

Article



# **Evaluation of Permeable Pavement Systems for Removing Heavy Metals from Stormwater**

Upeka Kuruppu and Ataur Rahman \*

School of Engineering, Design and Built Environment, Western Sydney University, XB.3.43, Kingswood (Penrith Campus), Locked Bag 1797, Penrith, NSW 1797, Australia; u.kuruppu@westernsydney.edu.au

\* Correspondence: a.rahman@westernsydney.edu.au

Abstract: This study examines a modified permeable pavement system (PPS) for enhanced heavy metal attenuation from stormwater. A laboratory model consisting of six PPS columns has been tested under varying rainfall intensities. The PPS structures are arranged based on the following hypotheses for enhancing heavy metal attenuation: (i) addition of a natural zeolite layer in the subbase for promoting heavy metal attenuation by adsorption and ion exchange; (ii) addition of a bark chip layer as an organic carbon source for promoting biosorption of heavy metals; (iii) maintaining a saturated zone in order to maintain the required humidity level and decrease the level of oxygen for increased biodegradation; and (iv) inclusion of thin sand layers to restrict the transport of oxygen to create an anoxic zone in the PPS and to enhance filtration. Successful treatment of metals such as Ba, Co, Mn, Ni, and Zn has been observed under various rainfall conditions using a conventional PPS. The rainfall intensity greatly influences the attenuation of Al, Cr, Cu, Mo and Sr. During heavy rains through the conventional PPS structure, chromium is found to be leached back into the infiltrate. The results indicate that by changing the subbase material and layer setting, biosorption of heavy metals can be encouraged in the PPS structure. The results of this study suggest that the PPS structure be amended by adding into its subbase a saturated region, an organic carbon donor and thin sand layers for enhanced heavy metal attenuation. Compared to the conventional structure, the proposed structure reduces Cr desorption and improves the attenuation of Al, Cu and Mo.

Keywords: permeable pavement; heavy metals; biosorption; adsorption

## 1. Introduction

The growth of urbanisation contributes to a rise in environmental pollutants. Heavy metals are among the priority pollutants that could have harmful effects on water bodies. In stormwater, heavy metals can exist as dissolved, colloid, suspended matter and sedimentary loads [1]. From the literature, it can be found that heavy metals present in road and pavement runoff in different concentrations, such as As (0.1–340 µg/L), Ba (40–87 µg/L), Cd (0.04–13,730 µg/L), Co (0.08–6.7 µg/L), Cr (0.05–2300 µg/L), Cu (0.06–1410 µg/L), Mn (0.5–3800 µg/L), Mo (1–20 µg/L), Ni (0.02–49,000 µg/L), Pb (0.5–26,000 µg/L), V (7.2–29 µg/L), Zn (0.7–25,500 µg/L) and Fe (9.76–57,325 µg/L) [2–6]. Many research studies show that the larger components of heavy metals present in stormwater runoff exist in particulate forms [1,7]. These particulate heavy metals are attached to fine sediments due to the higher adsorption rate (due to the high surface area per unit mass), lower density and higher organic minerals in sediments [8]. Heavy metal removal from stormwater and wastewater has been examined by many researchers [9–11].

In accordance with water-sensitive urban design (WSUD) concepts, traditional storm drainage systems are being replaced by more eco-friendly alternatives, such as permeable pavement systems (PPSs) [12,13]. With the SSMC, improving the runoff quality is a must, in addition to controlling the runoff quantity. The literature shows the capability of PPSs to



Citation: Kuruppu, U.; Rahman, A. Evaluation of Permeable Pavement Systems for Removing Heavy Metals from Stormwater. *Water* **2023**, *15*, 1573. https://doi.org/10.3390/ w15081573

Academic Editor: Craig Allan

Received: 8 March 2023 Revised: 13 April 2023 Accepted: 15 April 2023 Published: 17 April 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). treat various contaminants, such as nitrogen, phosphorus and heavy metals, to a certain extent [14]. Brattebo and Booth [15] found that the levels of Zn, Cu and mineral oil infiltrated by PPSs were considerably lower. Pagotto et al. [16] demonstrated that the conventional PPS structure can attenuate 20% Cu and 74% Pb. Melbourne Water [17] revealed that 70% of heavy metals can be retained using properly built and maintained PPSs. The mechanisms for treating particulate heavy metals are well-established; however, mechanisms for attenuating dissolved heavy metals are still mostly in an investigational phase [18–20].

