



A mixed-flow bioretention system amended with water treatment residuals to enhance nitrogen and phosphorus removal performance

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ABSTRACT

Bioretention is a stormwater management practice that can effectively remove several urban runoff pollutants, but the extent of nitrogen and phosphorus removal varies. In this study, 10% (v/v) water treatment residuals (WTRs) and a submerged zone were used to enhance phosphorus and nitrogen removal, respectively, and a mixed-flow bioretention column filled with WTRs that enhances simultaneous phosphorus and nitrogen removal. A semi-synthetic runoff experiment, which included 10 rainfall events, showed that setting a submerged zone and adding wood chips to the bioretention columns increased the volume reduction efficiency and enhanced the infiltration rate, but adding WTRs had a negative effect on both. However, the addition of WTRs in column media significantly improved the removal efficiency of various phosphorus forms, and setting a submerged zone negatively affected particulate phosphorus (PP) and total phosphorus (TP) removal efficiency, but the effect on dissolved phosphorus removal efficiency was limited. Setting a submerged zone produced a significant improvement in nitrate ($\text{NO}_3\text{-N}$) removal ($p < 0.05$), but negatively affected ammonia ($\text{NH}_4\text{-N}$) removal. When WTRs and submerged zones existed simultaneously, total nitrogen (TN) removal was weakened compared with the column with only a submerged zone, but $\text{NO}_3\text{-N}$ removal was not affected significantly ($p > 0.05$). The mixed-flow bioretention column had higher phosphorus removal than conventional systems, and TP mass removal efficiency increased from $83.33\% \pm 3.64\%$ (conventional) to $97.58\% \pm 0.91\%$ (mixed-flow), and PP increased from $75.38\% \pm 7.26\%$ (conventional) to $98.21\% \pm 1.82\%$ (mixed-flow). The $\text{NH}_4\text{-N}$ and TN removal efficiencies in the mixed-flow bioretention column was also higher than the conventional column, but this was not the case for $\text{NO}_3\text{-N}$. The mixed-flow bioretention filled with WTRs provides an alternative approach to achieve a better simultaneous removal of nitrogen and phosphorus.

Keywords: Bioretention; Submerged zone; Water treatment residual; Mixed-flow; Nitrogen and phosphorus removal

1. Introduction

Rapid urbanization increases the imperviousness of drainage areas, resulting in higher peaks and volume

of runoff. Increased runoff conveys additional pollutants from watersheds, negatively affecting water quality when it is discharged [1]. Increased nutrient (such as nitrogen (N) and phosphorus (P)) wash-off is conveyed to receiving

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lakes, rivers and estuaries downstream; these increased inflows stimulate excessive and unbalanced plant and algal growth, leading to oxygen depletion and eventual eutrophication of the water body [2]. Runoff pollution can be effectively controlled by various technical practices, among which bioretention is one of the most commonly used [3].

Bioretention has been reported to be one of the most effective runoff management practice for water quantity and quality [4]. Bioretention systems can effectively reduce peak flow and runoff volumes [5,6]. The pollutant removal performance of bioretention systems has been widely investigated [7,8]. Total suspended solids (TSS), chemical oxygen demand (COD) and organic matter in runoff are effectively removed in a bioretention system [3,9–11]; however, the removal of nutrients, such as N and P, is less certain [4,12–15]. Several approaches that aim to enhance the N and P removal performance of a bioretention have been investigated, including media amendments to improve P removal [16], and submerged zones or a layered structure to improve N removal, respectively [17,18]. In addition, plants play an important role in N removal [19]. As reported in previous research, N and P removal can be improved, but differences in effectiveness still exist [17,18,20,21]. Therefore, a method of how best to achieve stable N and P removal still needs to be further investigated.

To improve the P removal performance of a bioretention system, a variety of materials have been investigated. Kandel et al. [13] found that fly ash can effectively adsorb P, and bioretention schemes using sand and 5% fly ash as mixed media can improve P removal whereby total phosphorus (TP) concentrations and outflow mass decreased by 68%–75% and 76%–93%, respectively. Zhang et al. [22] found that water treatment residuals (WTRs) and fly ash demonstrated good adsorption capacity for soluble reactive phosphorus (SRP), and the adsorption capacity of a modified mixture (10% WTRs) was a significant improvement (~3.5–4.5 times) over other mixed fillers. Jiang et al. [20] investigated P adsorption on to bioretention media with the addition of 5% modified material, including green zeolite, WTRs, fly ash and medical. The adsorption capacity of WTRs (18.859 mg/kg) was greater than fly ash (13.340 mg/kg), medical (12.062 mg/kg) and green zeolite (10.989 mg/kg) when SRP was 1.0 mg/L. Thus, WTRs has been shown to be an efficient material to enhance P adsorption. Zhang et al. [23] explored the feasibility of river sediment, which is rich in aluminum (Al) and iron (Fe) oxides, to be used as bioretention media in a laboratory study, and the results showed that bioretention columns with 6% (volume ratio) of river sediment in upper reaches achieved $81.86\% \pm 9.91\%$ TP mass removal efficiencies. Commercially available activated carbon and river sediment-derived biochar can improve the P removal performance of bioretention media [24]. Overall, these reported materials can improve TP removal, although the degree of improvement varies.

Among the materials that enhance P adsorption, WTRs is an effective media to improve the P removal efficiency of a bioretention system. Dayton et al. [25] examined 21 types of Al-based WTRs; their results showed that the adsorption of P in runoff was related to Al or Fe oxide contents. O'Neill and Davis [26] found that the adsorption of TP and

dissolved phosphorus (DP) in bioretention media containing WTRs were higher than the adsorption capacity of TP and DP without WTRs under equilibrium conditions. They established a long-term column experiment to confirm that 93.3% of the TP mass can be removed by bioretention media filled with WTRs, which was a substantial significant improvement when compared with media without WTRs [27]. This improvement in TP removal was confirmed by other studies [12,28–31].

