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Using a Laboratory Column Experiment to Explore the Influence of an Antecedent Dry Period on the Nutrient Removal of a Bioretention Filter

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Abstract Various factors, such as rainfall conditions, may influence nutrient removal by bioretention filters. The aim of this study was to evaluate how antecedent dry periods (ADP) affected the removal of nutrients by a laboratory-scale bioretention system. A bioretention filter system comprising columns with different media, treatment, and submerged zone combinations was set up. The treatments included 10% (v/v) water treatment residual to enhance the phosphorus (P) removal and 10% (v/v) zero-valent iron to enhance the nitrogen (N) removal. Semi-synthetic runoff was applied to explore how ADPs (from 1 to 10 days) affected the N and P removal. The denitrification efficiency was determined from the variations in the N concentrations in the submerged zone over 14 days. Without a submerged zone, the total nitrogen (TN) removal increased, the chemical oxygen demand (COD) removal decreased, and there was no clear trend for total phosphorus (TP), dissolved P, or particulate P as the duration of the ADP increased. When the bioretention filter had a submerged zone, the TN removal peaked at 82.64 ± 0.24% and 84.50 ± 0.28% for an ADP of 10 days. When zero-valent iron was added to a filter with a submerged zone, the denitrification improved significantly, and the TN removal reached 92.95 ± 1.50% and 92.16 ± 2.28% for an ADP of 5 days. The iron also

Highlights
- Influence of ADP on the nutrient removal was explored by column experiment.
- As the ADP increased, the TN removal increased, but the COD removal decreased.
- The denitrification in submerged zone and TN removal were the highest with a long ADP.
- Zero-valent iron can improve the TN, COD, and TP removal in bioretention.
- TN concentrations in submerged zone provide a reference for bioretention designing.

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significantly promoted the COD and TP removal efficiencies of the bioretention filter, but was not significantly related to the ADP. The TN and ammonia concentrations in a filter with a submerged zone decreased significantly in the first 3 days of the ADP, and then stabilized after 5 days. These results provide a reference for determining the effectiveness of a submerged zone in bioretention systems.

Keywords Bioretention · Submerged zone · Zero-valent iron · Nitrogen and phosphorus removal · Antecedent dry period · Water treatment residual

1 Introduction

Urban runoff pollution can be effectively controlled by various measures, including source control technologies such as bioretention filters (Wang et al., 2022). While suspended solids, heavy metals, organic matter, and pathogenic microorganisms in urban runoff can be removed effectively by bioretention systems, the removal of nutrients such as nitrogen (N) and phosphorus (P) can vary significantly (Chen et al., 2022; Davis et al., 2009).

Various approaches, including media improvements, have been tested to enhance the N and P removal performance of bioretention systems. For example, water treatment residuals (WTR), fly ash (Kandel et al., 2017), river sediment (Zhang et al., 2019b), activated carbon (Mai & Huang, 2021; Sang et al., 2019), and other materials have been tested for their P removal properties. Studies have shown that the P removal performance increased significantly when WTR was added to the media of a bioretention system (O'Neill & Davis, 2012; Yan et al., 2017). Similarly, studies reported that zero-valent iron enhanced the removal of phosphate from runoff (Lechner, 2016), and supported denitrification in a bioretention system as an electron donor (Tian et al., 2019).

The removal of N can be enhanced by amending the media and improving the media structure. For example, when a submerged zone was set at the bottom of a bioretention system, the denitrification was enhanced and the nitrate (NO_3^--N) removal reached 71% when the inflow concentration of NO_3^--N was 0.403 mg/L (Palmer et al., 2013). Wan et al. (2017) investigated an innovative two-layered bioretention system, and found that more than 80% of the NO_3^--N could be removed when the total nitrogen (TN) concentration of the influent reached 8 ~ 9 mg/L. Zhang et al. (2019a) found that when the average TN concentrations of inflow pollutants were 8.49 ± 0.80 mg/L, TN removal was 14% higher, and the inflow paths and hydraulic retention time (HRT) were better, in a mixed-flow bioretention system than in a conventional system. Studies have also shown that the N removal in bioretention systems could be improved by plants (Li et al., 2019), but that the most effective way to enhance the denitrification was to improve the media structure (Wang et al., 2018a, 2018b; Zhang et al., 2019a).