This research study explores the possibility of enhancing dissolved heavy metal attenuation via design modifications to the PPS structure. PPSs are commonly regarded as effectively treating stormwater pollutants by adsorption, filtration and ion exchange. The attenuation of dissolved heavy metals can be accomplished in a PPS by adhering to the aggregate surfaces (or the biofilm on the surface) due to the van der Waals force and electrostatic force [21]. Gunawardana et al. [7] revealed that a considerable part of heavy metals are adsorbed through chemisorption to Fe, Al and Mn oxides; however, the adsorption of heavy metals to clay-forming minerals takes place via ion exchange. Adsorption is a surface mechanism that leads to a molecule being moved from a bulk of fluid to a solid surface. The adsorption mechanisms are influenced by factors such as the temperature, pH, redox potential, contact time, and other ions. Ion exchange is a chemical process where dissolved ions get exchanged for other ions with a similar charge. Cations in PPS products, such as lead, cadmium, zinc, and manganese, can be exchanged with cations in runoff. Similarly, anions in PPS materials can be exchanged with anions in runoff, such as nitrates and nitrites. Thus, the pollutant removal capacity of a PPS is highly dependent on the materials used during PPS construction, environmental conditions and runoff quality.

In some cases, by leaching contaminants back to the infiltrator, PPSs can pollute groundwater and underlying soil. Materials retained by filtration are eliminated from vegetated stormwater management systems such as biofilters by plant assimilation. In a PPS, pollutants removed by physical processes, especially heavy metals, can leach back to infiltrate, either because of altered flow conditions or after saturation. In addition to physical and chemical methods, biosorption is another method for removing heavy metals from aqueous solutions. It is assumed that heavy metal ion oxidation or reduction, as well as the metabolic activities of enzymes in microbial cells, convert metal ions into less soluble forms [21]. The redox potential impacts the separation of metals by decreasing the dissolved oxygen level in the saturated region [22]. Furthermore, the introduction of biological components, such as organic carbon, can improve the attenuation of metals [23]. From the above discussion, it is evident that maintaining a saturated zone and providing a carbon source can affect heavy metal attenuation. Although PPSs have been found to act as bioreactors, there is no research on the biosorption processes used in PPSs to treat heavy metals. Therefore, it is not easy to assess the impacts of these factors and the associated interactions on the attenuation of metals in PPSs from the available literature.

In the literature, studies that investigated the efficiency of various sorption and filter media for water treatment can be found. Although there is limited research to date on improving heavy metal attenuation in PPSs, it is possible in future research studies to integrate and evaluate similar findings from other sustainable stormwater management strategies, such as bio-retention systems. The results of some research studies on various sorption media that can also be used in PPSs are listed below. A promising adsorbent for attenuating heavy metals in wastewater, stormwater and other contaminated waters is activated carbon [24–26]. However, researchers have been inspired by its comparatively high price to explore low-cost and readily available adsorbents for extracting heavy metals in stormwater was investigated by Mohammed et al. [28]. In an experiment with columns, they used synthetic stormwater under intermittent runoff conditions. HFO has a high ability to eliminate Cu and Zn, which are present in higher levels in stormwater runoff, as found by this experiment. Single kinetics measurement on natural periodic

runoff, however, was not applicable, as the sorption of the coexisting metals and oxyanions varied with time. To assess the capacity of natural zeolite (clinoptilolite) to extract Pb, Cu and Zn from stormwater, Gray et al. [29] performed single component batch equilibrium experiments. This research showed that the inclusion of a small amount of clinoptilolite would dramatically increase the filtering performance of the powerful heavy metals. Genç-Fuhrman et al. [30] examined 11 sorbents in the treatment of heavy metals in stormwater, including alumina, activated bauxsol-coated sand (ABCS), bark, bauxsol-coated sand (BCS), fly ash (FA), granulated activated carbon (GAC), granulated ferric hydroxide (GFH), iron oxide-coated sand (IOCS), natural zeolite (NZ), sand and spinel (MgAl<sub>2</sub>O<sub>4</sub>). To compare the total heavy metal attenuation performance of the sorbents, calculated sorption constants were used, and a decreasing order was found as follows: alumina, BCS, GFH, FA, GAC, spinel, ABCS, IOCS, NZ, bark and sand. They also found that the Freundlich isothermal model in many instances fitted the data. The impacts of the solution pH, existence of humic acid (HA) and contact time on the combined removal of As, Cd, Cr, Cu, Ni and Zn were investigated by Genç-Fuhrman et al. [31]. The results showed that in order to eliminate the full spectrum of metals, the pH value of the runoff should be 6 to 7.

Most of these media showed positive results in the removal of contaminants, especially heavy metals, although they were not tested for PPSs. Thus, it is important to examine the suitability of integrating these materials into the PPS structure. In addition, as sorption media for handling heavy metals in contaminated water, waste materials such as sawdust [32], industrial waste [33], fly ash [34] and juniper fibre [35] have been tested and shown positive results.

