP)	A		2.34	0.233	**90**	0.005	N.D.	-	0.003	N.D.	-	0.172	0.031	**82**	2.10	0.291	**86**	0.016	0.004	**76**	0.002	0.002	**39**	0.068	0.002	**97**	0.316	0.023	**93**
	B		3.90	0.634	**84**	0.006	N.D.	-	0.006	N.D.	-	0.256	0.052	**80**	3.40	0.652	**81**	0.022	0.009	**58**	0.003	0.001	**59**	0.115	0.007	**94**	0.376	0.031	**92**
	C		5.11	0.589	**88**	0.006	N.D.	-	0.008	N.D.	-	0.282	0.046	**84**	4.46	0.589	**87**	0.028	0.006	**78**	0.004	0.001	**73**	0.128	0.004	**97**	0.388	0.022	**94**
	D		4.93	1.17	**76**	0.006	N.D.	-	0.007	N.D.	-	0.279	0.064	**77**	4.12	0.996	**76**	0.025	0.007	**71**	0.003	0.001	**69**	0.137	0.015	**89**	0.397	0.046	**88**
	5-yr		4.94	2.28	**54**	0.006	N.D.	-	0.007	N.D.	-	0.289	0.121	**58**	4.28	1.89	**56**	0.024	0.010	**57**	0.003	0.002	**53**	0.144	0.058	**60**	0.388	0.120	**69**
	Total		4.14	0.78	**81**	0.006	N.D.	-	0.006	N.D.	-	0.250	0.054	**78**	3.58	0.73	**80**	0.023	0.007	**70**	0.003	0.001	**61**	0.115	0.011	**91**	0.371	0.037	**90**
ADWG[1]			*0.2*			0.002			0.05			1			*0.3*			0.1			0.02			*0.01*			3		
ANZECC[2]	Fresh		*0.055*			0.0002			0.001			*0.0014*			-			1.9			*0.0011*			*0.0034*			*0.008*		
	Marine		-			0.0055			0.0044			*0.0013*			-			0.07			*0.0044*			*0.0044*			*0.015*		
	LTV		5			0.01			0.1			0.2			*0.2*			0.2			0.2			2			2		
	STV		20			0.05			1			5			10			10			2			5			5		

[1] ADWG - Australian Drinking Water Guideline Values (NHMRC-NRMMC, 2011); [2] ANZECC - Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECEPH&ARMCANZ, 2000): Fresh and Marine means trigger values for 95% protection of species in Fresh and Marine waters, respectively; LTV and STV are long-term trigger value and short-term trigger value for heavy metals in irrigation waters. Values in *italic 'Red'* means outflow concentrations of the heavy metal is above the trigger value.

3.1.2 Performance change over time and impact of clogging

For majority of the heavy metals, a general increasing trend of effluent concentrations with fluctuations was observed over the whole experiment (Figure 2); the fluctuations were due to the variable input flows and concentrations (that mimic reality), with six large 'storm events' contributed to the highest outflow peaks. With the accumulation of metals in the systems, adsorption sites became limited and desorption turned to be more prominent. Nevertheless, the outflow concentrations were still below the inflow concentrations until the end of the experiment (*e.g.* after 20-26 years of operation), indicating that these systems still have capacity for metal removal. Mn, exhibited surprisingly decreasing concentration over time (Figure 2), *e.g.* the effluent Mn concentrations were 2-3 times lower in the end compared with the start. Bradl (2004) suggested that Mn oxides are good sinks for Cu and Fe oxides, and can also form Pb-Mn formation, hence exhibit co-precipitation which enhances Mn removal over time.

Another important finding is that in the early stage of the system (1-2 years), the systems had poorer performance and exhibited larger variabilities especially for the first few sampling events (especially for Mn which even had net productions; Figure 2); for example, outflow Cu concentrations in the first two years were 0.076 ± 0.048 mg/L, which dropped to 0.045 ± 0.023 mg/L over the following two years. Therefore, porous pavement systems need time to mature for stable and improved performance. Clogging, which occurred in Year 11 in PA and Year 12 in HP had obvious impact on the system performance (Figure 2; Table 3). It is estimated that after clogging average outflow concentrations were 1.2 – 2.4 times higher than that before clogging for PA systems (and 1.3 - 3.6 times for HP system). As time progressed, clogging resulted in an increase in the detention time, allowing more time for the desorption process, which became more prominent (due to the accumulated heavy metals over time) than the adsorption. This is different from previous study by Myers *et al.* (2011) who found that longer residence time led to better removal of Zn, Cu and Pb. The study however only investigated one single large event (*i.e.* short-term) on a fresh permeable pavement that had no clogging issue; this reaffirms the importance of this study which looked into the long term performance of the pavement systems in removing heavy metals.