Denitrification in bioretention systems is limited by the availability of carbon sources (Goh et al., 2015; Kim et al., 2003; Lopez-Ponnada et al., 2020; Wang et al., 2018a, 2018b). Several studies have investigated the effectiveness of various materials as carbon sources. Kim et al. (2003) found that sawdust, wheat straw, and wood chips could be continuous sources of carbon. Of these, wood chips are currently commonly used as a carbon source, and studies have demonstrated their ability in this function (Lopez-Ponnada et al., 2017). Studies have shown, however, that pollutants, especially particulates, may leach from bioretention systems as the carbon source materials, such as wood chips, decompose (Kim et al., 2003; Zhang et al., 2021b). While we know that the submerged zone and the carbon supply affect the N and P removal in bioretention systems (Kim et al., 2003; Wang et al., 2018a, 2018b), it is also thought that the N and P removal might be affected by rainfall.

Rainfall characteristics, such as antecedent dry periods (ADP), may affect the nutrient removal in a bioretention system. Lopez-Ponnada et al. (2020) investigated how the inflowing hydraulic load and the ADP affected N removal in a bioretention system, and found that the TN removal was higher when the hydraulic load was low (4.1 cm/h), but that the NO_3^--N removal did not vary significantly with the duration of the ADP (0 to 13 days). Notably, an ADP may only influence the N removal in a bioretention system with a submerged zone (Subramaniam et al., 2021). Zinger et al. (2021) found that when the TN concentration of the inflow was 2.1 mg/L, the performance of N removal decreased significantly during the 2-week ADP for the bioretention without submerged zone, while the bioretention with submerged zone was able to retain high TN removal performance for up to four weeks of ADP. It has also been reported that, when the NO_3^--N concentration of inflow were 2.00 ± 0.22 mg/L and the ADP varied from 0 to 56 days, as the ADP increased, a bioretention system was more capable of controlling the water quantity because of evaporation and transpiration (Subramaniam et al., 2016), which meant that the NO_3^--N removal increased significantly as the ADP increased. However, Cho et al. (2011) reported that the NO_3^--N removal in a bioretention system with similar conditions did not increase continuously with ongoing increases in the ADP, but instead observed significant N leaching in a bioretention system when the ADP was 20 days.

When a bioretention system has a submerged zone, the ADP determines the HRT of the retention runoff in the submerged zone, which equates to the denitrification reaction time. An ADP may strongly influence the denitrification in a submerged zone, which in turn may affect the N removal. He et al. (2020) explored the N removal in a bioretention system under alternating wet and dry operation conditions, and found that when the dry period was 96 h, the NH_4^+-N concentration in the submerged zone decreased rapidly in the first 24 h of the dry period, then decreased slowly and approached 0 within 72 h. The influence of the ADP on N removal in bioretention systems has been mainly reflected in the variation in the concentrations of N pollutants in the submerged zone; the variations in the concentrations during dry periods may therefore help to explain how the ADP duration affects N removal.

In this study, the influence of the ADP duration on the nutrient removal of bioretention systems was investigated in a laboratory-scale column experiment. The objectives of this study were as follows: first, to determine whether the P and chemical oxygen demand (COD) removal in bioretention systems was affected by the media, structure, or ADP; second, to quantify the influence of the ADP on the removal of TN and NH_4^+-N; and third, to examine the concentrations of N compounds in the submerged zone of the bioretention system, to determine how the ADP influenced the N removal.

2 Materials and Methods

2.1 Bioretention Column Setting

Six columns with bioretention filters were established. The PVC columns were 100 cm long and had a diameter of 15 cm. The bioretention columns were placed in a greenhouse on the campus of the Beijing University of Civil Engineering and Architecture (BUCEA) to avoid any effects of natural rainfall or other factors during the experiment. The experiment ran from September 2020 to December 2020. During this time, the maximum temperature was 15 ± 11 °C and the minimum temperature was 4 ± 7 °C.