From the above, it can be stated that the effectiveness of PPSs in removing heavy metals is less understood and further research is needed in this area. Six laboratory models of PPSs are, therefore, evaluated in this study for heavy metal attenuation for various rainfall intensities and durations to investigate the treatment effectiveness and potential for leaching metals back to infiltration in order to close the current knowledge gaps concerning PPSs. This study also intends to examine the elimination of heavy metals from runoff by establishing favourable conditions for biosorption. Various modifications have been made to the traditional PPS subbase to achieve these goals, as noted below. (i) An added bark chip layer as an organic carbon source to assist metal uptake. (ii) Provided a saturated zone to supply the necessary moisture, anoxic environment and increased retention time to affect the separation of metals between the solution and the solid phase. (iii) Added thin sand layers to facilitate filtration, ion exchange, and adsorption and to obstruct oxygen transport to create an anoxic zone at the subbase of the structure to promote biosorption of heavy metals.

In this study, we have investigated the following: (i) the performance of the traditional PPS structure in relation to metal attenuation; (ii) the influence of the rainfall duration on metal attenuation; (iii) the influence of the rainfall intensity on metal attenuation; (iv) the effect of the subbase material and layer arrangement on metal attenuation; (v) the influence of the organic carbon content, pH and other pollutants on metal attenuation; and (vi) the possibility of absorbed metal elements leaching back to the infiltrate during high-intensity rainfall. Finally, recommendations for structural modifications of PPSs have been proposed for better heavy metal attenuation via PPSs.

### 2. Materials and Methods

In the laboratory, six PPS columns (600 mm long, 420 mm wide and 250 mm deep) with different subbase materials and layer settings (with a control designed according to the design guide for HydroStone, a local manufacturer) were built. Before building the columns, all of the materials used in the columns were washed to prevent misleading findings in the experiment due to trapped contaminants leaching from the materials. The subbase configurations of the six columns are presented in Figure 1.

Height in cm	Column 1	Column 2	Column 3	Column 4	Column 5	Co <b>lumn</b> 6
23					Porous concre	te
22					2-5mm no-fine	es aggregate
21					5-20mm no-fir	ies aggregate
20					Compost	
19					Clinoptilolite	
17					Saturated zone	•
16					Geotextile	
15						
14						
13						
12						
11						
10						
9						
8						
6						
5						
4						
3						
2						
1						

Figure 1. PPS column cross-section.

To evaluate the distinct effect of integrating sand layers, a zeolite layer and a saturated zone into the subbase, the following four columns were created.

- Column 1: Showing the traditional PPS structure. It contains a 15 cm layer of 5–20 mm no-fines aggregate at the bottom, followed by a 3 cm layer of 2–5 mm aggregates and 5 cm porous concrete pavers.
- Column 2: Having thin sand layers (1 cm).
- Column 4: Having a zeolite layer (2 cm).
- Column 5: Having a saturated zone (4 cm).

In order to investigate the dependent effect of maintaining a saturated region, an organic carbon donor and thin sand layers, Columns 3 and 6 were constructed.

- Column 3: Having a saturated zone and a layer of bark chip.
- Column 6: Having a layer of sand, a saturated zone and a layer of bark chip.

The columns were fitted with a rainfall simulator. The saturated zones in Columns 3, 5 and 6 were maintained by raising the outlet pipe. The outlet water quality of the newly built columns was checked by dosing tap water until all six columns reached a steady state. Synthesised runoff was continuously applied for 4 h to the PPS columns. Since the amounts of contaminants in real stormwater runoff differ during rainfall events, in our experiment, synthetic stormwater was used, allowing us to run duplicates and maintain varying levels of pollutants to mimic typical field conditions of runoff. The pH of the synthetic runoff was kept in the range of 5.5 to 6.5. For the pH adjustment, 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M NaOH were used. The runoff quality was simulated by adding pollutants to tap water.

A number of trials were performed over a 6-month period in the Western Sydney University laboratory using synthesised runoff with different contaminant concentrations and rainfall intensities to mimic realistic rainfall runoff conditions as follows.

- Stage 1: An average rainfall intensity of 38–40 mL/min (40 mm per 4 h) was maintained for 4 h.
- Stage 2: The experiment was further expanded by changing the rainfall intensity to 120 mm/4 h in order to investigate the outputs of the PPS columns under high-intensity rainfall.

For the first two stages of the experiment, the synthetic stormwater characteristics were as presented in Table 1.

Parameter	Average Concentration (mg/L)	Standard Deviation	
pH	5.5	1.4	
Ammonium Nitrogen (NH <sub>4</sub> -N)	0.53	0.01	
Nitrogen as Nitrites (NO <sub>2</sub> -N)	0.51	0.07	
Nitrogen as Nitrates (NO <sub>3</sub> -N)	0.56	0.04	
Total Inorganic Nitrogen (TIN-N)	1.59	0.12	
Organic Carbon (Org-C)	3.68	1.04	
Ba	0.22	0.08	
Со	0.34	0.06	
Cr	1.08	0.25	
Mn	0.36	0.05	
Pb	0.40	0.03	
Al	0.33	0.03	
Cu	0.76	0.15	
Мо	0.66	0.00	
Se	0.61	0.03	
Sr	0.51	0.13	
Ni	0.61	0.15	
Zn	0.70	0.05	
Fe	0.51	0.09	

 Table 1. Synthetic stormwater characteristics.