Figure 2 Change of outflow heavy metal concentrations over the course of 26 simulated years; "average inflow concentration ± standard deviation" indicated in brackets of the legends.

3.1.3 Impact of pavement type

The difference in average removal between the three types of porous pavements were very small (up to 5%; Figure 3A), with exception of the soluble metals – Cu, Zn and Mn. As discussed, system clogging had adverse impact on system performance, hence the PP (which was not clogged) performed best for removing these heavy metals; *e.g.* specifically the average outflow heavy metal concentrations from PP were only 71% and 56% of those from HP and PA, respectively (Table 3). In addition, the difference in sub-base materials may also contribute to the different observations. Dierkes *et al.* (2002) observed that paving stones of porous concrete and green apertures (similar to PP and PA in this study) had better heavy metal retention capacities than pavers with joints (similar to HP in this study). Although gravel and basalt as base material are usually more effective in removing pollutants (Dierkes *et al.*, 2002), the basalt used in PA system of this study used are much coarser than the stones in HP and gravel in PP, thus resulting the lowest removal for Cu, Zn and Mn.

3.1.4 Impact of flow rate

Figure 3B indicates the impact of flow rates on removal. As expected, the simulated flow representing 1 in 5-yr storm led to the poorest performance, *e.g.* the average removal of heavy metals (except for Mn) were usually within the range of 40-55%, while it was >70% under the other flow rates. The differences of average removal rates between other flow rates (Flow A, B, C and D) were small (<10%) for particulate metals (*i.e.* Pb, Al and Fe), but higher outflow concentrations usually corresponded to larger flow rates (*e.g.* Flow D had ~ 4 times higher average outflow concentrations than Flow A; Table 3), which has good agreement with previous study on the same systems for removal of TP (however opposite trend was found for TN) (Yong *et al.*, 2011). As for the soluble heavy metals (*i.e.* Cu, Zn, and Mn), relatively higher removals were observed at Flow C; surprisingly, it was found that the lowest rate (Flow A) had the largest variability in heavy metal removal compared with other flow rates (Figure 3B), which presumably due to the big reduction in removal after clogging (Table 3); in cases that clogging occurred, lower outflow rates were observed and it benefited to the desorption process of these weakly attached metals, or breakdown of trapped sediments in the clogging layer facilitated by longer detention (during the event) as previous reported to impact TN outflow concentration from the systems (Yong *et al.*, 2011); both processes may introduce more uncertainties and result in the higher variability.

Figure 3 Influence of (A) pavement types and (B) flow rates on heavy metal removal

3.2 Model testing results

The performance of the proposed model and values of calibrated parameters are summarized in Table 4, with the observed and simulated outflow concentrations presented in Figure 4. The overall upwards trend of heavy metal concentrations (downwards for Mn), the fluctuations and peaks were all reasonably modelled, with the Nash-Sutcliffe coefficient (NSE) values of 0.53 – 0.68 for PA and 0.56 – 0.64 for HP, respectively, indicating that the model can estimate the release of heavy metals from two porous pavements with satisfactory; Mn was again an exception and had the poorest model efficiency (E=0.13 for HP and 0.00 for PA), due to its complex potential removal processes and variable performance observed.

The calibrated values of adsorption rate (k_{ads}) and desorption rate (k_{des}) had good agreement with the pollutant removal performance observed, with higher k_{ads} and lower k_{des} values indicating relatively higher removal rates; *e.g.* the particulate heavy metals (Pb, Al, and Fe) are characterized as higher k_{ads} and lower k_{des} values, vice versa for the soluble ones (Zn, Cu and Mn).

