

Article

# Reduction and Accumulative Characteristics of Dissolved Heavy Metals in Modified Bioretention Media

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**Abstract:** Twelve bioretention filter columns with different media were designed to study the effects of media on dissolved heavy metals in bioretention systems by changing three test conditions (inflow concentration, discharge ratio, and recurrence interval). The results showed that the average load reduction efficiency of the bioretention soil media (BSM)+10%water treatment residue, BSM+10%green zeolite, and BSM+10%medicinal stone for Cu and Zn was larger than 80%. The highest volume reduction efficiency is 39.25% by BSM+coconut bran. Among the three factors selected in tests, inflow concentration had the biggest degree of influence, followed by discharge ratio and recurrence interval. The media of the upper, middle, and lower layers of each filter column were detected before and after the treatment to study the accumulative characteristics of heavy metals in the bioretention system. The accumulation of Cu, Zn, and Cd in the media of BSM+medicinal stone, BSM+fly ash, BSM+vermiculite, and BSM+turfy soil was relatively low. The contents of the three metals were positively correlated with urease and negatively correlated with protease in the media, but no obvious rule was showed in the accumulation of dissolved heavy metals with depth.

**Keywords:** bioretention; modified media; treatment effect; accumulative characteristic

## 1. Introduction

One of the major sources of heavy metals in surface and subsurface water is stormwater runoff [1]. Concentrations of heavy metals such as copper, zinc, cadmium in waterbodies and sediments receiving stormwater runoff from densely populated urban areas are high enough to impair the health of aquatic organisms [2,3]. Pollutants in runoff mainly exist in dissolved and particulate states [4,5]. Stormwater runoff pollution has conventionally been considered a problem related to particles [6]. A considerable number of studies have focused on particulate heavy metals, but the removal of dissolved metals has attracted significant attention in recent years [7]. Physical processes, such as settling and filtration, are effective at removal of particles and their associated pollutants [8,9]. Dissolved heavy metals are bio-available and rapidly impact the receiving water body and its biota [10,11]. Therefore, the removal of dissolved heavy metals is crucial in reducing runoff pollutants.

Bioretention is an important technology used for low-impact development (LID) stormwater management [12–15]. Most heavy metals accumulate inside the bioretention media, and media are critical in bioretention systems. However, a large amount of contaminants accumulated in the interior of the media may be re-infiltrated in the soil or groundwater to cause soil and groundwater contamination. Therefore, large-capacity and high-efficiency bioretention media should be developed, and the accumulative characteristics in the media should be investigated.

Increasingly, credence is being given to the use of amendments used in conjunction with soil either added as a blend within the soil matrix or layered at one or more depths within the soil profile [16,17]. Different soil amendments have demonstrated competence in various aspects of water-quality improvement. Work by Rahmani suggests that nanostructure alumina is able to absorb Zn [18]. Results show that the maximum removal rates achieved for individual metals were: 95%–100% Cd, Cu, Pb and Zn by calcite, zeolite and iron filings, 90% Ni by zeolite, and 100% Cr by iron filings. Sand produced low results with maximum levels of 8%–58% [19]. Lim assessed the Cu, Zn and Cd removal efficiency of compost, sludge, coconut coir and a proprietary material via a series of column tests [20]. Their findings concluded compost and the proprietary material performed best with reported removal efficiency exceeding 90%, and that metal leaching from all materials was negligible. The goethite-rich overburden and basic oxygenated furnace amendments were showed to remove 46%–98% of dissolved metals (Cu, Pb, and Zn) in repacked soil columns, and up to 72% of dissolved metals were removed by the first 7 cm of filter media [21].

The present work seeks to examine large-capacity and high-efficiency bioretention media, the influence of different factors on bioretention, and find out the accumulative characteristics of heavy metals in different media. In this study, 12 bioretention filters with different types of media are designed to perform water distribution tests by changing different test conditions (inflow concentration, discharge ratio, and recurrence interval). (1) The treatment effect of dissolved heavy metals in 12 filter columns is analyzed, and the effective modified media for bioretention are determined; (2) the treatment effects under different test conditions are compared to determine the influence of different test factors on the treatment efficiency of dissolved heavy metals in bioretention media; and (3) the contents of heavy metals and enzyme in upper, middle, and lower layers in different media are tested before and after the treatment to investigate the accumulative characteristics of heavy metals and correlation between enzymes and heavy metals in the bioretention system.

## 2. Materials and Methods

### 2.1. Media Preparation

In tests, local sand and soil were mixed in a ratio of 7:3 (by mass), and 5% wood chips (by mass) were added in the mixture to make traditional bioretention soil media (BSM). The local soil was obtained from Fengxi New City in Xi'an. Then, the modified media were prepared by mixing modifiers including water treatment residue (WTR), green zeolite (Gz), medicinal stone (Ms), vermiculite, turfy soil (Ts), coconut bran, and fly ash and BSM with different proportions [22]. Selection and proportion of modifiers are determined by previous adsorption experiments [23]. In the static adsorption experiments, the modifiers with good adsorption capacity were selected. In the dynamic adsorption experiments, the max adsorption capacity of modifiers was determined. The media are shown in Table 1. The chemical and physical specifications of media are shown in Table 2. The method for determination of soil organic matter is NY/T 85-1988 in China (<http://www.zbgb.org/27/StandardDetail855835.htm>).

**Table 1.** Twelve bioretention media.

Device Number	1#	2#	3#	4#	5#	6#
Media (by mass)	Local soil	30%Local soil+70%Sand	Bioretention soil media (BSM)	BSM+10%WTR	BSM+10%Gz	BSM+10%Ms
Device Number	7#	8#	9#	10#	11#	12#
Media (by mass)	BSM+10% fly ash	BSM+5% vermiculite	BSM+5%Ts	BSM+5% coconut bran	BSM+2.5%Ms+2.5%Ts	BSM+2.5%Gz+2.5%Ts