• Stage 3: Stage 3 was done to investigate the possibility of adsorbed metal elements leaching back to the infiltrate during high-intensity rainfall. Here, we compared a standard traditional PPS structure (Column 1) with Column 6 (which showed better performance over the other 4 columns). Trials were performed starting with a rainfall intensity of 20 mm per 4 h. It was continued for 1 h and then the average rainfall intensity was raised to 120 mm per 4 h. The characteristics of the synthesised runoff were set close to natural stormwater quality referring to the available literature (average values in mg/L were Al-70, Cr-77, Cu-348, Mo-107, Sr-136, Ba-72, Co-35, Mn-72, Ni-83, Zn-86).

The synthesised runoff was kept in a 300 L fiberglass tank and was well-mixed. To simulate the rainfall, stormwater was pumped into the columns from the top end through a weeper hose (for 20 mm and 40 mm per 4 h) or sprinkler nozzles (for 120 mm per 4 h) and the infiltrates were collected from the column outlets. The rainfall intensity was maintained by adjusting the pump speed and the manometer.

The infiltrates were obtained and checked from each column at 15-min intervals in all phases. By calculating the depth of the samples in the collection buckets, the infiltration rate was determined. The effluent flow rate, however, was very similar to the rainfall

intensity simulated, and there was not much difference between the six columns. To sample, polyethylene bottles were utilised. After collection, the samples were preserved by means of acidification using concentrated nitric acid at pH < 2 (5 mL of HNO3 was added to 1 L of the sample) and kept at 4 °C before the analysis was carried out.

For the metal analysis, Shimadzu inductively coupled plasma–optical emission spectrometry (ICP–OES) 710 was adopted here.

### 3. Results and Discussion

#### 3.1. Heavy Metal Treatment Performance of Column 1 (Traditional Structure)

The dissolved metal attenuation via Column 1 was investigated for rainfall of 40 mm/4 h (which is almost the most widely adopted design rainfall for Sydney, NSW, Australia) and 120 mm/4 h, as shown in Figure 2. It can be seen that the rainfall intensity significantly influences the dissolved metal attenuation performance via the conventional PPS structure. In removing Cr, Sr, Se and Mo, the typical conventional PPS structure is not successful. Thus, for Cr-, Sr-, Se- and Mo-rich sites, the stranded PPS structure needs to be upgraded.



Figure 2. Percentage dissolved metal attenuation performance of PPS Column 1.

3.2. The Effect of the Subbase Material and Layer Setting on the Total Dissolved Metal Attenuation under 40 mm/4 h and 120 mm/4 h Rainfalls

Figure 3 presents the average total dissolved metal concentrations at the column outlets at 40 mm/4 h of precipitation. It can be seen that the attenuation performance of the traditional structure is degraded with the rainfall duration. After the first hour of rainfall, the reduction of the total dissolved metal has significantly dropped. In order to promote filtration, ion exchange, and adsorption, to decrease the transfer of oxygen to the subbase and to form an anoxic region, the second column was constructed with two thin sand layers. It can be seen that during the first 90 min of rainfall, Column 2 has the best performance, and it has better performance than Column 1 (the conventional PPS structure) during the 4 h period of rainfall. The interaction of dissolved metal elements with surface functional groups of sand (silicates) can promote dissolved metal attenuation by adoption and ion exchange [36]. Unlike biological treatment processes, pollutants attenuated by physical mechanisms (filtration and adsorption) do not remove the pollutants from the system, as they are trapped within the pores of the PPS structure. Hence, the filtration, ion exchange and adsorption efficiencies will be reduced with time due to the changes in the surface characteristics and specifications of the sorbates, as noted by Kuruppu et al. [37]. While Column 3 shows a better performance at the beginning of the rainfall relative to the standard structure, it shows the worst performance compared to the other four columns. The fourth column has a layer of natural zeolite in its subbase. The zeolite frameworks consist of a  $SiO_4$  and  $AlO_4$  tetrahedra three-dimensional system. The aluminium ion can occupy the space of four oxygen atoms in the centre of the tetrahedron, and the isomorphic substitution of  $AI^{3+}$  for  $Si^{4+}$  raises a negative charge in the lattice. These cations are exchangeable with metal ions in the runoff [36,37]. Although there is better heavy metal attenuation at the beginning, the performance drops after about 130 min.



Figure 3. Concentrations of total metals at the PPS column outlets vs. time.

A better effect on improving the dissolved heavy metal attenuation is also seen in Column 5 with the inclusion of a saturated zone alone. The dissolved heavy metals are effectively extracted over a long operating period in Column 5, as shown in Figure 3. The complete metal attenuation in Column 3 (which is combined with an organic carbon layer and a saturated zone) can be seen to be enhanced over the 4 h rainfall cycle relative to the other five columns. This indicates that the presence of an organic carbon donor (bark chips), thin sand layers and a saturated zone has a substantial effect on increased heavy metal attenuation for a longer period of rainfall.