The conversion of different forms of nitrogen (i.e., total nitrogen (TN), ammonia ($\text{NH}_4^+\text{-N}$) and nitrate ($\text{NO}_3^-\text{-N}$)) in a bioretention system is complicated, and removal performance is variable [32]. Several design modifications have been widely investigated, including setting a submerged zone, adding additional carbon sources, and using layered media. Kim and Davis [33] set up a submerged zone and added a carbon source to enhance denitrification in the bioretention, and the subsequent $\text{NO}_3^-\text{-N}$ removal efficiency reached 80%. A double-layer bioretention system, in which each layer has high or low infiltration capacity, was proposed by Hsieh et al. [1]; the results indicated that a system with high infiltration in the upper layer and low infiltration in the lower layer was prone to form an anoxic environment, an affect similar to setting a submerged zone. Layered media were beneficial for denitrification and the $\text{NO}_3^-\text{-N}$ removal efficiency reached 84%. Wan et al. [18] improved on the double-layer bioretention system by adding wood chips in the upper layer because the oxygen consumption of wood chips enhances the activity of some heterogeneous bacteria in the upper layer, resulting in hypoxia in the surrounding environment and enhancing denitrification. During the experiment, the $\text{NO}_3^-\text{-N}$ removal efficiency exceeded 80% [18]. These results indicate that whether there is a submerged zone or double-layer bioretention system was created that enhanced microbial function and improved the removal of N.

Setting a submerged zone and adding a carbon source are commonly used methods at present to improve the removal of N pollutants in bioretention systems. When Peterson et al. [34] set a submerged zone and added a carbon source, the $\text{NO}_3^-\text{-N}$ removal efficiency significantly improved to $82.4\% \pm 0.4\%$. This improvement was confirmed in similar studies [35]. A submerged zone increases hydraulic retention time, promotes denitrification and improves the removal of N pollutants, whereas an additional carbon source is essential to enhance N pollutant removal [36]. A submerged zone is normally accomplished by setting a given depth zone at the bottom of the bioretention; denitrification is related to the size of the submerged zone. The up-flow and mixed-flow bioretention proposed in Zhang et al. [37] showed that the influence of the submerged zone was expanded and the TN mass removal efficiency was significantly increased compared with conventional bioretention schemes.

Amendments to bioretention media that enhance P removal, as well as submerged zone settings that enhance N removal, have mostly been studied separately and there are few studies that combine these two approaches to investigate them simultaneous N and P removal. Palmer et al. [28] found that submerged zone will affect the removal of P. However, Liu et al. [38] found that the P removal effect was

better when WTRs and submerged zones existed simultaneously. Qiu et al. [39] found that N and P removal can be improved by adding WTRs and setting a submerged zone. However, whether the submerged zone and added WTRs affect each other and whether they can achieve highly efficient simultaneous N and P removal needs further research. The mixed-flow bioretention system proposed by Zhang et al. [37] can effectively improve TN removal, but it is unclear whether high-efficiency simultaneous N and P removal can be achieved or whether there are differences in N and P removal between mixed-flow and conventional bioretention systems if a certain prescribed of WTRs is added to the media; this also merits further research.

Thus, our experiment explored N and P pollutant removal performance by simultaneously adding WTRs and setting a submerged zone in laboratory-based bioretention columns. The objectives of this study were to (a) investigate whether WTRs and a submerged zone can achieve simultaneous N and P removal, (b) evaluate the effects on N and P removal in a mixed-flow bioretention system with added WTRs and (c) quantify differences in the removal of N and P pollutants between a mixed-flow bioretention system and a conventional one with a submerged zone.

2. Materials and methods

2.1. Bioretention column setup

We established four bioretention columns in a greenhouse located at the Beijing University of Civil Engineering and Architecture (Fig. 1); thus, the influence of natural rainfall and other factors was intentionally avoided. The experiment ran from September 2019 to January 2020,

during which time the highest temperature was 27°C and the lowest temperature was -2°C. Each bioretention column consisted of a 150 mm diameter PVC pipe (Fig. 2). The flow direction of three columns (GaW, GaS and GWS) was downward. GWM was mixed-flow, where it first had upward flow and then downward flow. For the column named GaW, GaS, GWS and GWM, Ga and G represents garden soil; W represents WTRs; S represents submerged zone; M represents mixed-flow.

GaW and GWM had WTRs added to verify P removal. WTRs was provided by Changzhou CGE Water Co., Ltd., and the proportion added was 10% (volume ratio), as suggested by related research [29]. Garden soil was taken from a greenbelt area. A 300-mm deep submerged zone was set and wood chips were added in GaS and GWS to study N removal. The mixed-flow in GWM's two-column bioretention structure followed Zhang et al. [37]; the majority of the right column acted as a submerged zone during bioretention operations (Fig. 2c). The mixed-flow bioretention has been implemented in Guyuan, Ningxia province, a national pilot city of sponge city in China. Fig. 3 illustrates the working sketch of mixed-flow bioretention. The packing ratio of each column and the submerged zone settings is shown in Table 1. The details and characteristics of bioretention column media were measured using standard methods for soil bulk density, available nitrogen and phosphorus, and soil organic matter [40], and are shown in Table 2.

The drainage layer of each bioretention column consisted of 2–10 mm of gravel, and the drainage pipe (diameter = 20 mm) was wrapped with permeable geotextile to prevent fine particles from washing out. The media in the columns were mixed and filled by volume ratio. Media were placed above the geotextile and atop the gravel layer



Fig. 1. Bioretention columns (GaS, GaW, GWS and GWM) in the greenhouse.