**Table 2.** The chemical and physical specifications of media.

Media	Organic Matter %	Specific Surface Area m <sup>2</sup> /g	Ion Exchange Capacity cmol/kg	Pore Volume cm <sup>3</sup> /g	Packed Density g/mL
Loal soil	0.032	20.837	19.44	0.03	1.121
Sand	0.745	0.8037	11.76	0.0021	1.53
BSM	7.55	4.9909	34.45	0.0096	1.116
Water treatment residue (WTR)	10.3	28.433	9.31	0.0215	0.953
Green zeolite (Gz)	6.98	16.8707	27.50	0.0510	1.054
Medicinal stone (Ms)	4.14	1.2723	13.39	0.0033	1.297
Fly ash	2.66	1.3814	23.23	0.0066	1.008
Vermiculite	1.122	1.5942	17.38	0.0162	0.120
Turfy soil (Ts)	36.6	0.7400	14.44	0.0018	0.136
Coconut bran	4.65	0.8105	13.62	0.0026	0.092

## 2.2. Device Setting

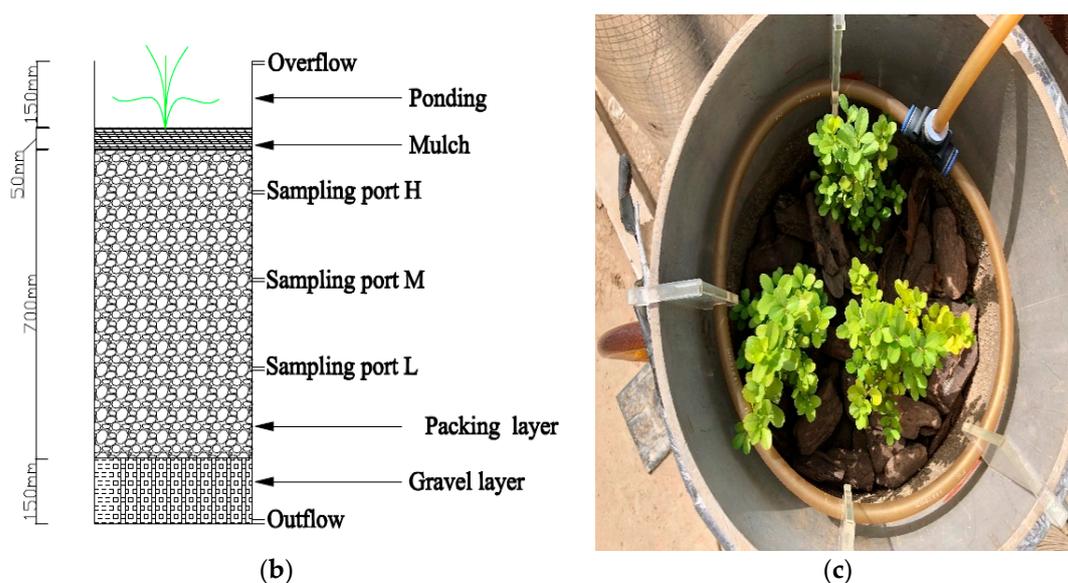
Twelve bioretention filter columns were established at the test site of Xi'an University of Technology. The 12 media were added to the columns. The partial site photo of the columns is shown in Figure 1a. The main body of the device is DN400 PVC tube with a thickness of 6 mm. Each column is 40 cm in diameter and 1.2 m in height. The PVC tube is from Daming Gong Palace building materials market, Xi'an, China.

The devices from bottom to top are as follows, 1. Gravel layer. The gravel layer is 15 cm high and consists of gravels with a diameter of 12–35 mm. The gravel layer is mainly used to protect perforated pipes, to prevent blockage, and to provide temporary storage space. The diameter of the perforated pipe is 25 mm, and it is placed at the bottom of the columns. 2. Packing layer. The height of packing layer is 70 cm. The 12 media were used to fill the packing layer. 3. Mulch. The thickness of mulch layer is 5 cm. Barks fill in the cover layer in this test. 4. Ponding. The (allowed) ponding depth is 15 cm. A water outlet and an overflow port were arranged at the bottom and top ends of the column, respectively. Three holes were set at 10, 30, and 50 cm below the packing layer to collect media. The same plants (three boxwood for every columns) were planted on the 12 columns. The sectional view and vertical view of the bioretention system are shown in Figure 1b,c.



(a)

**Figure 1.** Cont.



**Figure 1.** Schematic of the bioretention system; (a) sectional view; (b) partial site photos; (c) vertical view.

### 2.3. Experimental Design

The influence factors of bioretention on the treatment include the inflow concentration, discharge ratio, precipitation, duration, and antecedent dry time [24,25]. The tests mainly investigate the effects of inflow concentration, discharge ratio, and precipitation on treatment effect and ensure that other conditions (antecedent dry time, rainfall duration, plants, device and environment) keep constant. Antecedent dry period is 6 days, and rainfall duration is 60 min. Three levels of each factor were determined by comparing the results of water quality assessment with urban road surface runoff in Xi’an, China [26]. Nine orthogonal tests were designed. Precipitation was calculated in three recurrence intervals based on Formula (1), as follows [27]:

$$i = \frac{16.715 \times (1 + 1.1658 \lg P)}{(t + 16.813)^{0.9302}} \tag{1}$$

where  $P$  is recurrence interval,  $a$ ;  $t$  is rainfall duration, min.

Different levels of factors and orthogonal experimental design are showed in Tables 3 and 4.

**Table 3.** Different levels of factors.

Level	Factor A (Inflow Concentration, mg·L <sup>-1</sup> )			Factor B (Discharge Ratio)	Factor C (Recurrence Interval)
	Cu	Zn	Cd		
1	1	1.5	0.5	10:1	0.5a
2	0.5	1	0.3	15:1	2a
3	0.3	0.5	0.1	20:1	3a

Note: Cu, Zn, Cd are copper chloride, zinc sulfate, and cadmium chloride, respectively. “a” stands for age. “0.5a” means that the recurrence interval is 0.5 years.

Table 4. Test schedule.

Test	Inflow Concentration	Catchment Ratio	Recurrence Interval	Antecedent Dry Time/day	Rainfall Duration/min	Precipitation/L
1	A1	B1	C1	6	60	151.5
2	A1	B2	C2	6	60	227.3
3	A1	B3	C3	6	60	303.0
4	A2	B1	C2	6	60	315.3
5	A2	B2	C3	6	60	473.0
6	A2	B3	C1	6	60	630.7
7	A3	B1	C3	6	60	363.3
8	A3	B2	C1	6	60	544.9
9	A3	B3	C2	6	60	726.5

Note: Discharge ratio is the catchment area/bioretention surface area. A, B, and C and 1, 2, and 3 correspond to the corresponding values in Table 3.