When considering the metal elements Cr, Mo, Se and Sr (Figure 4), all six columns show an inferior performance in comparison to other metal species. However, Column 6 shows comparatively better attenuation performance. This proves the ability of the Column 6 PPS structure to perform as a bioreactor promoting the biosorption of heavy metals.



Figure 4. Average percentage of metals at the PPS column outlets at different rainfall intensities.

# 3.3. Influence of the Organic Carbon Content, pH and Other Pollutants on Dissolved Metal Attenuation

The mean concentrations of the organic carbon content, pH and other contaminants at the column outlets are shown in Table 2. A raised pH (due to the porous concrete pavers) can stabilise heavy metals chemically and decrease solubility. This stabilisation of heavy metals is likely to happen at the top region of the PPS structure, which is porous concrete pavers. The entrapped stabilised metals at the top region can be excluded at the time of PPS maintenance. In addition, with regard to the attenuation of heavy metals, Column 3, which is higher in the treatment of nitrogen compounds (Figure 5), shows substandard efficiency. These findings cast doubt on the impact of attenuated metals on limiting the effectiveness of nitrogen reduction in other columns. This phenomenon deserves more study, which is left for future research attempts.

	Org-C at Column Outlets (mg/L)	pH at Column Outlets	Percentage of Attenuated Total Inorganic Nitrogen as N
Column 1	4.62	9.6	35.35
Column 2	4.78	9.5	41.40
Column 3	10.78	8	75.97
Column 4	5.17	9.1	38.86
Column 5	4.23	9.8	36.82
Column 6	7.68	8.7	55.25

 Table 2. Organic carbon content, pH and other pollutants at the PPS column outlets.



Figure 5. EMC of metals at the PPS column outlets.

# 3.4. Comparison of the Standard Traditional PPS Structure (Column 1) with the Proposed PPS Structure (Column 6) for Metal-Rich Sites—Stage 2

With the stage 1 and 2 results, it can be seen that an organic carbon donor (bark chips), thin sand layers and a saturated zone have a considerable influence on better dissolved heavy metal attenuation for a longer rainfall duration. Thus, in stage 3, Column 1 and Column 6 were compared to investigate the possibility of the leaching back of the entrapped metal elements during high rainfall intensity. Inferior metal attenuation efficiency was

observed during stage 3 of the experiment due to decreased adsorption ability because the metal elements were already adsorbed (or saturated) by the material during stage 1. In addition, as discussed below, it was observed that the entrapped metals were leaching back to the infiltrate during stage 3.

The outlet concentrations of heavy metals through the standard traditional PPS structure (Column 1) over a 4 h period for low and high rainfall intensities are shown in Figure 6a. Moreover, it can be seen that, relative to the low rainfall rate, the attenuation of the metals was decreased during the high rainfall intensity.



**Figure 6.** (a) Metal attenuation over time for Column 1 [38]. (b) Metal attenuation over time for Column 6 [38].

Column 6, which has been upgraded to facilitate biosorption, has demonstrated a 100% reduction of Ba, Co, Mn, Ni, Cu, and Zn under low and high rainfall conditions, as shown in Figure 6b. With the exception of Al and Sr, when the rainfall intensity was low, both Column 1 and Column 6 displayed results that were comparable (Table 3). The unknown causes of Sr leaching from Column 6 need to be further researched. Column 6 has demonstrated improved metal attenuation, even in conditions of heavy precipitation, indicating that the conditions are favourable for biosorption.

	Average Attenuation (%)			
Pollutant	Low-Intensity Rainfall		High-Intensity Rainfall	
	Column 1	Column 6	Column 1	Column 6
Al	71.98	59.87	34.47	72.31
Cr	80.82	81.35	-78.14	-21.79
Cu	95.50	92.42	75.40	93.89
Мо	87.93	83.39	7.18	21.96
Sr	53.29	-13.10	23.83	-11.42
Ba	100.00	100.00	100.00	100.00
Со	100.00	100.00	100.00	100.00
Mn	100.00	100.00	100.00	100.00
Ni	100.00	100.00	100.00	100.00
Zn	100.00	100.00	100.00	100.00

Table 3. Percentage reduction of metals via Columns 1 and 6.

For Cr, Column 6 also revealed a negative percentage reduction, pointing to the potential for Cr desorption back into the runoff during intense rain. According to Mandiwana et al. [39], the existence of  $CO_3^{2-}$  ions controls the solubility of Cr(VI) species. This desorption can, therefore, be justified as a result of the additional carbon source in Column 6. The results of Kayhanian et al. [40] also showed that the concrete PPS leachate contained dissolved Cr. Given that Cr is one of the most hazardous pollutants in terms of ecological toxicity, only one-third of the standard traditional PPS structure's desorption occurs from Column 6. For Cr-rich sites, the PPS structure needs to be modified based on further research.