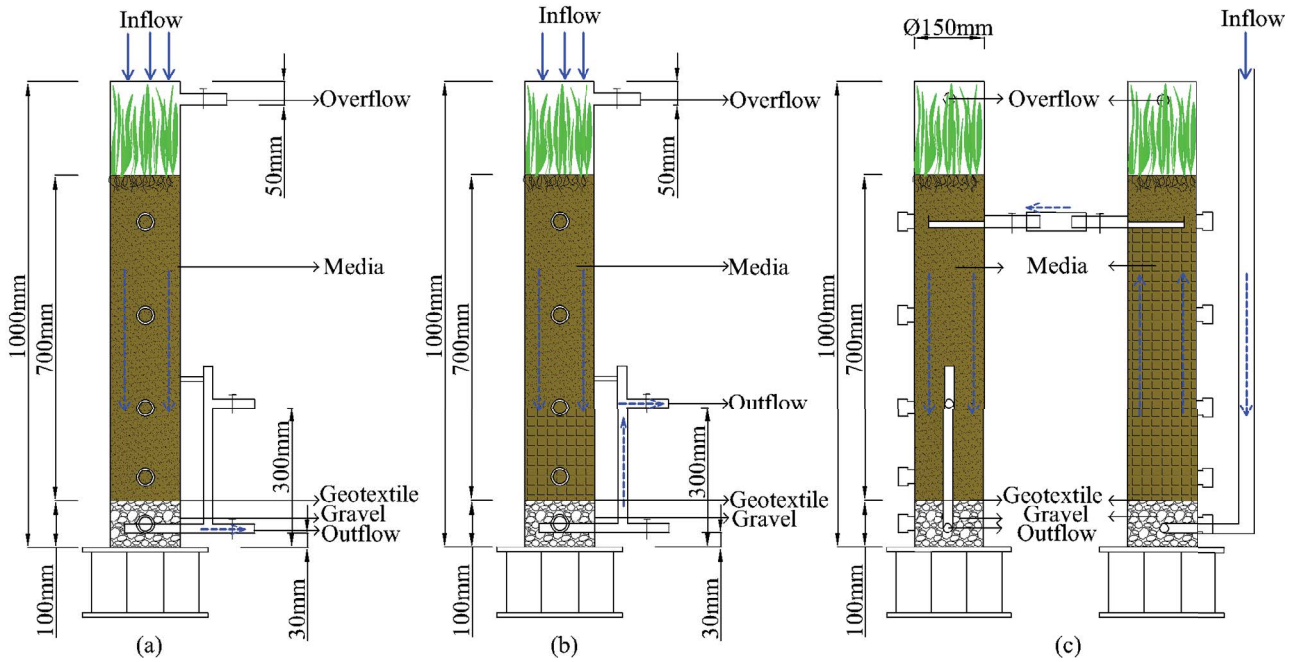


Fig. 2. Experimental operations and schematics of columns (a) GaW, (b) GaS and GWS, and (c) GWM.

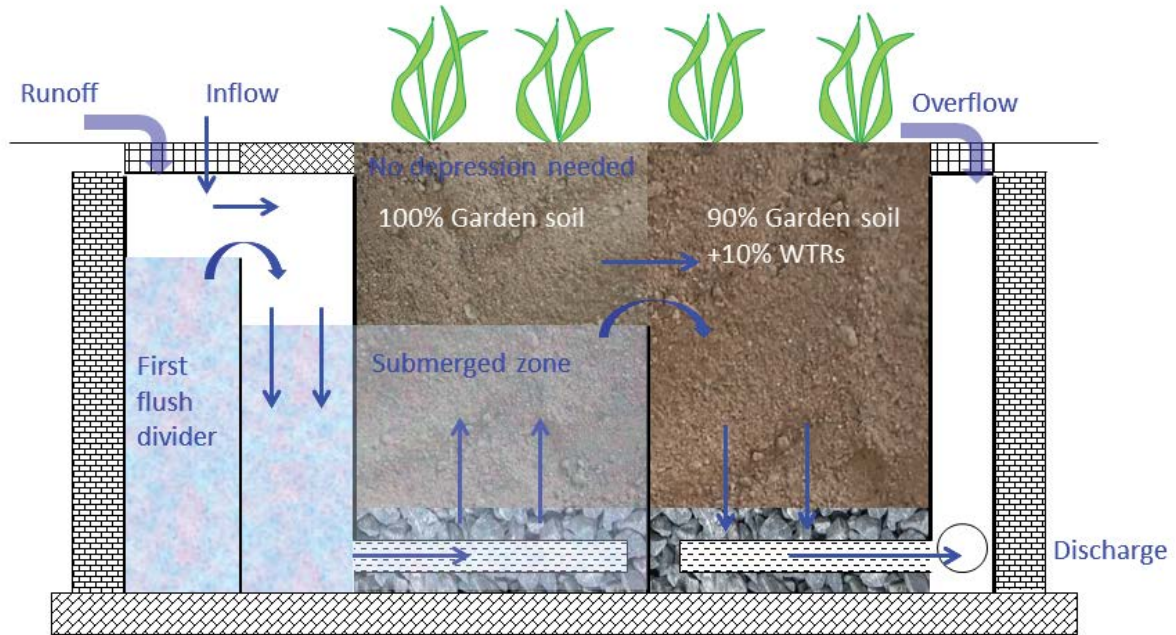


Fig. 3. Working sketch of mixed-flow bioretention.

to prevent the media from washing out. All the columns were planted with native vegetation (*Iris lactea* Pall. var. *chinensis* (Fisch.) Koidz.), which was a commonly used plant in bioretention systems in urban parts of northern China.