#### 2.4. Analysis Methods

Different concentration solutions of dissolved Cu, Zn, and Cd are shown in Table 3. The water distribution test is carried out according to the factors shown in Table 4. A certain amount of prepared solution was poured into the storage tank. The water flows evenly into each filter column by adjusting the valve. The water was evenly distributed in 60 min. Each test interval is 6 days. The tests monitored the complete process from the beginning to the end by monitoring the concentration and water volume, outflow and overflow every 5 min. Before and after the treatment, 500 g media were taken in the high, medium, and low holes on the columns for analysis. After each test, the inflow, outflow, and overflow concentrations of Cu, Zn, and Cd in 12 bioretention columns were measured by atomic absorption spectroscopy. The inflow and outflow water samples were filtered through a 0.45 µm membrane. Atomic absorption spectrometry was used to determine the contents of Cu, Zn, and Cd in the water samples. The contents of heavy metals in media before and after the treatment were determined by atomic absorption spectrometry. The urease was measured by indophenol-blue colorimetry, and the protease was measured by copper-salt colorimetry. Concentration removal efficiency  $R_C$ , load reduction efficiency  $R_L$  and content change rate (in media)  $R_m$  are calculated as follows:

$$R_C = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (2)$$

$$R_L = \frac{T_{in} - T_{out} - T_{over}}{T_{in}} \times 100\% \quad (3)$$

$$R_m = \frac{T_{after} - T_{before}}{T_{before}} \times 100\% \quad (4)$$

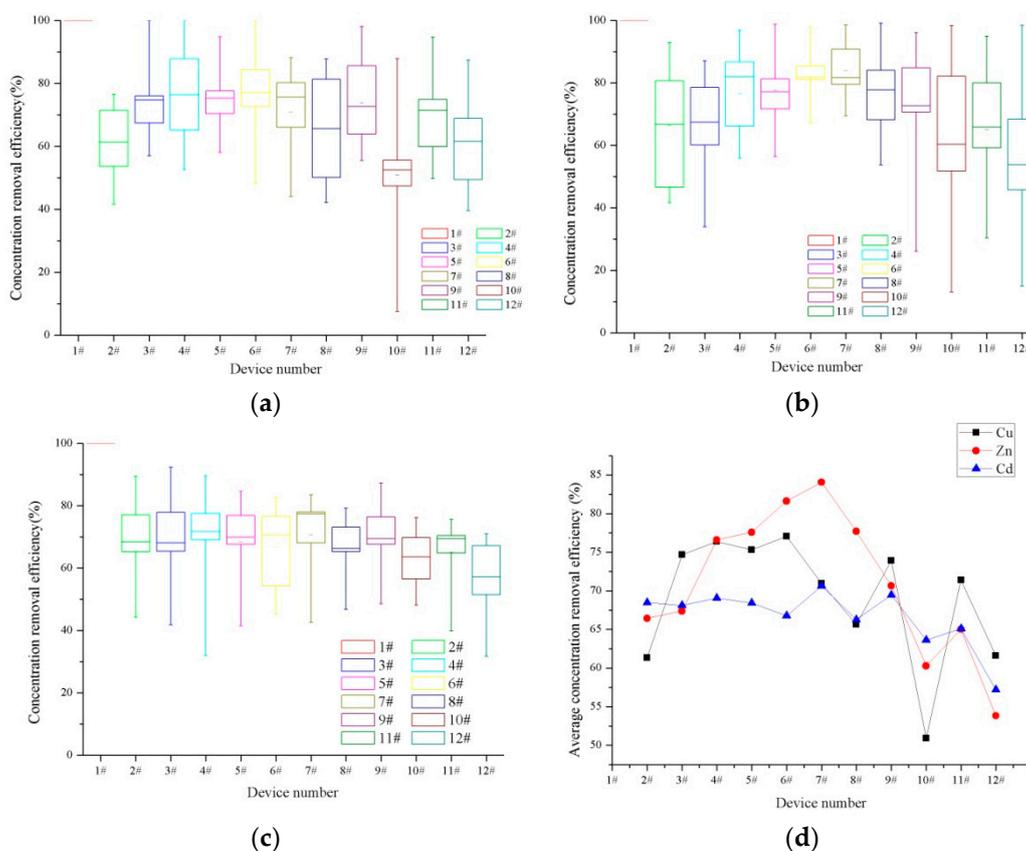
where  $C_{in/out}$  is the mean concentration in a single runoff event for inflow or outflow, mg/L.  $T_{in/out/over}$  is the inflow, outflow, and overflow pollutant load, mg.  $T_{before/after}$  is the content of heavy metal/enzyme in media before/after the 9 tests.

### 3. Results and Discussion

#### 3.1. Dissolved Heavy Metal Concentration Removal Effects

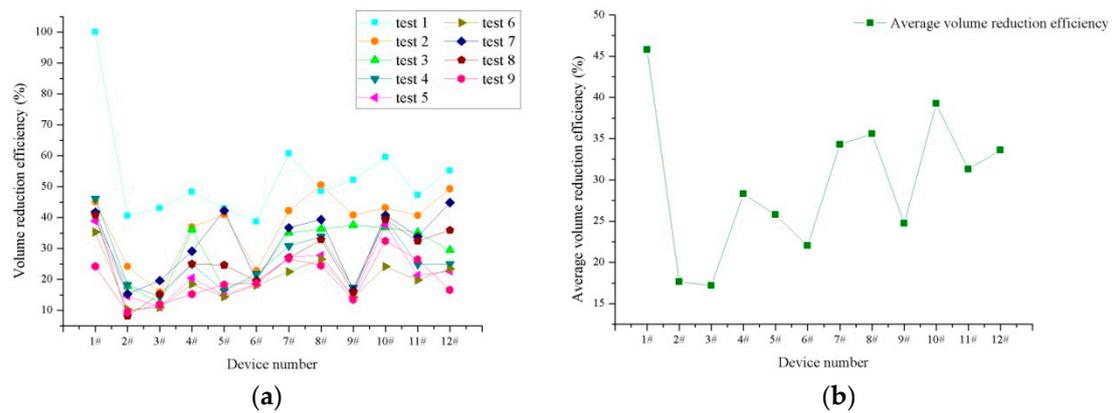
The concentration removal efficiency of Cu, Zn, and Cd in different media is shown in Figure 2. The experimental results showed that 1# (local soil) had no outflow. However, considerable overflows were observed in 9 tests, and it may be related with the infiltration efficiency of the fine and dense soil. The water scour led to the formation layer with low infiltration efficiency at the bottom. So the concentration removal efficiency of Cu, Zn, and Cd in 1# (local soil) was not considered. The concentration removal efficiency of Cu and Zn fluctuated greatly. The average removal efficiencies of 2# (local soil+sand) and 3# (BSM) were 61.31% and 74.67%. The 4# (BSM+WTR),