The bioretention filter in the column, from top to bottom, comprised a 150 mm ponding layer, a 700 mm media layer, and a 100 mm drainage layer. The drainage layer consisted of 2–10 mm of gravel, in which the drainage pipe (diameter = 20 mm) was laid. To prevent leaching of fine particles, the drainage pipe was wrapped with permeable geotextile, and was separated from the drainage layer by geotextile. The surface of the media layer was planted with a native plant species, *Iris lactea Pall. var. chinensis (Fisch.) Koidz.*, which is commonly used in bioretention cells in urban areas in northern China. Information about the columns in the greenhouse is provided in the Supplementary Data.

The six bioretention columns were labeled G, GS, GW, GWS, GIS, and GWI to indicate their different packing compositions and submerged zone settings, as shown in Table 1. In the column labels, G represents garden soil; W represents WTR; S represents a submerged zone, and I represents zero-valent iron. Columns G and GW did not have a submerged zone. Columns GS, GWS, GIS, and GWI had a 300 mm submerged zone and 3% (v/v) of wood chips as a carbon source to improve the N removal. Columns GW and GWS had 10% (v/v) WTR added to enhance the P removal. The WTR was provided by the Changzhou CGE Water Co. Ltd. (Zhang et al., 2021b). Columns GIS and GWI had 10% (v/v) zero-valent iron added to the media, to determine how zero-valent iron influenced the removal of N and P. All the materials in the media layer were passed through a 2-mm sieve before use. The characteristics of the media materials are shown in Table 2.

2.2 Experimental Methods

The experiment comprised a leaching stage and a semi-synthetic runoff stage. The leaching stage was designed to assess the media leaching characteristics, and the inflow in this stage was tap water (Sang et al., 2019). The semi-synthetic runoff stage was designed

Table 1 Composition of the packing in the bioretention columns and the submerged zone settings

Column	Media type (volume ratio)	Submerged zone depth (mm)
G	100% garden soil	—
GS	97% garden soil + 3% wood chips	300
GW	90% garden soil + 10% WTR	—
GWS	87% garden soil + 10% WTR + 3% wood chips	300
GIS	Infiltration zone: 97% garden soil + 3% wood chips Submerged zone: 90% (97% garden soil + 3% wood chips) + 10% zero-valent iron	300
GWI	Infiltration zone: 87% garden soil + 10% WTR + 3% wood chips Submerged zone: 90% (87% garden soil + 10% WTR + 3% wood chips) + 10% zero-valent iron	300

Table 2 Details and characteristics of the 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% WTR	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% WTR + 3% wood chips	1.33	102.65	8.14	8.72

to simulate the bioretention operation, and the inflow was semi-synthetic runoff. In both stages, the inflow water was supplied to the columns at a constant water head (10 cm) to realistically simulate the actual operation of the bioretention system. All the columns received an inflow volume of 4.3 L, which was based on a catchment area ratio of 10% and the design rainfall (27.3 mm), assuming an 80% capture ratio of the total annual runoff volume in Beijing (Zhang et al., 2019a).

The inflow tap water during the leaching experiment had a pH of 7.58 ± 0.15, and COD, TP, dissolved P (DP), particulate P (PP), TN, and NH_4^+-N values of 5 ± 1, 0.02 ± 0.01, 0.01 ± 0.00, 0.01 ± 0.01, 6.70 ± 1.04, and 1.00 ± 0.16 mg/L, respectively. The ADP in this stage was 4 days, and the leaching experiment was stopped once the pollutant concentrations in the outflow stabilized. A total of 6 experiments were conducted in this stage, and the cumulative rainfall depth was 163.8 mm. After the leaching stage, the semi-synthetic runoff stage was started.

The nutrient concentrations in the semi-synthetic runoff were chosen to mimic those reported elsewhere for road runoff in Beijing (Zhang et al., 2012, 2021a). The semi-synthetic runoff was prepared by adding street dust and soluble nutrients to tap water. Street dust was collected from the roads of the BUCEA and then was passed through a 200-mm standard sieve. The dust particles were added to tap water. Chemical compounds that represented soluble pollutants were then added. Glucose, KNO_3, NH_4Cl, and KH_2PO_4 were used to simulate COD, NO_3^--N, NH_4^+-N, and P, respectively. The mean concentrations of COD, TP, DP, PP, TN, and NH_4^+-N in the inflow during this stage were 204 ± 20, 0.65 ± 0.05, 0.43 ± 0.05, 0.22 ± 0.04, 8.81 ± 0.57, and 4.03 ± 1.23 mg/L, respectively.