2.2. Experimental methods

Our experiment used two stages: leaching and semi-synthetic runoff. The leaching stage used tap water as

inflow to assess media leaching characteristics. The semi-synthetic runoff stage used semi-synthetic runoff as inflow to estimate the performance of the bioretention columns. All columns received the same inflow volume (4.3 L) based on the assumption that they were 10% of the size of the impervious catchment [41]; the runoff coefficient (0.9) was based on the design rainfall (27.3 mm), according to an 80% capture ratio of total annual runoff volume in Beijing [23]. The average rainfall intensity was set as 0.2275 mm/

Table 1
Bioretention column packing composition and submerged zone setting

Column	Media type (volume ratio)	Submerged zone depth (mm)
GaS	97% Garden soil + 3% wood chips	300
GaW	90% Garden soil + 10% WTRs	–
GWS	87% Garden soil + 10% WTRs + 3% wood chips	300
GWM	Upward flow zone (right column): 100% Garden soil Downward flow zone (left column): 90% Garden soil + 10%WTRs	700

Table 2
The details and characteristics of bioretention column media

Media type (volume ratio)	Bulk density (g/cm ³)	Available nitrogen (mg/kg)	Organic matter (g/kg)	Available phosphorus (mg/kg)
100% Garden soil	1.25	44.89	1.30	2.35
90% Garden soil + 10% WTRs	1.30	65.29	1.89	5.61
97% Garden soil + 3% wood chips	1.20	95.23	7.68	8.34
87% Garden soil + 10% WTRs + 3% wood chips	1.33	102.65	8.14	8.72

min according to the rainfall pattern with constant rainfall intensity.

2.2.1. Leaching experiments

All the columns received tap water (4.3 L) with constant water head as inflow. A water head of 50 mm was maintained throughout the inflow process. During the leaching stage, the simulated rainfall event was repeated eight times to ensure the pollutant concentrations in the outflow did not varies.

In our experiment, the soil moisture in the packing layer basically returned to its initial state ($0.23 \pm 0.02 \text{ m}^3/\text{m}^3$) after 24–48 h; the antecedent dry period (ADP) was determined to be 4 d. The inflow tap water mean parameters during this stage were: pH = 7.46 ± 0.15 , TN = $7.89 \pm 0.47 \text{ mg/L}$, TP = $0.02 \pm 0.00 \text{ mg/L}$, COD = $5 \pm 1 \text{ mg/L}$ and turbidity = 0.49 ± 0.11 nephelometric turbidity units (NTU).

During the leaching stage, the outflow from the bioretention columns gradually decreased and became stable. Over five to eight rainfall events, the main pollutant concentrations in the outflow were stable (Table 3). The semi-synthetic runoff stage was implemented after the eighth rainfall event in the leaching experiment.

2.2.2. Semi-synthetic runoff experiments

During the semi-synthetic runoff stage, all the columns received 4.3 L of semi-synthetic runoff as inflow. A water head of 50 mm was maintained throughout the inflow process. This stage included 10 rainfall events, and the ADP was 4 d. The pollutant concentrations in the semi-synthetic runoff were determined similar to road runoff pollution reported in previous studies in China [42,43]. Road dust was collected from a road on the campus using a brush. This road at the campus was a two-way road of two lanes with a width of 5 m. The average daily traffic was

Table 3
Pollutant concentrations in outflow from the bioretention columns during five to eight rainfall events

Column	TN (mg/L)	TP (mg/L)	COD (mg/L)	Turbidity (NTU)
GaS	3.19 ± 0.37	0.56 ± 0.04	35 ± 4	35.63 ± 4.57
GaW	4.46 ± 1.12	0.04 ± 0.02	26 ± 3	0.88 ± 0.11
GWS	3.25 ± 0.59	0.16 ± 0.01	28 ± 5	39.15 ± 5.19
GWM	4.51 ± 0.96	0.14 ± 0.01	28 ± 1	38.46 ± 1.30

approximately 700 vehicles/d taken in 2019 by two-way traffic count. The dust was passed through a 0.10 mm standard sieve and added to the semi-synthetic runoff to simulate particulate pollutants. Additionally, appropriate chemical reagents, such as glucose, KNO_3 , NH_4Cl , and KH_2PO_4 , were added to simulate soluble pollutants in urban stormwater runoff.

Across all the 10 repeated rainfall events during this stage, the mean inflow water quality indicators were pH = 7.54 ± 0.18 , $\text{NH}_4^+\text{-N}$ = $6.63 \pm 1.07 \text{ mg/L}$, $\text{NO}_3^-\text{-N}$ = $3.25 \pm 0.81 \text{ mg/L}$, TN = $16.5 \pm 1.15 \text{ mg/L}$, DP = $0.28 \pm 0.08 \text{ mg/L}$, PP = $0.39 \pm 0.08 \text{ mg/L}$, TP = $0.67 \pm 0.11 \text{ mg/L}$, COD = $268 \pm 16 \text{ mg/L}$ and turbidity = $41.05 \pm 4.02 \text{ NTU}$.

2.3. Water quality analysis

In the leaching and semi-synthetic runoff stages, polyethylene sample bottles were used to collect the outflow every 10 min. The total outflow volume was calculated after each column outflow sample was collected. Collect composite water samples from each column and immediately tested (within 24 h of collection) for COD, TN, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, TP, DP, PP, pH and turbidity using standard methods [44]. If concentrations were below the detection limit, the detection limit was used in the statistical analysis.

2.4. Data analysis

Water volume reduction efficiency only included the reduction of water from evaporation, media absorption and storage facility during rainfall events. The water volume reduction efficiency (R_v) was defined and calculated as:

$$R_v = \frac{V_{in} - V_{out}}{V_{in}} \quad (1)$$

where V_{in} is the inflow volume (L), particularly the water ponding in depressions during a rainfall event, and V_{out} is the outflow volume (L).

The mass removal efficiency (R_L), for the constituent of interest was used to estimate the bioretention column performance, was calculated as:

$$R_L = \frac{C_{in} \cdot V_{in} - C_{out} \cdot V_{out}}{C_{in} \cdot V_{in}} \quad (2)$$

where C_{in} is the inflow concentration (mg/L), V_{in} is the inflow volume (L), C_{out} is the outflow concentration (mg/L) and V_{out} is the outflow volume (L).