5# (BSM+Gz), 6# (BSM+Ms), and 7# (BSM+fly ash) had higher removal efficiency of Cu than 3# (BSM). The average removal efficiencies were 76.38%, 75.29%, and 77.04%. The removal efficiencies of 8# (BSM+vermiculite), 9# (BSM+Ts), and 11# (BSM+Ms+Ts) for Cu were lower than that of 3# (BSM) but higher than that of 2# (local soil+sand), and the average removal efficiencies were 65.65%, 73.89%, and 71.62%. The removal efficiencies of 10# (BSM+coconut bran) and 12# (BSM+Gs+Ts) for Cu were relatively low. The removal efficiencies of 4# (BSM+WTR), 5# (BSM+Gz), 6# (BSM+Ms), 7# (BSM+fly ash) and 8# (BSM+vermiculite) for Zn were higher than those of 2# (local soil+sand) and 3# (BSM), and the average removal efficiencies were 74.06%, 74.93%, 79.61%, 82.27%, and 75.03%. The removal efficiencies of 9# (BSM+Ts), 10# (BSM+coconut bran), 11# (BSM+Ms+Ts), and 12# (BSM+Gs+Ts) for Zn were relatively low. The removal efficiency of Cd fluctuated slightly, which may be related to low inflow concentration. The 7# (BSM+fly ash) and 9# (BSM+Ts) had high Cd removal efficiency, and their average removal efficiencies were 70.64% and 69.45%, respectively. The removal efficiencies of 10# (BSM+coconut bran) and 12# (BSM+Gs+Ts) for Cd were low, and the rest were relatively stable.

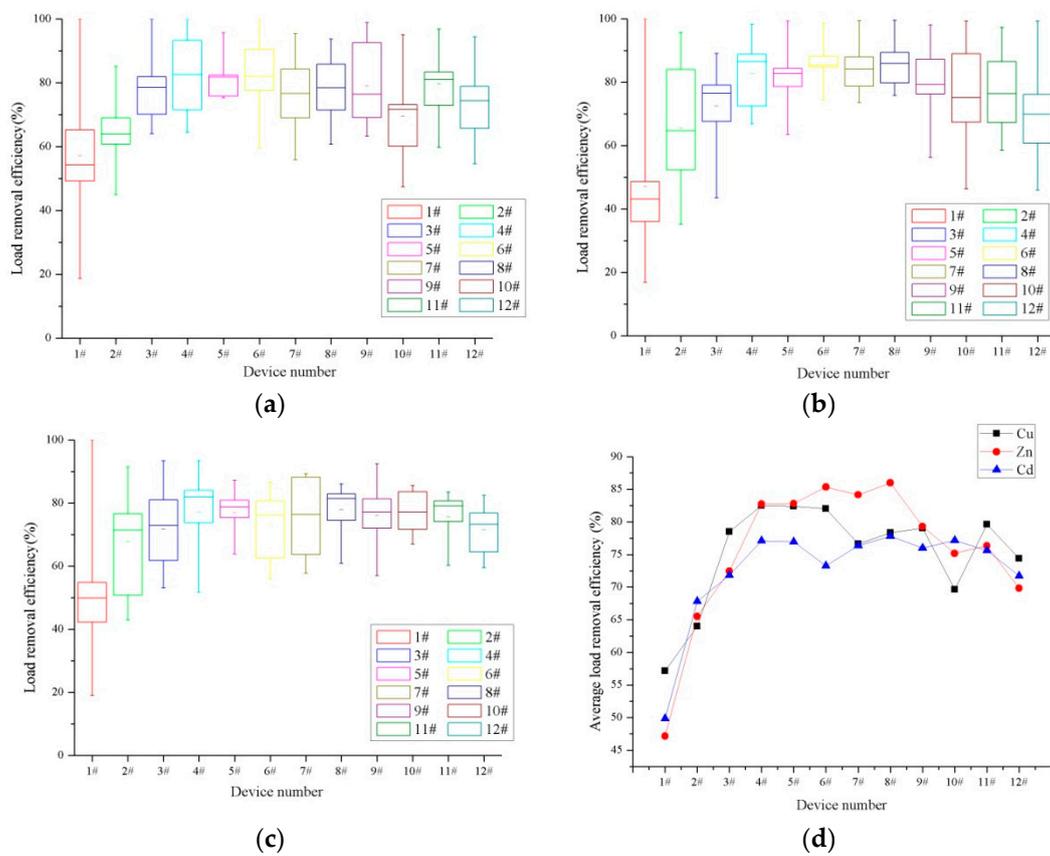


**Figure 2.** Concentration removal efficiency in different media combinations; (a) Cu; (b) Zn; (c) Cd; (d) average concentration removal efficiency.

The difference in inflow, outflow, and overflow water volumes leads to different load reduction efficiency and accumulation of heavy metals in the media. The volume reduction efficiency for the 9 tests is shown in Figure 3. The load reduction efficiency in different media combinations is shown in Figure 4.



**Figure 3.** Volume reduction efficiency in different media combinations; (a) volume reduction efficiency in each test; (b) average volume reduction efficiency.



**Figure 4.** Load reduction efficiency in different media combinations; (a) Cu; (b) Zn; (c) Cd; (d) average concentration removal efficiency.

The first test volume reduction efficiency of the 12 columns was generally high. This condition is due to the fact that the media inside the columns were dry before test 1. The volume reduction efficiencies in the remaining 8 tests of 1#–12# columns fluctuated within the range of 24%–46%, 8%–24%, 10%–19%, 15%–36%, 14%–42%, 18%–22%, 22%–42%, 24%–50%, 13%–40%, 24%–43%, 19%–40%, and 16%–49%, respectively. The 1# (local soil) had overflow and no outflow. The 2# (local soil+sand), 3# (BSM), and 7# (BSM+fly ash) also overflowed at different degrees when the inflow volume was large. The average volume reduction efficiencies of 4#–12# were higher than those of 2# (local soil+sand) and 3# (BSM). The 10# (BSM+coconut bran) had the highest average volume reduction efficiency of 39.25%. Low volume reduction efficiency and high overflow concentration decreased load reduction efficiency.