Table 4 *Performance of the model and calibrated parameters*

	Porous Asphalt (PA)						Hydrapave (HP)					
	Calibration				Prediction		Calibration				Prediction	
	k_{ads} (-)	k_{des} (1/L)	k (day/L)	NSE	Max NSE*	Obs. within prediction band (%)	k_{ads} (-)	k_{des} (1/L)	K (day/L)	NSE	Max NSE	Obs. within prediction band (%)
Al	0.892	0.041	29.5	**0.63**	0.44	64	0.931	0.024	35.1	**0.56**	0.74	82
Cu	0.831	0.061	34.5	**0.59**	0.48	91	0.896	0.058	38.4	**0.62**	0.62	50
Fe	0.919	0.076	34.6	**0.56**	0.42	27	0.944	0.045	39.1	**0.53**	0.69	46
Pb	0.986	0.016	25.8	**0.64**	0.20	77	0.974	0.005	44.3	**0.53**	0.39	27
Zn	0.873	0.158	26.3	**0.64**	-0.62	46	0.952	0.126	44.2	**0.68**	0.04	22
Mn	0.455	0.214	5.21	**0.00**	-3.3	46	0.432	0.001	1288.1	**0.13**	-4.1	9

* max NSE – the best of 100 model runs during model validation (*i.e.* prediction)

Figure 4 illustrates the 90% prediction bands as well as the best fit of prediction. Best performance was observed for Al and Cu in both systems, with 50%-91% of observations covered by the prediction bands (Table 4), and the trends and fluctuations were simulated reasonably well (max NSE = 0.44-0.74). Fe concentrations was over-predicted by the model, and the best fit of prediction in PA system extended slightly outside of the lower bound of the 90% prediction band; nevertheless, the overall prediction performance for Fe was acceptable, evidenced by the NSE of 0.42 for PA and 0.69 for HP. As for Pb, the peak concentrations after Year 15 were under predicted by the model, with relatively poorer model performance (77% and 27% observations within prediction band, max NSE of 0.20 and 0.39 for PA and HP respectively). The model did not predict Zn concentrations well (NSE<0.04), especially for that in HP systems (best fit of the predictions were out of the 90% prediction bands and only 22% observations within the band), indicating that other important removal processes of these heavy metals not considered in the model (*e.g.* complexation with other compounds or biological transformation) might occur. Although the model predicted same decreasing trend of Mn concentrations as observed, it produced the worst model results, *e.g.* 46% and 9% for HP observations within prediction band, max NSE of <0 for PA and HP respectively. It should be acknowledged that 90% prediction bands were generated in a strict way, *i.e.* using GLUE method based on top 1% parameter sets (corresponding to cut-off thresholds of NSE>0.45 for all the metals), which in some cases caused the best fit prediction fell out of the 90% prediction bands (*e.g.* Zn in HP system – it was checked that the whole prediction band overlapped with the best fit prediction); it however provides a stronger verification of the proposed model. Overall, the results indicate that model has abilities to predict long term performance of porous pavements for some heavy metals, *e.g.* most promisingly for Al and Cu with high NSE values and coverage of observations within the 90% bands, followed by Fe and Pb with lower coverage of observed data within the 90% prediction bands. The proposed model has to be improved further for predicting Zn and Mn removal by the porous pavements; *e.g.* it is suggested to include more removal processes of these two metals in model.

Figure 4 *Calibration and prediction results of outflow concentrations of the model. For PA, the 1-10 year, and 1-13 year data were used for calibration of PA and HP respectively. The shaded areas indicate the 90% prediction band. Solid lines with symbols represent the best calibrated concentrations, while the solid lines without symbols represent predictions from max NSE.*

The efficiency of the proposed model performance (NSE values equal to 0.44-0.74 for Al and Cu, 0.42-0.69 for Fe and 0.20-0.29 for Pb) are reasonably good except for Zn and Mn (NSE from negative to 0.04) and have good agreements to previous reported water quality models for porous pavements; e.g. Newton (2005)'s one-parameter first decay model adapted from filtration theory can predict particle removal efficient from pavement systems under several individual events with different levels of satisfactory: low flow rates with NSE=0.36-0.98 and high flow rates with NSE from negative to 0.39. He et al. (2015)'s empirical model developed based on laboratory data also provided good prediction on six field tests results for TSS and TP removal by porous concrete pavement with errors of up to 2.9% for average removal rates; the same study also tested a sediment removal conceptual model and reported prediction errors of 1.3% and 5.8% for TSS removal rates for two validation field events. As seen, these existing models are simple and can perform well; they however were just validated against individual events and could not be used for predicting long term performance of pavement systems that are exposed to continuous stormwater events. The current proposed model however has overcome these shortcomings and this study for the first time developed a new process-based model specifically for heavy metals involving both adsorption and desorption processes; more importantly its greater utility has been supported by the ability to simulate long-term treatment performance, thus can assist in better design of pavement systems.