The infiltration rate (IR), used to estimate the performance of the bioretention column, is calculated as:

$$IR = \frac{10 \cdot Q_n}{t_n \cdot S} \quad (3)$$

where Q_n is the volume that permeated in the interval (mL), t_n is infiltration interval time (min) and S is the cross-sectional area of bioretention column (cm^2).

One-way analysis-of-variance was used to identify significant differences in removal efficiencies for among different bioretention columns (accepted at $p > 0.05$). A paired sample t test was used to evaluate the significance of differences between the inflow/outflow concentrations (accepted at $p > 0.05$).

3. Results and discussion

3.1. Runoff volume retention

The mean R_v and mean IR from 10 rainfall events are illustrated in Fig. 4. The mean R_v of GaW (WTRs only) was $6.25\% \pm 1.16\%$, which was significantly lower ($p < 0.05$) than GWS (submerged zone and WTRs; $7.68\% \pm 1.07\%$). In addition, the IR of GaW was also lower than GWS. This indicates that setting a submerged zone and adding wood chips increased the R_v and enhanced the IR. The R_v and IR are related to media porosity, and wood chips increase media porosity, which then increases the IR and water retention capacity. Furthermore, a submerged zone has been shown to improve the R_v of bioretention systems [45].

The mean R_v values of GaS (submerged zone only) and GWS were $11.12\% \pm 0.69\%$ and $7.68\% \pm 1.07\%$, respectively, and the IR of GaS (0.53 ± 0.06 mm/min) was significantly ($p < 0.05$) higher than GWS (0.37 ± 0.01 mm/min). This indicates that adding WTRs decreased the R_v and weakened

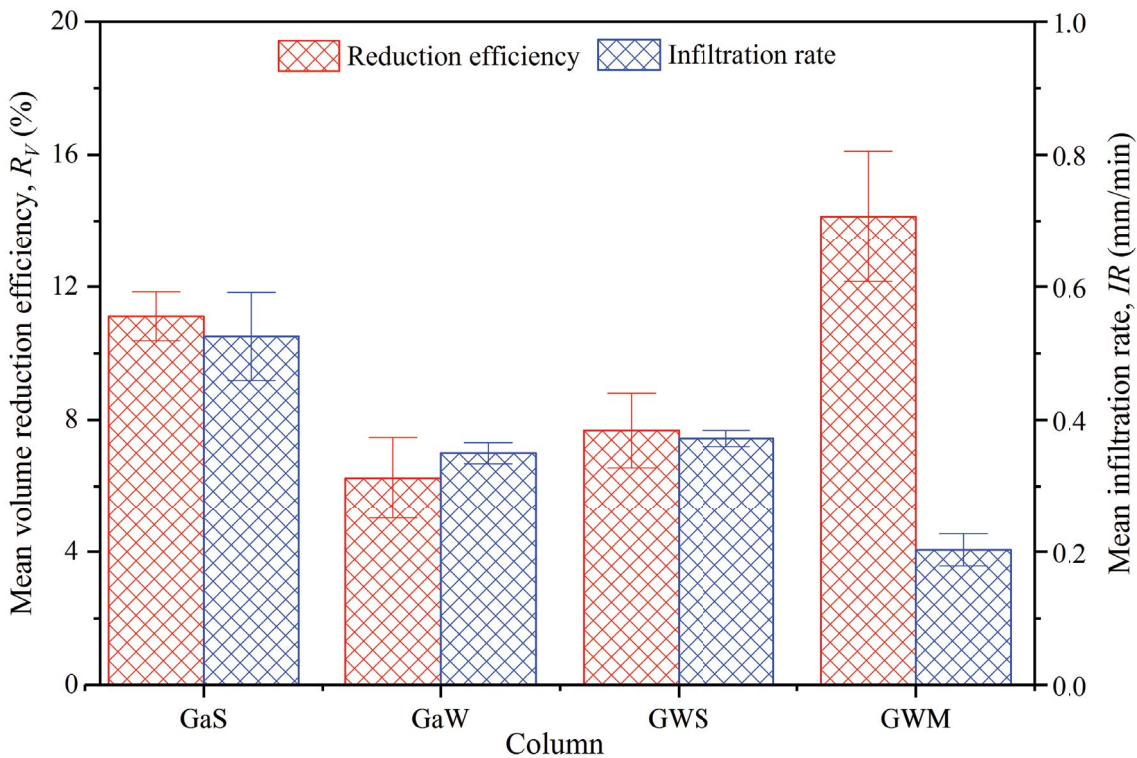


Fig. 4. Mean volume reduction efficiency (R_v) and mean infiltration rate (IR) of the four bioretention columns in the semi-synthetic runoff stage of the experiment. Each column and error bar represents the mean and standard deviation ($n = 10$), n represents the number of rainfall events.

the IR. The bulk density of GWS media was 1.33 g/cm^3 , which was higher than GaS (1.20 g/cm^3). The addition of WTRs reduced media porosity, which decreased IR and water retention capacity. Davis et al. [45] also found that the media porosity and moisture can produce unique column R_v values.

The mean R_v of GWM was $12.89\% \pm 3.03\%$, which was the highest of the four bioretention columns. It was almost twice that of GWS, and may be attributed to the fact that the volume of GWM was basically double that of GWS. In addition, the media type and proportion of the submerged zone in GWS and GWM were similar, although there were structural differences between the two columns. Hence, under the premise that the media type and the submerged zone proportion were the same, we interpret our results to reflect that larger column volumes led to higher R_v values.