The load reduction efficiencies of 3#–12# on Cu, Zn, and Cd were all more than 70%. The load reduction efficiencies of 4# (BSM+WTR), 5# (BSM+Gz), and 6# (BSM+Ms) on Cu can reach more than 80%. The load reduction efficiencies of 4# (BSM+WTR), 5# (BSM+Gz), 6# (BSM+Ms), 7# (BSM+fly ash) and 8# (BSM+vermiculite) on Zn reached more than 80%. The load reduction efficiencies of 4#–11# were higher than those of 2# (local soil+sand) and 3# (BSM), and the highest was that of 8# (BSM+vermiculite), which reached 77.83%.

The modified media had a better treatment effect on dissolved Cu, Zn, and Cd. The treatment effect of 4# (BSM+WTR), 5# (BSM+Gz), 6# (BSM+Ms), 9# (BSM+Ts), and 11# (BSM+Ms+Ts) in dissolved Cu, Zn, and Cd was better than the traditional BSM, which can replace the traditional BSM as the new modified media.

### 3.2. Relationship between Treatment Effect and Test Factors

Nine orthogonal tests were conducted to change the inflow concentration, discharge ratio, and precipitation, and the other conditions were kept constant. The influence of the three factors on the treatment effect of biological retention facilities was analyzed. Combining the load reduction efficiency of the nine tests, the best test results were screened for each of the three factors, and the corresponding factor levels were the optimal test condition. The range of load reduction efficiencies under the three factors of each column was calculated, and the best configuration level was determined. The results are shown in Table 5 and Figure 5.

**Table 5.** Range of the three factors and optimal test condition in different media.

Device Number	Range/A	Range/B	Range/C	Optimal Test Condition
1#	0.377	1.109	0.588	A1B1C1
2#	0.771	0.425	0.245	A1B2C2
3#	0.588	0.383	0.085	A1B2C3
4#	0.590	0.322	0.210	A1B2C2
5#	0.380	0.127	0.145	A1B2C2
6#	0.388	0.331	0.276	A1B2C2
7#	0.465	0.353	0.195	A1B1C2
8#	0.276	0.208	0.129	A1B2C2
9#	0.502	0.359	0.227	A1B2C2
10#	0.374	0.392	0.367	A1B2C2
11#	0.439	0.294	0.237	A1B2C2
12#	0.425	0.242	0.392	A1B2C1

The greater the range is, the easier the treatment effect by this factor. The treatment effects of 2#–9# and 11# (BSM+Ms+Ts) were most affected by inflow concentration, followed by discharge ratio and recurrence interval. The ranges of the three conditions for 10# (BSM+coconut bran) were close. The optimal test conditions of 1#–12# were obtained by comparing the load reduction efficiency of different factors and different levels. The optimal test conditions for 1# (local soil), 3# (BSM), 7# (BSM+fly ash), and 12# (BSM+Gs+Ts) were A1B1C1, A1B2C3, A1B1C2, and A1B2C1, respectively, and for the other 8 devices are A1B2C2. For the optimal test conditions of 12 devices, A1, B2, and C2 appeared 12, 10, and 9 times, respectively. The optimal setting levels that correspond to the three factors were  $1 \text{ mg}\cdot\text{L}^{-1}$  for Cu,  $1.5 \text{ mg}\cdot\text{L}^{-1}$  for Zn,  $0.5 \text{ mg}\cdot\text{L}^{-1}$  for Cd, 15:1, and 2a.

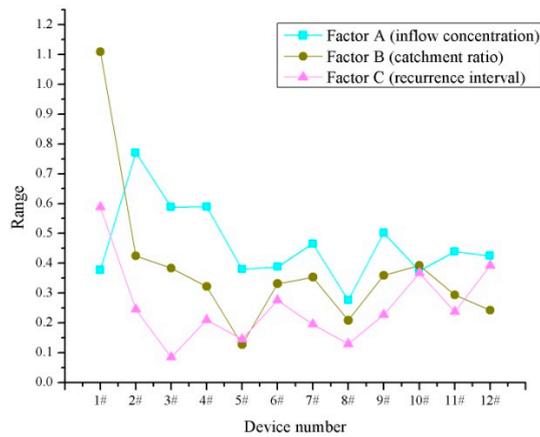


Figure 5. Comparison of range among the three factors.

### 3.3. Adsorption and Accumulation of Heavy Metals and Difference of Enzyme Activity in Different Media

Removal of heavy metals from stormwater runoff in bioretention is mainly caused by filtration, sorption, and plant/microorganism uptake. Most heavy metals accumulate inside the media. The study showed that 88%–97% of Cu, Zn, and Cd in stormwater are trapped in the media and 0.5%–3.3% are absorbed by plants [28]. Cu, Zn, and Cd contents in the upper and middle layers were determined. Meanwhile, the contents of urease and protease in 1# (local soil), 4# (BSM+WTR), 5# (BSM+Gz), 7# (BSM+fly ash), and 10# (BSM+coconut bran) were analyzed by colorimetry. The content of heavy metals in media before and after treatment is shown in Figure 6. The content change rates of heavy metal/enzyme with depth are shown in Figure 7.