4. Conclusions

This study tested the long-term treatment performance of three porous pavements - Porous Asphalt (PA), Hydrapave (HP) and Permapave (PP) in removing heavy metals, using accelerated laboratory experiments spanning over 1 year simulating 26 years of operations. Intermittent dry/wetting periods were also simulated with varying flow conditions to represent a realistic operational scheme. A water quality model that includes adsorption and desorption processes was proposed and tested using experimental data. The main findings are:

- All three porous pavements were good in removing heavy metals, with average cumulative removal rates over 26 years of operations being: 84±14% for Pb, 79±13% for Al, 77±13% for Fe, 68±19% for Fe, 66±20% for Zn, and 35±35% for Mn; metals with higher particulate fractions (Pb, Al and Fe) usually were easier to be retained by the pavements compared to soluble ones (*e.g.* Cu, Zn and Mn);
- Over the simulated 26-year period, effluent concentrations generally increased, indicating the long term release of heavy metals as a result of adsorption and desorption process; it was found that the porous systems took 1-2 years to mature for better and more stable performance. Clogging led to poorer system performance with higher variability.
- Permapave (PP) had the best performance as it was never clogged over the period, followed by Hydrapave (HP) and Porous Asphalt (PA); lower removals of soluble heavy metals was observed in the pavements with coarser sub-materials in PA;
- Flow rates influenced the heavy metal removal, with higher outflow concentrations usually corresponded to higher flowrate, especially for the soluble heavy metals; low flow rates was also not preferred especially after clogging occurred as it benefited to desorption processes and breakdown of accumulated sediments, leading to higher variability in heavy metal outflow concentrations.
- The proposed model was successfully calibrated against the data collected from first half of the accelerated experiment (*e.g.* 10~13 years), with the estimated NSE values 0.53 – 0.68 (except for Mn which had NSE of 0.0-0.13);
- The prediction results indicate that the proposed model was promising for predict the releasing of Al and Cu from the porous pavements (50%-91% of observations covered by the prediction bands, max NSE = 0.44-0.74); it can also be applied for Fe and Pb, but with lower confidence (NSE= 0.42-0.69 for Fe and 0.20-0.29 for Pb) and smaller coverage of observed

data within the 90% prediction bands. The proposed model has to be improved further if it is to be used for predicting Zn and Mn removal by the porous pavements.

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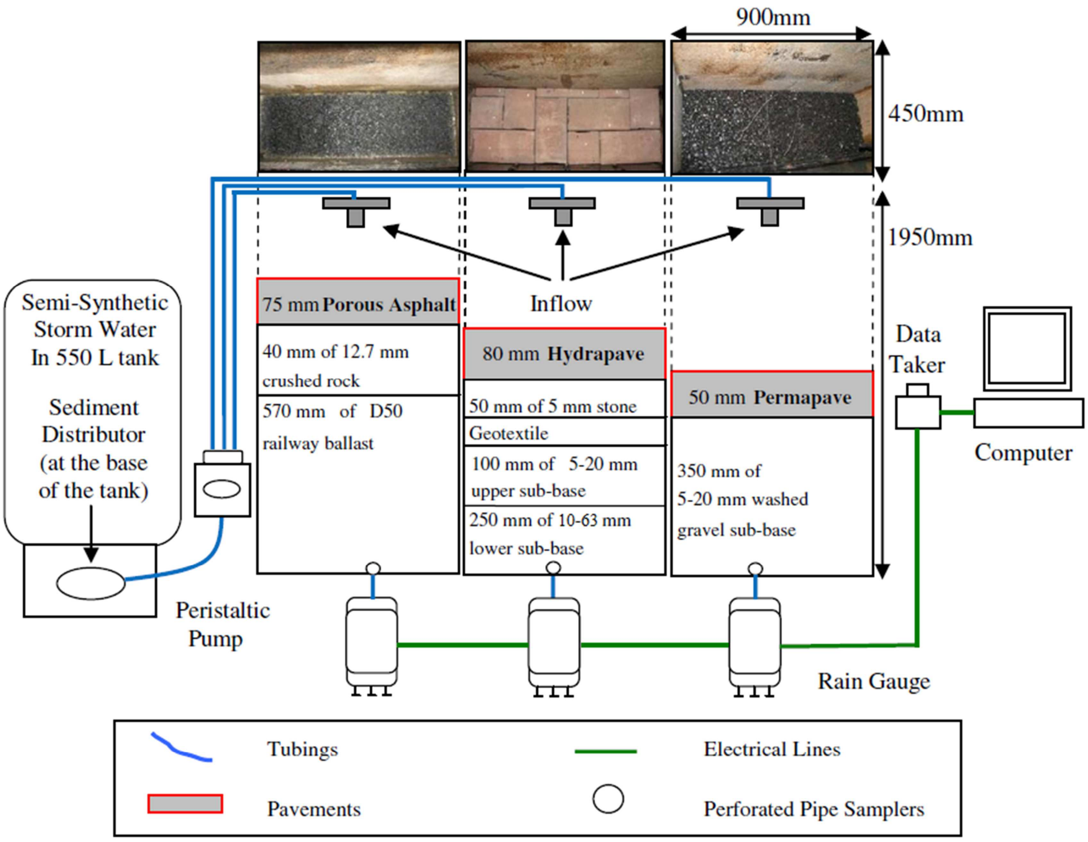