3.2. Influence of WTRs on P removal

The outflow concentrations and mean R_L for TP, PP and DP after 10 rainfall events are shown in Fig. 5. GWS

(submerged zone and WTRs) and GaW (WTRs only) had relatively stable removal efficiencies for TP, PP and DP. The R_L values of GaW for TP ($95.53\% \pm 3.31\%$), PP ($95.30\% \pm 4.62\%$) and DP ($96.10\% \pm 2.84\%$) were significantly higher than GWS ($p < 0.05$). This indicates that the submerged zone setting negatively affects the R_L for PP, TP and DP. It worth noting that the difference between GWS and GaW for DP R_L was relatively small. Hence, the submerged zone affected the PP and TP R_L , but the effect on DP R_L was limited. Qiu et al. [39] found no significant difference in the TP R_L between bioretention systems with submerged zones and 15% WTRs and bioretention systems with WTRs only. The reason may be related to the fact that the submerged zone extends hydraulic retention times, which led to P being efficiently absorbed. In this study, decomposition of the added carbon (wood chips) may lead to particulate leaching, which might affect the removal of P, especially PP.

By comparing GWS (submerged zone and WTRs) and GaS (submerged zone only), it was clear that the R_L values of TP ($26.38\% \pm 11.89\%$), PP ($-17.93\% \pm 25.10\%$) and DP ($87.25\% \pm 4.88\%$) from GaS were lower than GWS (TP, $83.33\% \pm 3.64\%$; PP, $75.38\% \pm 7.26\%$; DP, $93.73\% \pm 2.76\%$),

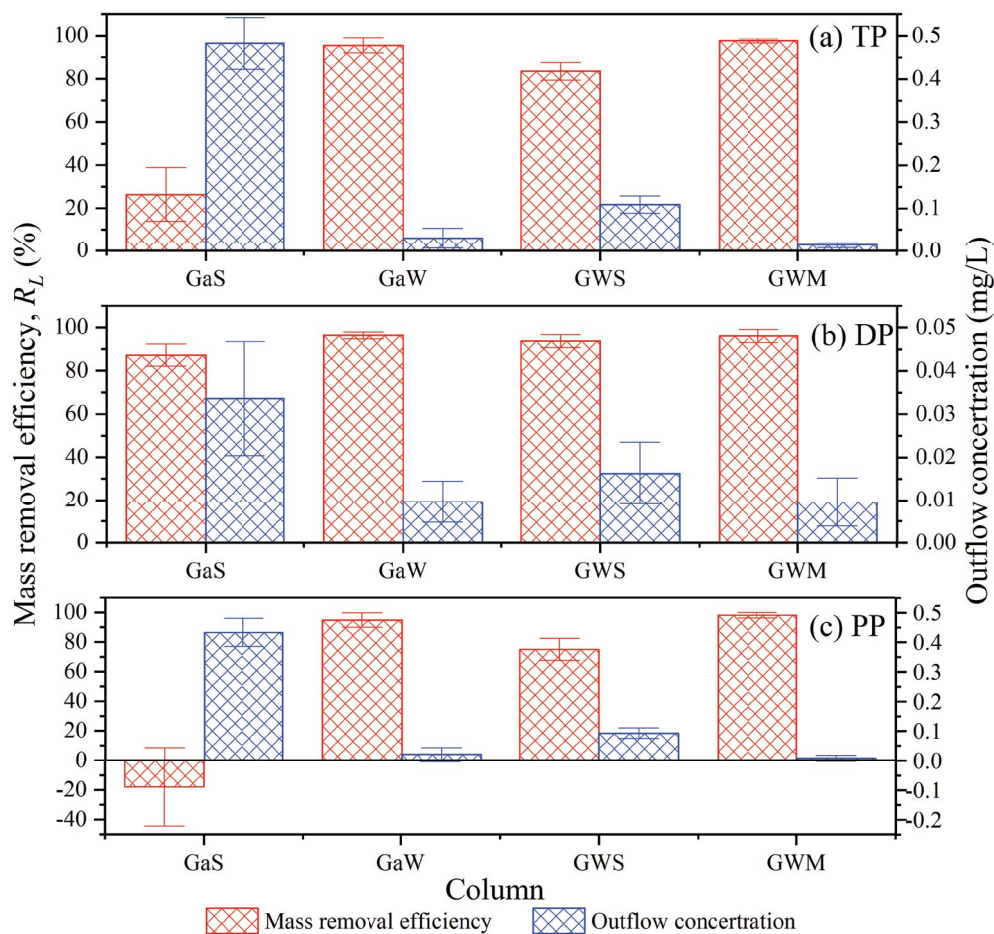


Fig. 5. Outflow concentrations and mean mass removal efficiencies (R_L) for total phosphorus (TP), dissolved phosphorus (DP) and particulate phosphorus (PP) in four bioretention columns during the semi-synthetic runoff stage. Each column and error bar represents the mean and standard deviation ($n = 10$), n represents the number of rainfall events.

and the removal efficiencies in GWS were significantly improved ($p < 0.05$) when WTRs was added. The mean outflow concentration of TP from GWS was only 0.11 ± 0.02 mg/L, which shows that media including WTRs can significantly improve the R_L of different forms of P. This is because WTRs contains Fe and Al oxides, which promote the adsorption of P [46]. It is worth noting that the PP R_L from GaS was negative; this is attributed to the degradation of wood chips that resulted in PP leaching out.

Mixed-flow GWM had a significantly higher ($p < 0.05$) R_L for TP and PP than a conventional column with the same media (GWS). The R_L of TP increased from $83.33\% \pm 3.64\%$ (GWS) to $97.58\% \pm 0.91\%$ (GWM), and PP increased from $75.38\% \pm 7.26\%$ (GWS) to $98.21\% \pm 1.82\%$ (GWM; Fig. 5a and c). Additionally, the R_L of DP did not vary significantly ($p > 0.05$) between GWS and GWM (Fig. 5b). Overall, GWM had better PP removal performance than GWS. This was attributed to PP being filtered out by the media because a mixed-flow bioretention system extends the flow path compared with conventional bioretention [37].