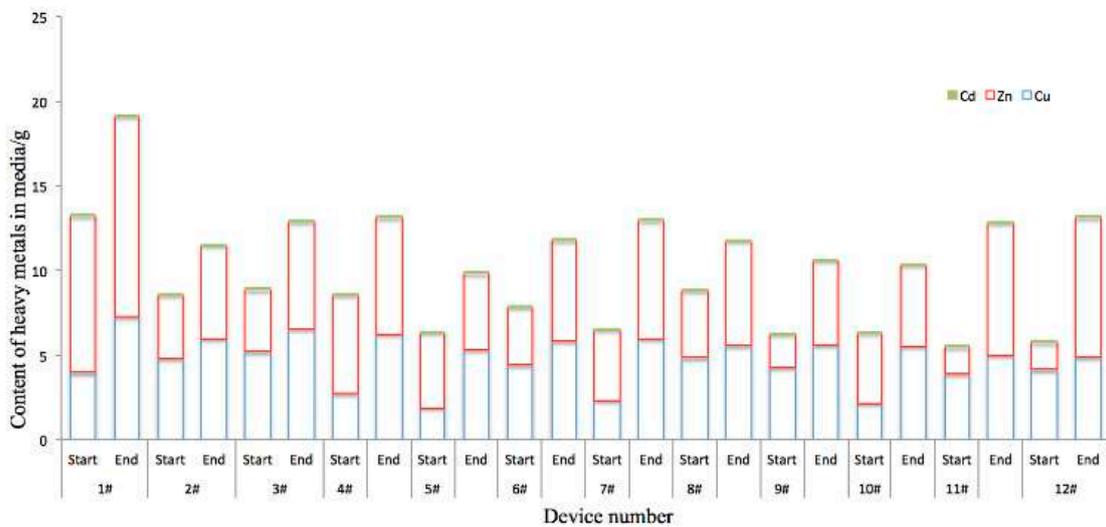
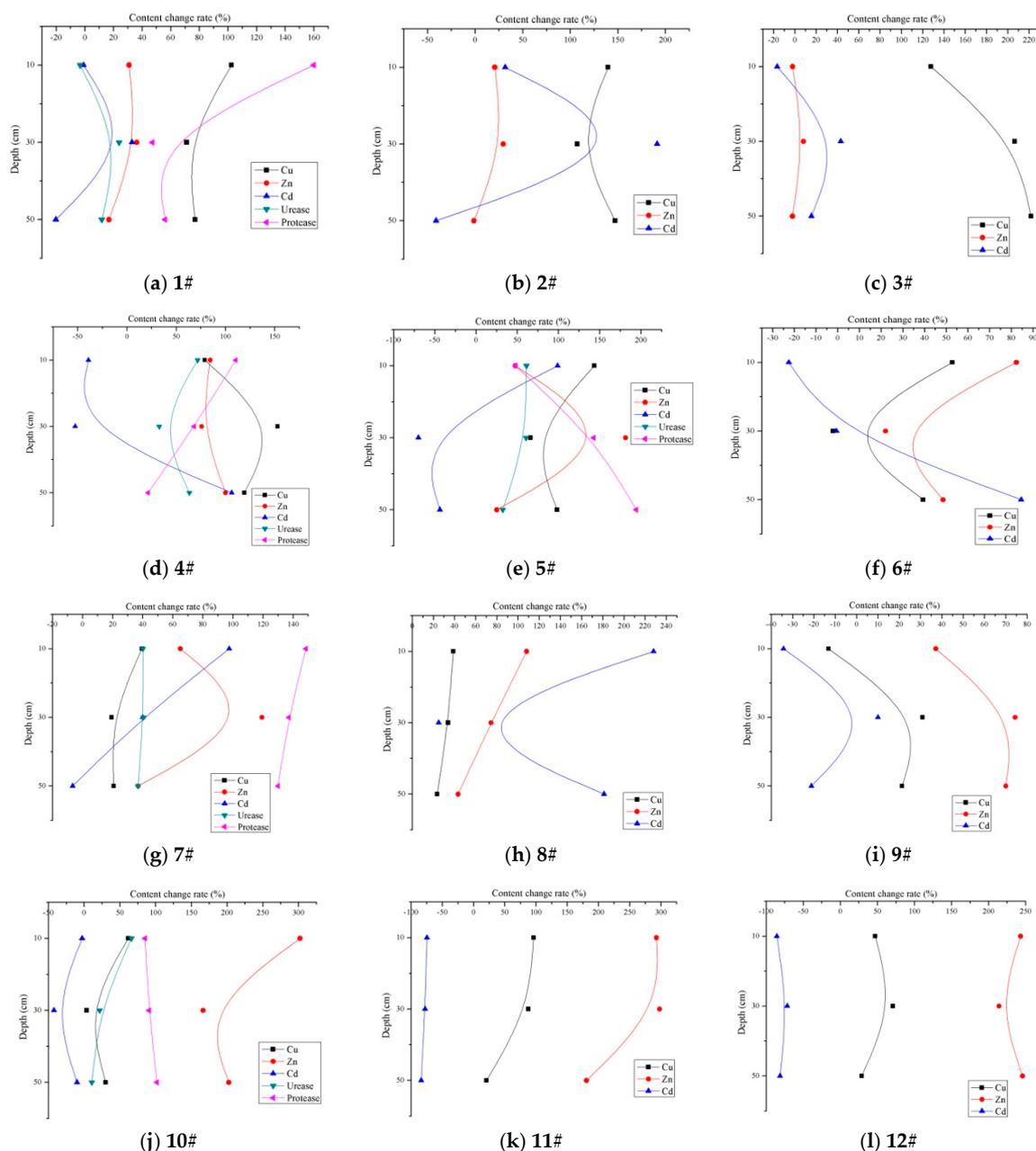


Figure 6. Content of heavy metals in media.



**Figure 7.** Content change rates of heavy metal/enzyme with depth; (a) 1#; (b) 2#; (c) 3#; (d) 4#; (e) 5#; (f) 6#; (g) 7#; (h) 8#; (i) 9#; (j) 10#; (k) 11#; (l) 12#.

The inflow concentrations of Zn, Cu, and Cd in this test were sequentially decreased. The average load difference of 4#–12# was Zn>Cu>Cd and the average load difference of 1# (Local soil), 2# (local soil+sand), and 3# (BSM) was Cu>Zn>Cd, as determined by comparing the average load difference of three depths in Figure 6 (4#). The accumulations of Cu, Zn, and Cd in 6# (BSM+Ms), 7# (BSM+fly ash), 8# (BSM+vermiculite), and 9# (BSM+Ts) were relatively low. This conclusion is inconsistent with the high load reduction efficiency of 6# (BSM+Ms), 7# (BSM+fly ash), and 9# (BSM+Ts), which is related to the absorbed heavy metals by plants or microorganisms. Future studies on the uptake of heavy metals by plants or microorganisms should be conducted. For vertical comparison of media in each column, the content change rate of Cd was volatile, which is related to small influent concentration. The content of Cd in a large number of columns is less than that before the test, which is due to the growth and absorption of plants and microorganisms. For Cd and Zn, the curve slightly fluctuates but does not show the law of depth. For Cu, the content change rates of the