Figure 1 *The experimental set-up for testing Porous Asphalt, Hydrapave and Permapave (adapted from Yong et al. (2013))*

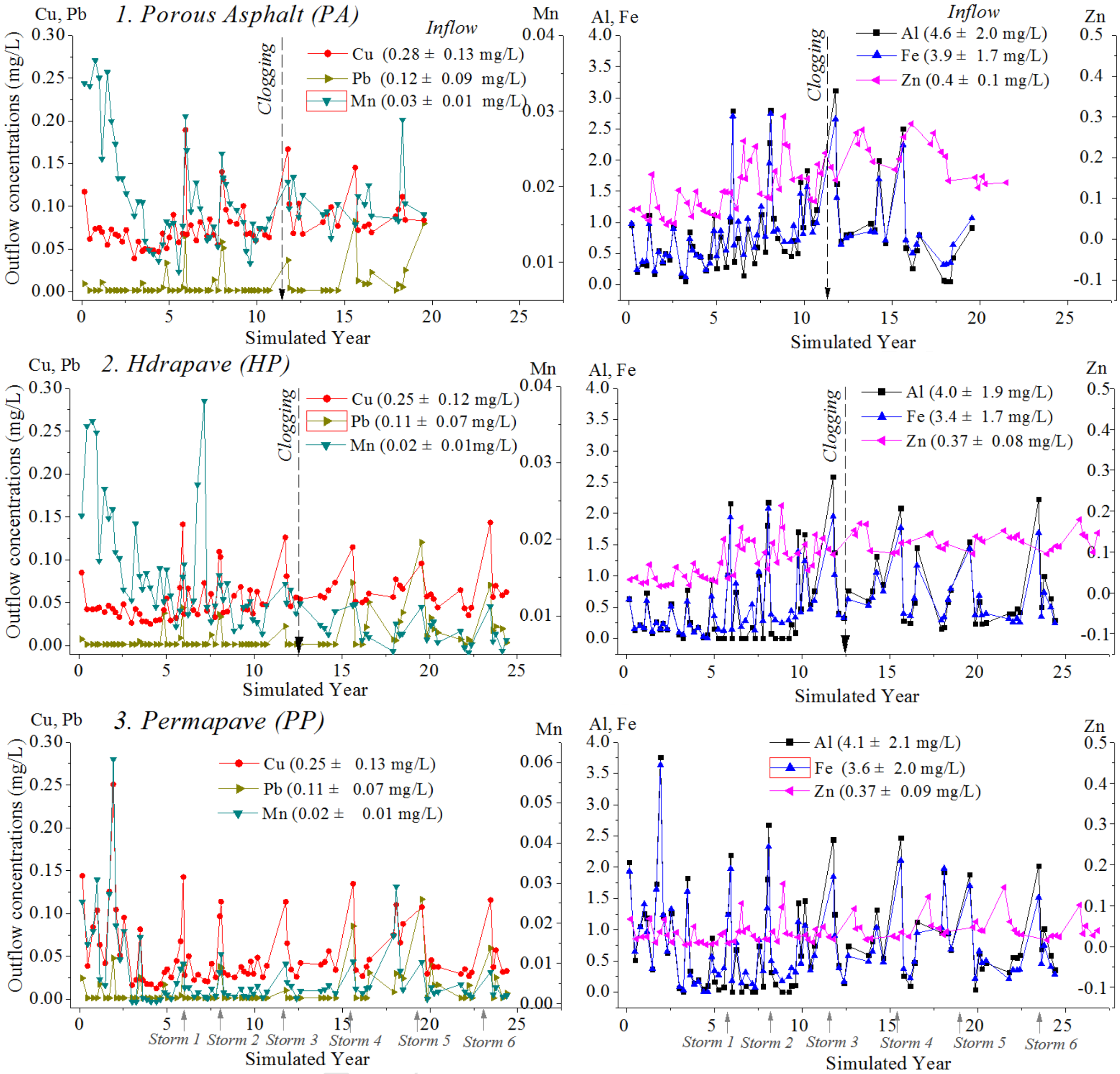

Figure 2 Change of outflow heavy metal concentrations over the course of 