Except for the change from low to high intensity rainfalls, Column 6 had stable outlet concentrations with little to no effect from the rainfall duration when considering the impact of the rainfall duration on metal attenuation. However, during periods of heavy rainfall, Column 1 revealed a sharp rise in the levels of heavy metals at the outlet.

When the rainfall intensity was raised to 45 mL/min, the percentage reduction of Cr was decreased from about 80% during the first hour (i.e., at 20 mL/min rainfall intensity), as shown in Table 3, to 56% (Table 4), and it then further decreased to 11% during the fourth hour. As shown in Table 4, the attenuation of Sr and Mo was also stopped.

Math	Average Reduction (%)			
Metal Element	1st Hour	2nd Hour	3rd Hour	4th Hour
Cr	56.64	18.18	14.10	11.51
Мо	80.26	48.05	40.13	39.28
Sr	36.66	19.12	14.10	11.51

Table 4. Average percentage reduction of metals for Cr, Mo and Sr.

There have only been a few studies on enhancing the dissolved heavy metal attenuation in PPSs. However, sorption media such as activated carbon [25,26,41], hydrous ferric oxide [28], alumina, activated bauxsol-coated sand, bark, granulated ferric hydroxide, iron oxide-coated sand, and humic acid [29], as well as waste materials such as sawdust [32], industrial waste [30], fly ash [34], and juniper fibre [35], have demonstrated successful results for the removal of heavy metals from wastewater. For PPSs, these sorption media can also be examined. The quality of stormwater is site-specific, and the capacity of various materials to remove various pollutants varies. As a result, the PPS structure needs to be carefully designed, taking into account the requirements of the environment, the proposed site's conditions, design rainfall, and water quality standards.

## 4. Conclusions

This study examines the effectiveness of permeable pavement systems (PPSs) in attenuating heavy metals. It has been found that the amount of rainfall has an impact on how well the conventional permeable pavement structure attenuates heavy metals such as Al, Cr, Cu, Mo, and Sr. When it rains heavily, Cr can be desorbed and returned to the runoff. In addition, Mo's attenuation decreased from 87% to 7% during heavy rain. The length of a rainfall event has a sizable impact on the attenuation of metals such as Cr, Sr, and Mo. These findings imply that heavy metals in stormwater runoff can be transferred without treatment from traditional permeable pavement structures to nearby groundwater and surface waters.

Physical treatment processes depend mainly on the physical properties of the materials used in the pavement system. The attenuation of contaminants can be improved by the correct choice of aggregate materials, particle size, particle distribution and layer configuration. Filter/adsorption media have an effective lifetime, after which they need to be regenerated or changed. Investigation of the effective lifetimes of aggregates for physical stormwater treatment and the possibilities of regeneration need future research. The chemical processes for dissolved heavy metal attenuation, which is possible in PPSs, are the interaction of metals with mineral or organic particles in the surface and subbase materials through chemical precipitation and ion exchange. Materials can be selected during the mix design of concrete pavers and as aggregates in the subbase to promote chemical treatment processes. As was already mentioned, the addition of organic matter in the form of a carbon source encouraged improved dissolved metal attenuation.

By incorporating a saturated zone, an organic carbon donor, and thin sand layers into its subbase, a PPS can promote the biosorption of heavy metals. In our experiment, this resulted in less Cr desorption than the conventional PPS structure and improved attenuation of Al, Cu, and Mo. The Sr attenuation, however, was adversely impacted by this subbase modification. The findings of this study will enable local councils to establish PPS design specifications in order to meet the necessary stormwater guidelines, taking into account elements such as pavement system material selection, layering, and design rainfall conditions.

**Author Contributions:** Conceptualization: U.K.; Methodology: U.K. and A.R.; Drafting of manuscript: U.K.; Review of manuscript: A.R.; Supervision: A.R. All authors have read and agreed to the published version of the manuscript.

Funding: No funding was received for this study.

Data Availability Statement: Authors do not have permission to share the data.

Conflicts of Interest: Authors declare that there is no conflict of interest.