upper layer in 1# (Local soil), 5# (BSM+Gz), 6# (BSM+Ms), 7# (BSM+fly ash), 8# (BSM+vermiculite), 10# (BSM+coconut bran), and 11# (BSM+Ms+Ts) are more than that of the middle and lower layers. However, the difference between the three layers in 1# (Local soil), 2# (local soil+sand), 7# (BSM+fly ash), 8# (BSM+vermiculite), 10# (BSM+coconut bran), and 12# (BSM+Gs+Ts) is not obvious. For Zn, the content change of the middle layer in 1# (Local soil), 2# (local soil+sand), 3# (BSM), 5# (BSM+Gz), 7# (BSM+fly ash), 9# (BSM+Ts), and 11# (BSM+Ms+Ts) are the highest. However, the difference between the three layers in 1# (Local soil), 2# (local soil+sand), 3# (BSM), 4# (BSM+WTR), and 12# (BSM+Gs+Ts) is not obvious. This result is due to the fact that dissolved heavy metals can only be adsorbed by media or absorbed by plants and microbes.

Pearson correlation analysis was conducted on heavy metal content and enzyme activity in media (Table 6). Heavy metals and enzymes were correlated. The contents of the three metals were positively correlated with urease and negatively correlated with protease. The correlation between each metal content and enzyme was low, whereas the correlation between the summation of the three heavy metals and enzyme was relatively high. The Pearson correlation coefficient of summation and urease was 0.52, and that of the summation and protease was  $-0.45$ .

**Table 6.** Pearson correlation of enzymes and heavy metals in media.

Content Difference	Cu	Zn	Cd	Summation
Urease	0.20	0.32	0.21	0.52
Protease	$-0.34$	-	$-0.36$	$-0.45$

Currently, no systematic study is reported on the existing forms and transformation rules of heavy metals in bioretention. Granular heavy metals are mainly accumulated in the upper media of bioretention and gradually decrease by depth [29]. However, no obvious rule is established for the accumulation of dissolved heavy metals. This condition is because dissolved heavy metals can only be absorbed by fillers and absorbed by microbes and plants and cannot be intercepted by fillers. Metals adsorbed to organic matter in the bioretention media are not permanently immobilized. Any processes that result in leaching of the media organic matter, such as dissolution or biotransformation, can result in mobilization of the organic matter-associated metals. The release of Cu from bioretention media has been linked to the release of dissolved organic matter [30,31].

#### 4. Conclusions

The present work seeks to examine large-capacity and high-efficiency bioretention media, influence of different factors on bioretention, and find out the accumulative characteristics of heavy metals in different media by comparing the treatment of 12 different media on Cu, Zn and Cd. The results show that (a) the bioretention soil media achieve better treatment effects of dissolved heavy metals by mixing water treatment residue, green zeolite, and medicinal stone as modifiers; (b) inflow concentration is the most significant effect for most of the bioretention media on the treatment effect of dissolved heavy metals followed by discharge ratio and recurrence interval; and (c) different media lead to different accumulative characteristics of heavy metals, and the media with low accumulations are more suitable for long-term use.

The correlation of accumulation and microorganism has also been noted in this study. A correlation was observed between heavy metal elements and enzymes. The media with high load reduction efficiency but low accumulation may be related to its microorganism content. The adsorption capacity of bioretention media is limited, and the long-term bioretention system may pose a threat to plant growth. Heavy metals cause ecological risks, such as soil and groundwater pollution, when they are accumulated to a certain degree [32,33]. Therefore, the migration and transformation of heavy metals between the fillers, microorganisms, and plants inside the bioretention have significant prospects for pollution. According to the minor contribution of plants, more work is needed to investigate

whether the incorporation of hyper accumulating plant species into bioretention cells [34,35] would improve overall metal capture and metal uptake via this mechanism.

**Author Contributions:** Y.L. designed the research scheme and wrote the manuscript. M.W. processed the data, analyzed the results, and wrote the manuscript. J.L., B.C. and C.J. improved the results analysis.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Hu, A.; Li, Z.; Zhang, S.; Liu, J.; Chen, J. Research Progress on urban road rain water quality. *Geomat. World* **2010**, *46*, 123–127. [[CrossRef](#)]
2. Ma, Y.; Egodawatta, P.; Mcgree, J.; Liu, A.; Goonetilleke, A.; Goonetilleke, A. Human health risk assessment of heavy metals in urban stormwater. *Sci. Total Environ.* **2016**, *557*, 764–772. [[CrossRef](#)] [[PubMed](#)]
3. Hwang, H.M.; Fiala, M.J.; Park, D.; Wade, T.L. Review of pollutants in urban road dust and stormwater runoff: Part 1. Heavy metals released from vehicles. *Int. J. Urban Sci.* **2016**, *20*, 1–27. [[CrossRef](#)]
4. Grogoglione, A.; Bombardelli, F.A.; Pitton, B.J.L.; Oki, L.R.; Haver, D.L.; Young, T.M. Role of Sediments in Insecticide Runoff from Urban Surfaces: Analysis and Modeling. *Int. J. Environ. Res. Public Health* **2018**, *15*, 1464. [[CrossRef](#)] [[PubMed](#)]
5. Jiang, W.; Gan, J. Importance of Fine Particles in Pesticide Runoff from Concrete Surfaces and Its Prediction. *Environ. Sci. Technol.* **2012**, *46*, 6028–6034. [[CrossRef](#)] [[PubMed](#)]
6. Bressy, A.; Gromaire, M.-C.; Lorgeoux, C.; Saad, M.; Leroy, F.; Chebbo, G. Towards the determination of an optimal scale for stormwater quality management: Micropollutants in a small residential catchment. *Water Res.* **2012**, *46*, 6799–6810. [[CrossRef](#)] [[PubMed](#)]
7. Lefevre, G.H.; Paus, K.H.; Natarajan, P. Review of dissolved pollutants in urban storm water and their removal and fate in bioretention cells. *J. Environ. Eng.* **2015**, *141*. [[CrossRef](#)]
8. Davis, A.P.; Traver, R.G.; Hunt, W.F. Improving urban stormwater quality: Applying fundamental principles. *Water Res.* **2010**, *44*, 3–10. [[CrossRef](#)]
9. Clark, S.E.; Pitt, R. Targeting treatment technologies to address specific stormwater pollutants and numeric discharge limits. *Water Res.* **2012**, *46*, 6715–6730. [[CrossRef](#)] [[PubMed](#)]
10. Erickson, A.J.; Gulliver, J.S.; Weiss, P.T. Enhanced sand filtration for storm water phosphorus removal. *Environ. Eng.* **2007**, *133*, 485–497. [[CrossRef](#)]
11. Kayhanian, M.; Fruchtmann, B.D.; Gulliver, J.S.; Montanaro, C.; Ranieri, E.; Wuertz, S. Review of highway runoff characteristics: Comparative analysis and universal implications. *Water Res.* **2012**, *46*, 6609–6624. [[CrossRef](#)] [[PubMed](#)]
12. Sun, Y.; Wei, X.; Pomeroy, C.A. Review of current research and future directions of low impact development practices for storm water. *Adv. Water Sci.* **2011**, *22*, 287–293.
13. Sheoran, A.S.; Sheoran, V. Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review. *Miner. Eng.* **2006**, *19*, 105–116. [[CrossRef](#)]
14. Ranieri, E.; Grogoglione, A.; Montanaro, C.; Iacovelli, A.; Gikas, P. Removal capacity of BTEX and metals of constructed wetlands under the influence of hydraulic conductivity. *Desalin. Water Treat.* **2015**, *56*, 5. [[CrossRef](#)]
15. De Macedo, M.B.; Rosa, A.; Do Lago, C.A.F.; Mendiondo, E.M.; de Souza, V.C.B. Learning from the operation, pathology and maintenance of a bioretention system to optimize urban drainage practices. *J. Environ. Manag.* **2017**, *204*, 454–466. [[CrossRef](#)] [[PubMed](#)]
16. Ingvertsen, S.T.; Cederkvist, K.; Jensen, M.B. Assessment of existing roadside swales with engineered filter soil: II. Treatment efficiency and in situ mobilization in soil columns. *J. Environ. Qual.* **2012**, *41*, 1970–1981. [[CrossRef](#)] [[PubMed](#)]
17. Hsieh, C.; Davis, A.P. Evaluation and optimization of bioretention media for treatment of urban storm water runoff. *J. Environ. Eng.* **2005**, *131*, 1521–1531. [[CrossRef](#)]