3.3. Influence of a submerged zone on N removal

The outflow concentrations and mean R_L for TN, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ of the four bioretention columns after 10 rainfall events are illustrated in Fig. 6. The R_L values of $\text{NO}_3^-\text{-N}$ for GaW (WTRs only) and GWS (submerged zone and WTRs) were $83.33\% \pm 3.64\%$ and $95.53\% \pm 3.31\%$, and the setting of the submerged zone produced a significant ($p < 0.05$) improvement in $\text{NO}_3^-\text{-N}$ removal. This is because the submerged zone and carbon sources enhance denitrification [36,47]. However, the R_L of $\text{NH}_4^+\text{-N}$ for GWS was significantly lower ($p < 0.05$) than GaW, showing a decrease from $90.58\% \pm 3.95\%$ (GaW) to $54.28\% \pm 7.98\%$ (GWS). This shows that the submerged zone setting affects $\text{NH}_4^+\text{-N}$ removal negatively, and the existence of anoxic environments in the submerged zone reduces $\text{NH}_4^+\text{-N}$ conversion [48].

The R_L values of $\text{NO}_3^-\text{-N}$ for GaW (submerged zone only) and GWS (submerged zone and WTRs) were $92.37\% \pm 3.89\%$ and $93.96\% \pm 2.82\%$, respectively, and the R_L of $\text{NH}_4^+\text{-N}$ were $62.51\% \pm 9.03\%$ (GaW) and $54.28\% \pm 7.98\%$ (GWS). The addition of WTRs to the base of the submerged zone did not significantly ($p > 0.05$) affect $\text{NO}_3^-\text{-N}$ and $\text{NH}_4^+\text{-N}$ removal, and a similar conclusion has been found in previous research [39]. However, the R_L of TN decreased significantly from $66.72\% \pm 4.79\%$ (GaS) to $58.54\% \pm 7.25\%$ (GWS) when WTRs was added to the media, which shows that with WTRs and a submerged zone, TN removal performance may be weakened compared with a submerged zone alone.

For mixed-flow GWM, the mean R_L of $\text{NO}_3^-\text{-N}$ did not vary significantly ($p > 0.05$) compared with a conventional column (GWS) with a submerged zone and WTRs (Fig. 6c). It indicates that $\text{NO}_3^-\text{-N}$ removal was not affected by the depth of the submerged zone, although the submerged zone in GWM was obviously deeper than GWS. However, for the mean R_L of $\text{NH}_4^+\text{-N}$ and TN, there were significant ($p < 0.05$) differences between GWS and GWM. The flow path is extended in a mixed-flow bioretention system, which contributes to the adsorption of $\text{NH}_4^+\text{-N}$

by the media [48], and effectively improves TN and $\text{NH}_4^+\text{-N}$ removal.

3.4. Particulate pollutant leaching

The turbidity of inflow and outflow during the semi-synthetic runoff stage is illustrated in Fig. 7. During the 10 rainfall events, the mean outflow turbidity of GaW and GWS were 0.84 ± 0.49 NTU and 48.07 ± 7.43 NTU, respectively, which represent over an order of magnitude difference. It indicates that the submerged zone setting and additional carbon source (wood chips) in GWS increased the outflow turbidity. High outflow turbidity (39.34 ± 5.02 NTU) was observed in GaS outflow because wood chips were added to this column. It is worth noting that the outflow turbidity was even higher than the inflow turbidity during the 4th and 8–10th rainfall events. Higher outflow than inflow turbidity was observed in GWS since the second rainfall event, and there may be a contribution of wood chip decomposition that produces particulate pollutant leaching [34].

N is removed in the submerged zone by denitrification, and the carbon source is an essential parameter. Wang et al. [36] found that $\text{NO}_3^-\text{-N}$ removal efficiency of bioretention systems with carbon sources was 11% higher than bioretention systems without carbon sources within 1 d hydraulic residence time. Furthermore, turbidity leaching have been found in the outflow of the bioretention systems with added carbon sources [36]. We confirmed a similar finding in GaS and GWS, columns that had added wood chips in this study, and our results are consistent with other research [33]. Although the addition of carbon may result in turbidity leaching in the outflow, it was indispensable for the removal of $\text{NO}_3^-\text{-N}$. Additional approaches that control particulate pollutant leaching under new carbon source conditions need to be further explored.

4. Conclusions

The removal of N and P by simultaneously adding WTRs and setting a submerged zone were assessed with a laboratory-based experiment. The main findings were:

- Setting a submerged zone and adding wood chips increased the volume reduction efficiency and enhanced the infiltration rate. The addition of WTRs reduced the media porosity, which then decreased the infiltration rate and water retention capacity.
- Setting a submerged zone negatively affected PP and TP removal efficiency, but the effect on DP removal was limited because decomposition of the added carbon source (wood chips) led to PP leaching. The added WTRs in column media significantly improved the removal efficiency of different forms of P. The mixed-flow bioretention column (GWM) had better PP removal than a similar conventional bioretention column (GWS), and the R_L of TP increased from $83.33\% \pm 3.64\%$ (GWS) to $97.58\% \pm 0.91\%$ (GWM), and PP increased from $75.38\% \pm 7.26\%$ (GWS) to $98.21\% \pm 1.82\%$ (GWM).
- A submerged zone produced a significant ($p < 0.05$) improvement in $\text{NO}_3^-\text{-N}$ removal, but negatively affected $\text{NH}_4^+\text{-N}$ removal. WTRs addition to the submerged