26 simulated years; "average inflow concentration ± standard deviation" indicated in brackets of the legends.

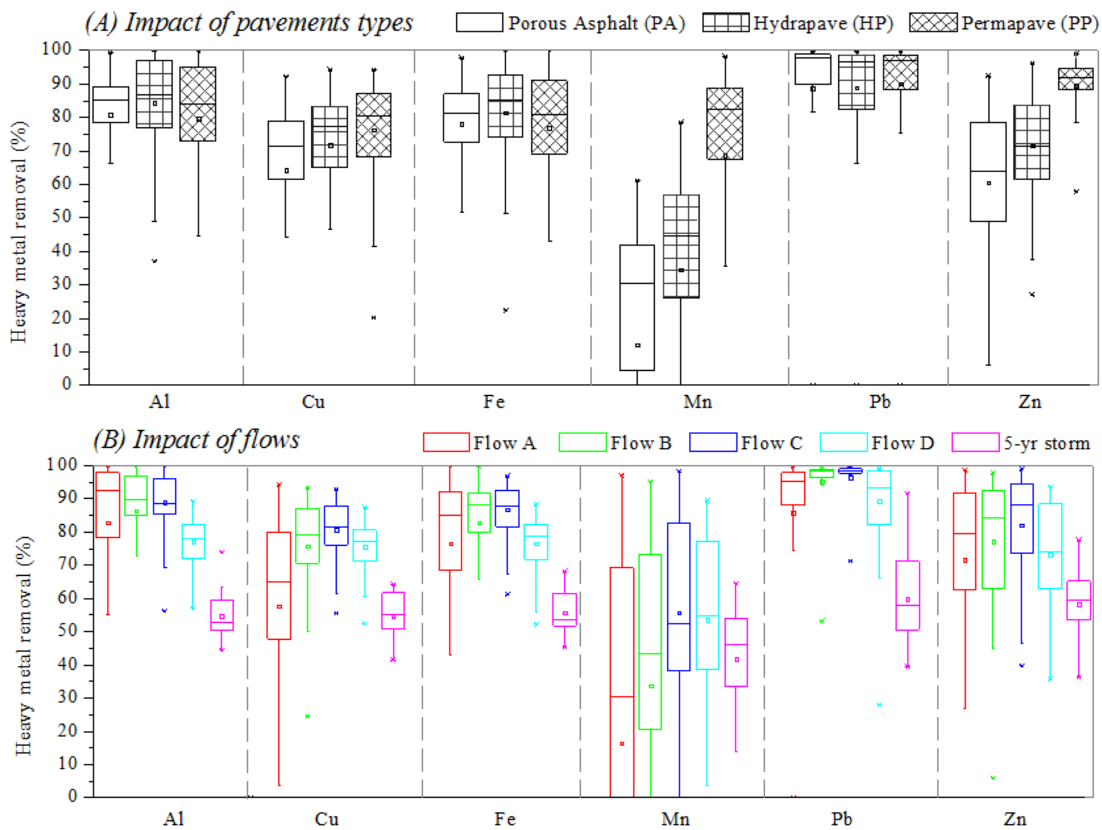

Figure 3 Influence of (A) pavement types and (B) flow rates on heavy metal removal