18. Rahmani, A.; Mousavi, H.Z.; Fazli, M. Effect of nanostructure alumina on adsorption of heavy metals. *Desalination* **2010**, *253*, 94–100. [[CrossRef](#)]
19. Reddy, K.R.; Xie, T.; Dastgheibi, S. Removal of heavy metals from urban stormwater runoff using different filter materials. *J. Environ. Chem. Eng.* **2014**, *2*, 282–292. [[CrossRef](#)]
20. Lim, H.S.; Lim, W.; Hu, J.Y. Comparison of filter media materials for heavy metal removal from urban stormwater runoff using biofiltration systems. *J. Environ. Manag.* **2015**, *147*, 24–33. [[CrossRef](#)] [[PubMed](#)]
21. Trenouth, W.R.; Gharabaghi, B. Soil amendments for heavy metals removal from stormwater runoff discharging to environmentally sensitive areas. *J. Hydrol.* **2015**, *529*, 1478–1487. [[CrossRef](#)]
22. Bratieres, K.; Fletcher, T.D.; Deletic, A. Nutrient and sediment removal by stormwater biofilters: A large-scale design optimization study. *Water Res.* **2008**, *42*, 3930–3940. [[CrossRef](#)] [[PubMed](#)]
23. Zhang, B.; Li, J.; Li, Y. Adsorption Characteristics of Several Bioretention-Modified Fillers for Phosphorus. *Water* **2018**, *10*, 831. [[CrossRef](#)]
24. Berndtsson, J.C. Green roof performance towards management of runoff water quantity and quality: A review. *Ecol. Eng.* **2010**, *4*, 351–360. [[CrossRef](#)]
25. Read, J.; Wevill, T.; Fletcher, T. Variation among plant species in pollutant removal from storm water in biofiltration systems. *Water Res.* **2008**, *42*, 893–902. [[CrossRef](#)] [[PubMed](#)]
26. Zhou, J. *Study on the Changes in Rainfall Patterns in Xi'an*; Xi'an University of Architecture & Technology: Xi'an, China, 2015.
27. Lu, J.; Cheng, Y.; Deng, Q.; Du, R.; Wang, S.; Wang, J. Derivation of rainstorm intensity Equation in Xi'an city. *Chin. Water Wastewater* **2010**, *26*, 82–84.
28. Sun, X.; Davis, A.P. Heavy metal fates in laboratory bioretention systems. *Chemosphere* **2007**, *66*, 1601–1609. [[CrossRef](#)] [[PubMed](#)]
29. Al-Ameri, M.; Hatt, B.; Coustumer, S.L. Accumulation of heavy metals in stormwaterbioretention media: A field study of temporal and spatial variation. *J. Hydrol.* **2018**. [[CrossRef](#)]
30. Li, H.; Davis, A.P. Water quality improvement through reductions of pollutant loads using bioretention. *J. Environ. Eng.* **2009**, *135*, 567–576. [[CrossRef](#)]
31. Blecken, G.T.; Marsalek, J.; Viklander, M. Laboratory study of stormwater biofiltration in low temperatures: Total and dissolved metal removals and fates. *Water Air Soil Pollut.* **2011**, *219*, 303–317. [[CrossRef](#)]
32. Mullane, J.M.; Flury, M.; Iqbal, H. Intermittent rainstorms cause pulses of nitrogen, phosphorus, and copper in leach ate from compost in bioretention systems. *Sci. Total Environ.* **2015**, *537*, 294–303. [[CrossRef](#)] [[PubMed](#)]
33. Chen, G.; Zeng, G.; Du, C. Transfer of heavy metals from compost to red soil and groundwater under simulated rainfall conditions. *J. Hazard. Mater.* **2010**, *181*, 211–216. [[CrossRef](#)] [[PubMed](#)]
34. Dietz, M.E.; Clausen, J.C. Saturation to Improve Pollutant Retention in a Rain Garden. *Environ. Sci. Technol.* **2006**, *40*, 1335–1340. [[CrossRef](#)] [[PubMed](#)]
35. Muthanna, T.M.; Viklander, M.; Gjesdahl, N. Heavy Metal Removal in Cold Climate Bioretention. *Water Air Soil Pollut.* **2007**, *183*, 391–402. [[CrossRef](#)]