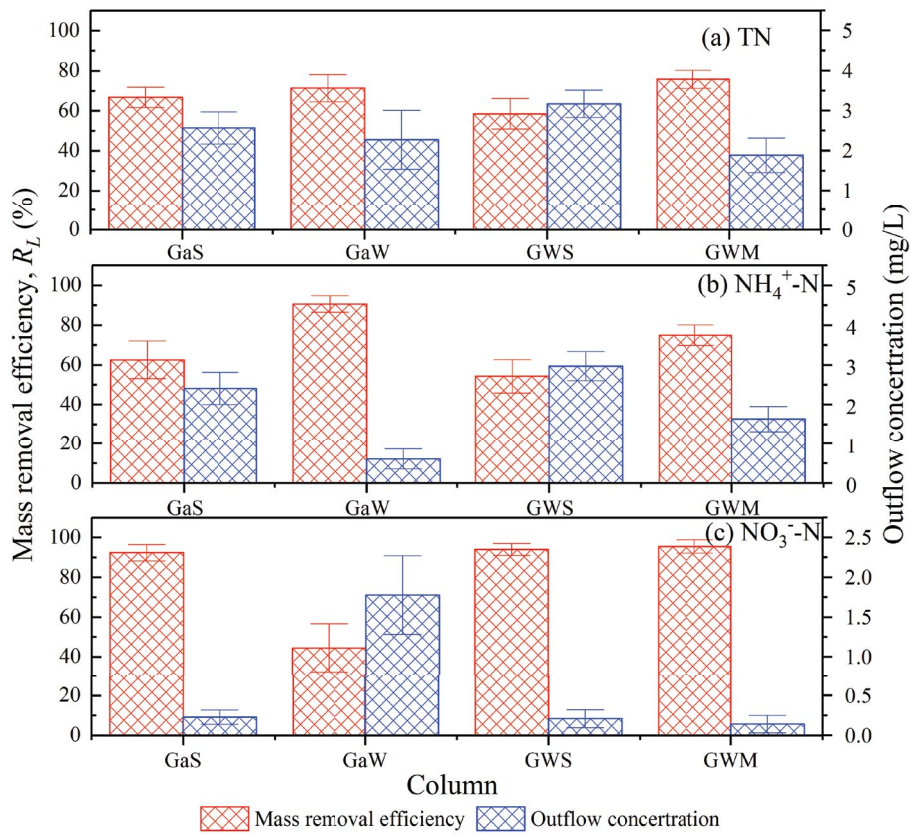


Fig. 6. Outflow concentrations and mean mass removal efficiency (R_t) for total nitrogen (TN), ammonia (NH_4^+-N) and nitrate ($NO_3^- - N$) in the four bioretention columns from the semi-synthetic runoff stage. Each column and error bar represents the mean and standard deviation ($n = 10$), n represents the number of rainfall events.

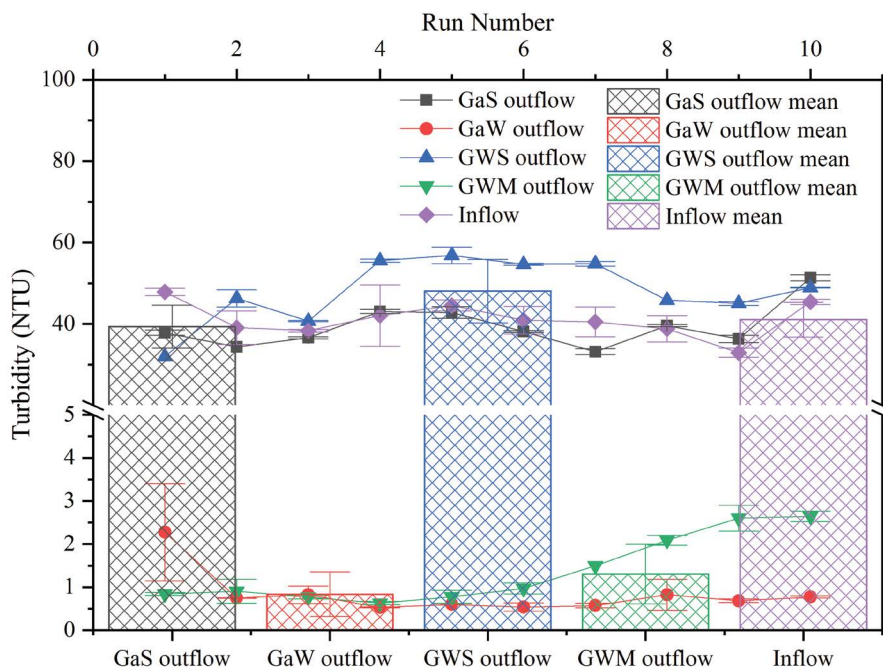


Fig. 7. The outflow and inflow turbidity of four bioretention columns in the semi-synthetic runoff stage. Each column and error bar represents the mean and standard deviation ($n = 10$), n represents the number of rainfall events. The run number represents rainfall event.

zone did not significantly ($p > 0.05$) affect $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ removal, but TN removal decreased significantly from $66.72\% \pm 4.79\%$ (GaS) to $58.54\% \pm 7.25\%$ (GWS). When both WTRs and a submerged zone were present (GWS), TN removal was weakened compared with the bioretention column with only a submerged zone (GaS). The mixed-flow column (GWM) had better $\text{NH}_4\text{-N}$ and TN removal than the conventional column (GWS), but not for $\text{NO}_3\text{-N}$ removal.

- The submerged zone setting and additional carbon increased outflow turbidity by an order of magnitude. Although the addition of carbon may result in turbidity leaching in the outflow, it was indispensable for the removal of $\text{NO}_3\text{-N}$. Additionally, nitrogen and phosphorus removal performance of the mixed-flow bioretention filled with WTRs was promising in this laboratory study. However, the column experiment results may be affected by several factors, such as the edge effects. Hence, a field study may be needed to confirm the nutrient removal performance.

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