During the semi-synthetic runoff experimental stage, the ADP was set as 1, 3, 5, and 10 days, and the same experiment was repeated each time. Samples were collected from columns GS, GWS, GIS, and GWI at the water outlet that was 300 mm from the bottom, while samples were collected from columns G and GW at the water outlet at the bottom. After the inflow, the total volume of the rainfall outflow was measured, and the outflow sample was completely mixed and retained for water quality analysis. HOBO rain gauge data logger (RG3-M) of Onset HOBO was used to obtain soil moisture. The pollutant concentrations in the inflow and outflow are provided in the Supplementary Data.

After the rainfall experiment for an ADP of 10 days, water samples were collected and the TN and NH_4^+-N contents were measured in the submerged zones of columns GS, GWS, GIS, and GWI, according to the preset sampling interval. Samples were collected at 0.5, 1, 3, 5, 10, and 14 days respectively. These times were the accumulation time after the rainfall occurred. Detailed data are provided in the Supplementary Data.

2.3 Water Quality Analysis

The water samples were immediately tested for COD, TP, DP, PP, TN, and NH_4^+-N in the laboratory after collection using standard methods (APHA, 2012). If the water samples were not analyzed immediately, they were stored in the refrigerator at 4 °C, and then measured within 24 h. Samples were analyzed in duplicate to ensure the results were accurate. If the concentrations were below the detection limit, the detection limit was used in the statistical analysis.

2.4 Data Analysis

The pollutant mass removal efficiency (R_L), which was an estimate of the efficiency of the removal of a specific pollutant by bioretention, was calculated as:

$$R_L = \frac{C_i \bullet V_i - C_o \bullet V_o}{C_i \bullet V_i} \times 100\% \quad (1)$$

where R_L is the pollutant mass removal efficiency (%), C_i is the inflow concentration (mg/L), C_o is the outflow concentration (mg/L), V_i is the inflow volume (L), and V_o is the outflow volume (L).

The independent sample t test was used to evaluate the difference in the pollutant mass removal efficiency in the different bioretention columns, and the results were significant when $p < 0.05$.

3 Results and Discussion

3.1 Influence of the ADP on COD and P Removal

The R_L values for COD from the six bioretention columns are illustrated in Fig. 1a. No significant differences in the COD removals were found between columns G and GS for ADP durations of 1 to 10 days ($p > 0.05$). When the column media comprised only garden soil, the submerged zone had no significant effect on the COD removal.

The COD R_L of column GW (modified with WTR) was higher than that of column G (without WTR) for ADPs of 1, 3, and 5 days. However, when the ADP was 10 days, the COD R_L of column GW was lower than that of column G. The pollutant concentrations in the outflow during the semi-synthetic runoff experiments are shown in Fig. 2. The average COD outflow concentration (42.44 mg/L) for the eight rainfall events in column GW was lower than that of column G (52.63 mg/L), but the standard deviation ($\sigma = 30.93$) for column GW was larger than that of the column G ($\sigma = 18.97$), indicating that the overall removal efficiency of COD in column GW was better than that of column G, but it was not stable. Zhang et al. (2021b) observed that, when WTR was added into the media of a bioretention filter without a submerged zone, the infiltration capacity generally decreased, because the particle size of the WTR was usually smaller than that of garden soil. The average infiltration rate of column GW was 0.35 ± 0.02 mm/min during this experiment, which was significantly lower than that of column G without WTR (0.43 ± 0.04 mm/min) ($p < 0.05$). Therefore, when the ADP was between 1 and 5 days, the column media had a high moisture content during the initial period of the rainfall event. The infiltration rate was low, meaning the contact time between the pollutants and media was considerable, resulting in enhanced COD removal. However, for an ADP of 10 days, the column media had a low moisture content and a high infiltration rate during the initial period of a rainfall event, giving low COD removal. When the ADP was 10 days, the COD R_L of column GW was lower than that of column G, which presented a different pattern than that for other ADPs. The high content of organic matter might be one of the reasons for the high leaching. However, COD leaching rule of columns for different ADPs was a complex process, related to many factors, such as time and particle size of organic constituents. Therefore, the mechanism of COD leaching needs to be further explored in the future research.