## References

- Djukić, A.; Lekić, B.; Rajaković-Ognjanović, V.; Veljović, D.; Vulić, T.; Djolić, M.; Naunovic, Z.; Despotović, J.; Prodanović, D. Further insight into the mechanism of heavy metals partitioning in stormwater runoff. *J. Environ. Manag.* 2016, 168, 104–110. [CrossRef] [PubMed]
- Erickson, A.J.; Gulliver, J.S.; Weiss, P.T. Capturing phosphates with iron enhanced sand filtration. *Water Res.* 2012, 46, 3032–3042. [CrossRef] [PubMed]
- Grant, S.B.; Rekhi, N.V.; Pise, N.R.; Reeves, R.L.; Matsumoto, M.; Wistrom, A.; Moussa, L.; Bay, S.; Kayhanian, M. A review of the contaminants and toxicity associated with particles in stormwater runoff. *Terminology* 2003, 2, 1–173.
- 4. Göbel, P.; Dierkes, C.; Coldewey, W. Storm water runoff concentration matrix for urban areas. J. Contam. Hydrol. 2007, 91, 26–42. [CrossRef] [PubMed]
- Hallberg, M.; Renman, G.; Lundbom, T. Seasonal Variations of Ten Metals in Highway Runoff and their Partition between Dissolved and Particulate Matter. *Water Air Soil Pollut.* 2007, 181, 183–191. [CrossRef]
- Nielsen, K. Characterisation and Treatment of Nano-Sized Particles, Colloids and Associated Polycyclic Aromatic Hydrocarbons in Stormwater. Ph.D. Thesis, Department of Environmental Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark, 2015.

- 7. Gunawardana, C.; Egodawatta, P.; Goonetilleke, A. Adsorption and mobility of metals in build-up on road surfaces. *Chemosphere* **2015**, *119*, 1391–1398. [CrossRef]
- 8. Hvitved-Jacobsen, T.; Vollertsen, J.; Nielsen, A.H. *Urban and Highway Stormwater Pollution: Concepts and Engineering*; CRC Press: Boca Raton, FL, USA, 2010.
- Liu, S.; Yang, T.; Wang, E.; Wang, H.; Du, Z.; Cao, S.; Zhang, Q.; Chou, K.-C.; Hou, X. Ultra-stable and bifunctional free-standing SiC photoelectrocatalyst for water remediation. J. Clean. Prod. 2023, 396, 136484. [CrossRef]
- Bai, F.; Zhang, X.; Hou, X.; Liu, H.; Chen, J.; Yang, T. Individual and simultaneous voltammetric determination of Cd (II), Cu (II) and Pb (II) applying amino functionalized Fe3O4@ carbon microspheres modified electrode. *Electroanalysis* 2019, *31*, 1448–1457. [CrossRef]
- 11. Wu, Y.; Yang, T.; Chou, K.-C.; Chen, J.; Su, L.; Hou, X. The effective determination of Cd(ii) and Pb(ii) simultaneously based on an aluminum silicon carbide-reduced graphene oxide nanocomposite electrode. *Analyst* **2017**, *142*, 2741–2747. [CrossRef]
- 12. Rahman, A.; Imteaz, M.A.; Arulrajah, A.; Piratheepan, J.; Disfani, M.M. Recycled construction and demolition materials in permeable pavement systems: Geotechnical and hydraulic characteristics. *J. Clean. Prod.* **2015**, *90*, 183–194. [CrossRef]
- Lu, G.; Liu, P.; Wang, Y.; Faßbender, S.; Wang, D.; Oeser, M. Development of a sustainable pervious pavement material using recycled ceramic aggregate and bio-based polyurethane binder. *J. Clean. Prod.* 2019, 220, 1052–1060. [CrossRef]
- 14. Xie, N.; Akin, M.; Shi, X. Permeable concrete pavements: A review of environmental benefits and durability. *J. Clean. Prod.* 2019, 210, 1605–1621. [CrossRef]
- Brattebo, B.O.; Booth, D.B. Long-term stormwater quantity and quality performance of permeable pavement systems. *Water Res.* 2003, 37, 4369–4376. [CrossRef]
- 16. Pagotto, C.; Legret, M.; Le Cloirec, P. Comparison of the hydraulic behaviour and the quality of highway runoff water according to the type of pavement. *Water Res.* **2000**, *34*, 4446–4454. [CrossRef]
- Melbourne Water. 2017. Available online: https://www.melbournewater.com.au/planning-and-building/stormwatermanagement/wsud\_treatments/pages/porous-paving.aspx (accessed on 3 May 2021).
- Wium-Andersen, T.; Nielsen, A.H.; Hvitved-Jacobsen, T.; Kristensen, N.K.; Brix, H.; Arias, C.A.; Vollertsen, J. Sorption Media for Stormwater Treatment—A Laboratory Evaluation of Five Low-Cost Media for Their Ability to Remove Metals and Phosphorus from Artificial Stormwater. *Water Environ. Res.* 2012, *84*, 605–616. [CrossRef]
- 19. Sounthararajah, D.P.; Loganathan, P.; Kandasamy, J.; Vigneswaran, S. Removing heavy metals using permeable pavement system with a titanate nano-fibrous adsorbent column as a post treatment. *Chemosphere* **2017**, *168*, 467–473. [CrossRef]
- Liu, J.; Borst, M. Performances of metal concentrations from three permeable pavement infiltrates. *Water Res.* 2018, 136, 41–53. [CrossRef]
- Srivastava, N.; Majumder, C. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. J. Hazard. Mater. 2008, 151, 1–8. [CrossRef]
- 22. Warren, L.A.; Haack, E.A. Biogeochemical controls on metal behaviour in freshwater environments. *Earth-Sci. Rev.* 2001, 54, 261–320. [CrossRef]
- 23. Yin, Y.; Impellitteri, C.A.; You, S.-J.; Allen, H.E. The importance of organic matter distribution and extract soil:solution ratio on the desorption of heavy metals from soils. *Sci. Total Environ.* **2002**, *287*, 107–119. [CrossRef]
- 24. Jusoh, A.; Shiung, L.S.; Ali, N.; Noor, M. A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. *Desalination* **2007**, *206*, 9–16. [CrossRef]
- 25. Kang, K.C.; Kim, S.S.; Choi, J.W.; Kwon, S.H. Sorption of Cu<sup>2+</sup> and Cd<sup>2+</sup> onto acid- and base-pretreated granular activated carbon and activated carbon fiber samples. *J. Ind. Eng. Chem.* **2008**, *14*, 131–135. [CrossRef]
- Sounthararajah, D.P.; Loganathan, P.; Kandasamy, J.; Vigneswaran, S. Column studies on the removal of dissolved organic carbon, turbidity and heavy metals from stormwater using granular activated carbon. *Desalination Water Treat.* 2016, 57, 5045–5055. [CrossRef]
- 27. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. J. Environ. Manag. 2011, 92, 407–418. [CrossRef]
- Mohammed, T.; Aryal, R.; Vigneswaran, S.; Loganathan, P.; Kandasamy, J.; Naidu, R. Removal of heavy met-als in stormwater by hydrous ferric oxide. *Proc. Inst. Civ. Eng.* 2012, 165, 171–178.
- 29. Gray, C.S.; Burns, S.E.; Griffith, J.D. The Use of Natural Zeolites As a Sorbent for Treatment of Dissolved Heavy Metals in Stormwater Runoff. *Bridges* 2014, *10*, 3978–3987.
- Genç-Fuhrman, H.; Mikkelsen, P.S.; Ledin, A. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents. *Water Res.* 2007, 41, 591–602. [CrossRef]
- Genç-Fuhrman, H.; Mikkelsen, P.S.; Ledin, A. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater using high-efficiency industrial sorbents: Effect of pH, contact time and humic acid. *Sci. Total Environ.* 2016, 566–567, 76–85. [CrossRef]
- 32. Kaczala, F.; Marques, M.; Hogland, W. Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto Pinus sylvestris sawdust. *Bioresour. Technol.* **2009**, *100*, 235–243. [CrossRef]
- 33. Ahmaruzzaman, M. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv. Colloid Interface Sci.* **2011**, *166*, 36–59. [CrossRef]
- Zhang, W.; Brown, G.O.; Storm, D.E. Enhancement of Heavy Metals Retention in Sandy Soil by Amendment with Fly Ash. *Trans.* ASABE 2008, 51, 1247–1254. [CrossRef]