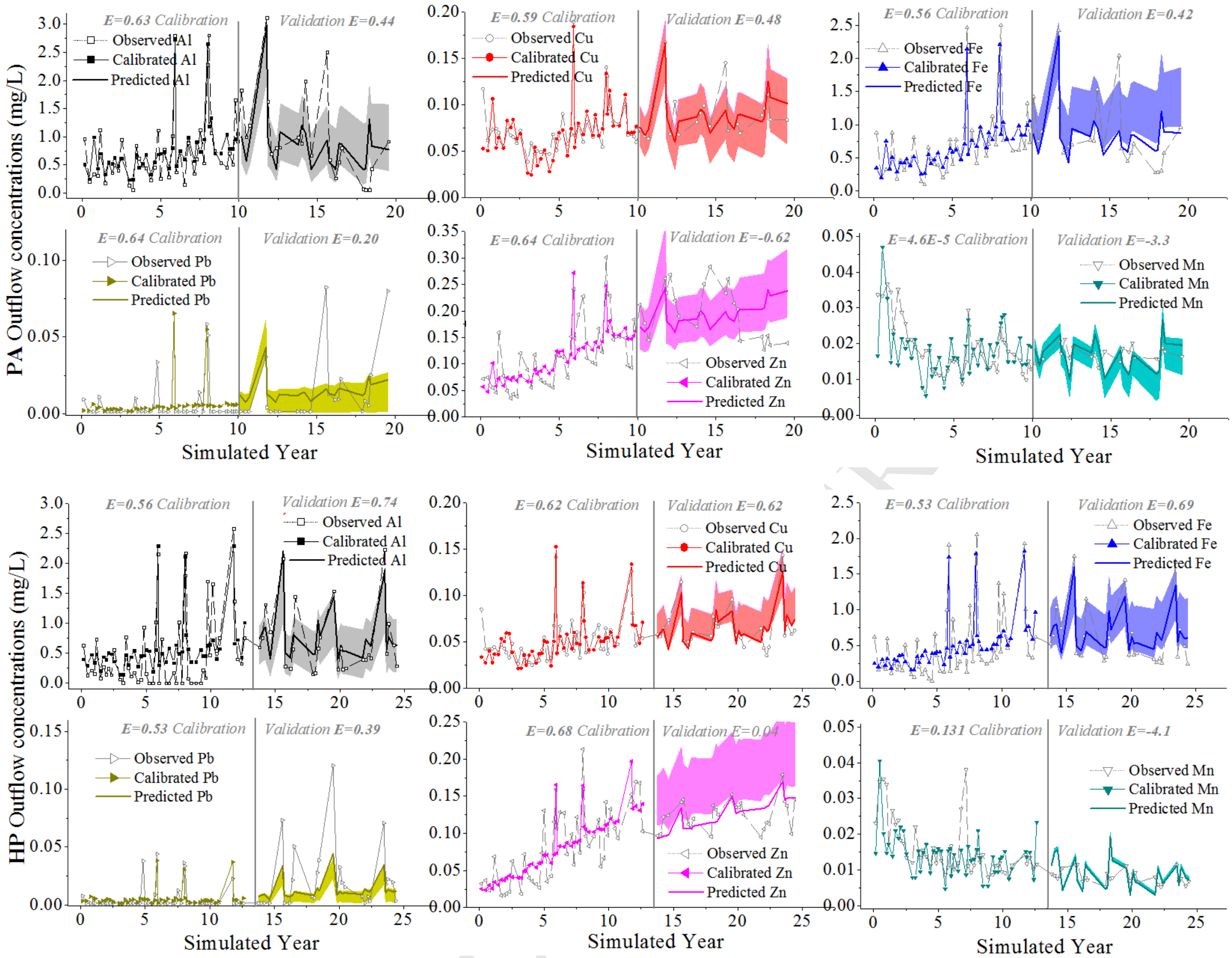

Figure 4 *Calibration and prediction results of outflow concentrations of the model. For PA, the 1-10 year, and 1-13 year data were used for calibration of PA and HP respectively. The shaded areas indicate the 90% prediction band. Solid lines with symbols represent the best calibrated concentrations, while the solid lines without symbols represent predictions from max NSE.*

Highlights

- Long term metal removal by porous pavement was studied at varying conditions
- An increasing trend of outflow concentrations from was observed except for Mn
- Clogging led to poorer system performance with higher variability
- The first processed-based model was developed to predict heavy metal performance
- The model was promising in predicting Al and Cu removal, followed by Fe and Pb