The WTR affected the COD removal in the bioretention filter. When the submerged zones were the same, the COD R_L values of column GWS (with

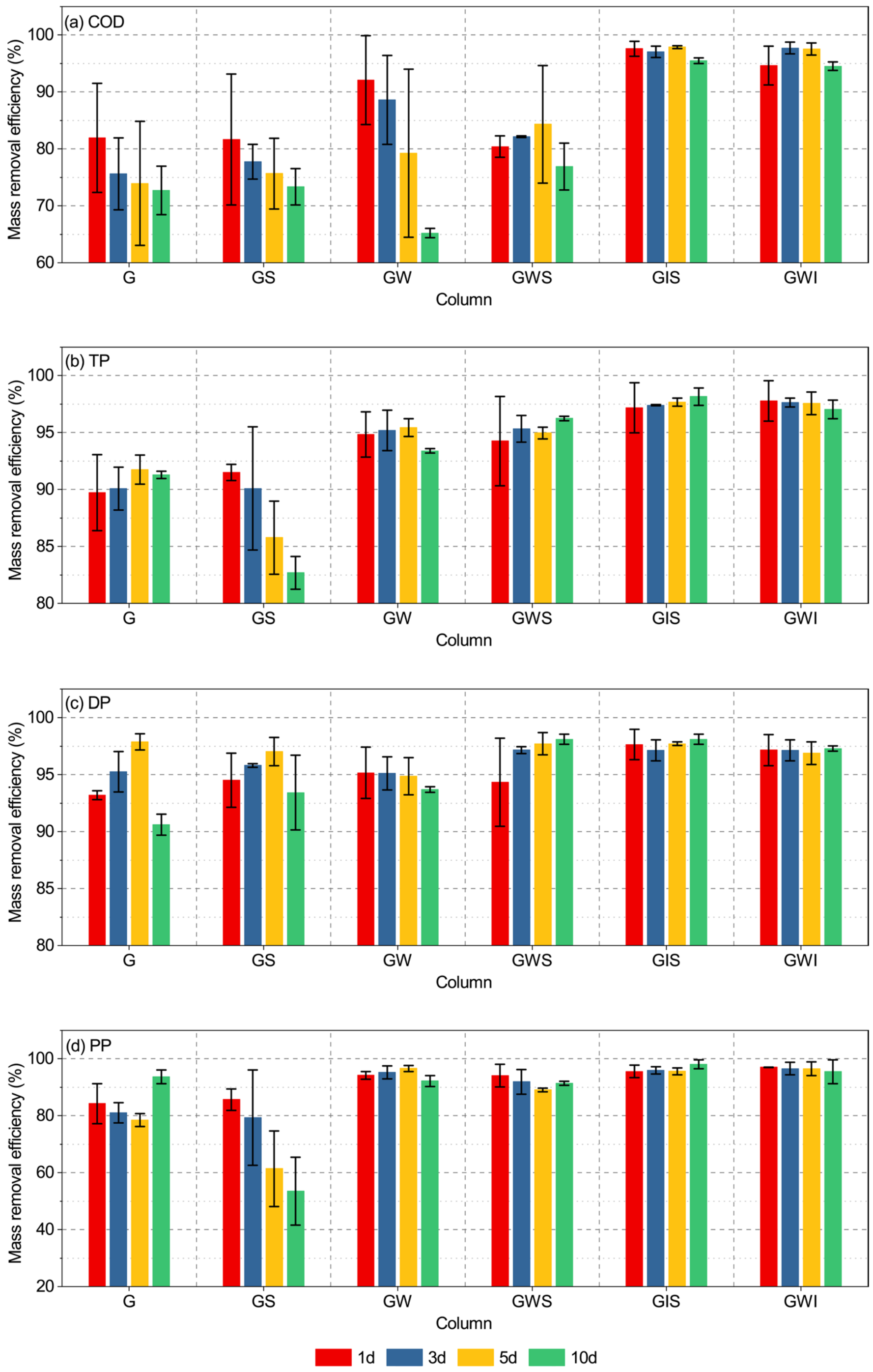

Fig. 1 Mean mass removal efficiencies (R_L) of COD, TP, DP, and PP in the bioretention columns for ADPs of different durations