- 35. Min, S.H.; Eberhardt, T.L.; Jang, M. Base-treated juniper fiber media for removing heavy metals in stormwater runoff. *Pol. J. Environ. Stud.* **2007**, *16*, 731–738.
- Čurković, L.; Cerjan-Stefanović, Š.; Filipan, T. Metal ion exchange by natural and modified zeolites. Water Res. 1997, 31, 1379–1382.
   [CrossRef]
- Kuruppu, U.; Rahman, A.; Sathasivan, A. Enhanced denitrification by design modifications to the standard permeable pavement structure. J. Clean. Prod. 2019, 237, 117721. [CrossRef]
- 38. Kuruppu, U.; Rahman, A.; Sathasivan, A. Modifications to permeable pavement structure to achieve improved heavy metal attenuation in stormwater runoff. In Proceedings of the 11th Annual TechConnect World Innovation Conference and Expo, Held Jointly with the 20th Annual Nanotech Conference and Expo, the 2018 SBIR/STTR Spring Innovation Conference, and the Defense TechConnect DTC Spring Conference, Anaheim, CA, USA, 13–16 May 2018; pp. 168–171.
- Mandiwana, K.; Panichev, N.; Kataeva, M.; Siebert, S. The solubility of Cr(III) and Cr(VI) compounds in soil and their availability to plants. J. Hazard. Mater. 2007, 147, 540–545. [CrossRef]
- Kayhanian, M.; Vichare, A.; Green, P.G.; Harvey, J. Leachability of dissolved chromium in asphalt and concrete surfacing materials. J. Environ. Manag. 2009, 90, 3574–3580. [CrossRef]
- Shanker, A.K.; Cervantes, C.; Loza-Tavera, H.; Avudainayagam, S. Chromium toxicity in plants. *Environ. Int.* 2005, *31*, 739–753. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.