WTR) and column GS (without WTR) were at the same level for ADPs of 1 and 3 days. However, for ADPs of 5 and 10 days, the COD R_L values of column GWS were 84.32 ± 7.29% and 76.89 ± 2.90%, respectively, which were significantly higher than the equivalent values of 75.65 ± 4.37% and 73.34 ± 2.24% observed at 5 and 10 days in column GS, respectively ($p < 0.05$). For the column with a submerged zone, the effect of WTR on COD removal became more pronounced as the ADP duration increased. Notably,

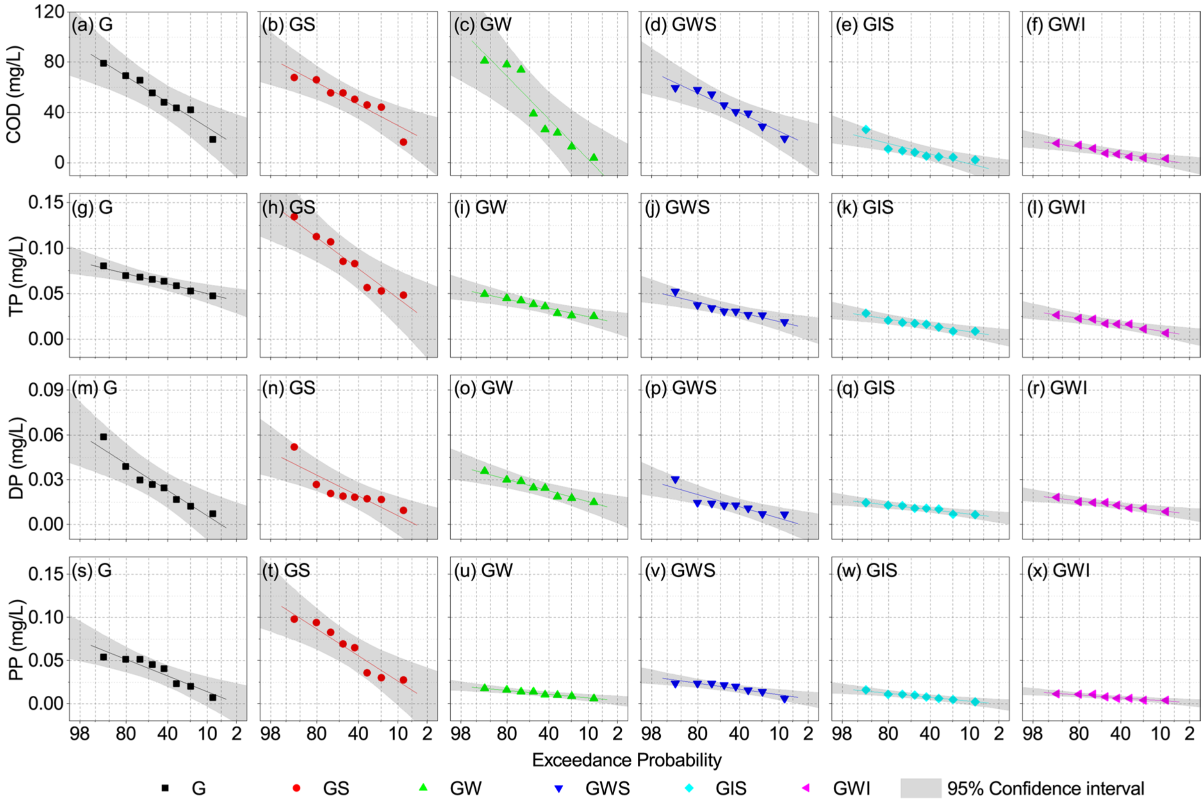

Fig. 2 COD, TP, DP, and PP concentrations in the outflow through the semi-synthetic runoff experiments

with zero-valent iron in the submerged zone, the COD at the outflows of columns GIS and GWI ranged from 2.5 to 26.5 mg/L and from 3.5 to 15.5 mg/L, respectively, which were significantly lower than those from other columns (Fig. 2a–f). The COD removal R_L of columns GIS and GWI improved and reached more than 92% for ADPs from 1 to 10 days when zero-valent iron was added, and these removals were significantly higher than those in columns GS and GWS, which were the same types of columns without zero-valent iron ($p < 0.05$).

We explored whether the ADP duration influenced the COD removal, and found that the COD R_L of columns G and GS decreased as the ADP duration increased. As the ADP increased, the moisture content in the media decreased, and the microbial activity decreased, which limited the biodegradation process and thus reduced the COD removal efficiency (Cruz-Paredes et al., 2021; Rahman et al., 2020). The COD R_L of column GW also decreased as the ADP duration increased, but the range of the decrease was greater, which may have been related to the decrease in the hydraulic conductivity in the column caused by the WTR. The COD R_L of column GWS did not change noticeably as the ADP duration increased, which may have been related to the COD leaching mentioned earlier. Similarly, the COD R_L of columns GIS and GWI improved significantly when zero-valent iron was added, but the changes observed as the ADP duration changed were not significant ($p > 0.05$). The relationship between the ADP duration and COD removal deserves further study.

The R_L values for TP, DP, and PP of the six bioretention columns for ADPs of different durations are shown in Fig. 1b–d. The TP R_L of columns G and GS did not differ significantly ($p > 0.05$) for ADPs of 1 and 3 days, but the TP R_L values of column GS ($85.77 \pm 2.27\%$ and $82.69 \pm 1.01\%$) were significantly lower than those of column G ($91.73 \pm 0.90\%$ and $91.29 \pm 0.22\%$) when the ADPs were 5 and 10 days ($p < 0.05$). The carbon source influenced the PP removal, which in turn affected the TP removal (Kim et al., 2003). The results show that, when there was a submerged zone and a carbon source, the PP outflow concentration increased, and the PP R_L of the column decreased significantly (Fig. 1d) as the operation time increased (Fig. 2s–t), reflecting the leaching of fine particles from the carbon source (wood chips) (Zhang et al., 2021b). As shown in Fig. 2m–n, the submerged zone was not related to any change in the DP outflow concentrations. Elsewhere, the TP outflow concentration of column GWS (with WTR) decreased significantly and was lower than 0.05 mg/L for ADP durations of 1–10 days, which showed a relatively stable removal efficiency. This significant decrease is thought to reflect enhanced P sorption by WTR (O'Neill & Davis, 2012; Zhang et al., 2021b). The TP R_L value of column GWS was not significantly different from that of column GW, which had the same submerged zone and carbon source ($p > 0.05$), and was significantly higher than that of column GS (without WTR, $p < 0.05$), when the ADP was between 1 and 10 days. This result indicates that WTR can significantly improve the P removal efficiency and mitigate the decrease in the TP removal efficiency as the denitrifying carbon source leaches, and that the submerged zone did not significantly affect the ability of the WTR to remove P.

We also examined the P removal efficiency of column GW without a submerged zone, and found that the TP R_L of column GW was significantly higher than that of column G for ADP durations of 1–10 days ($p < 0.05$), again confirming that the iron and aluminum compounds in the WTR contributed to improved P removal efficiency in a bioretention filter (Palmer et al., 2013). The average TP, DP, and PP outflow concentrations of columns GIS and GWI were lower than those of the other columns, and the outflow concentrations were also very stable (Fig. 2). As shown in Fig. 1b, the TP R_L values of columns GIS and GWI were more than 95% for ADP durations of 1 to 10 days, and they did not differ significantly ($p > 0.05$). The TP R_L of column GIS, which contained zero-valent iron, was significantly higher than that of column GS, which had no zero-valent iron ($p < 0.05$), reflecting the ability of zero-valent iron to promote phosphate removal (Luo et al., 2020; Sun et al., 2021) and to improve the TP removal. The TP R_L of column GWI with zero-valent iron was greater than that in a column of the same type, GWS, but the increase was limited, perhaps because the P removal in column GWI was already improved by WTR, and there was little additional benefit from the zero-valent iron.

We explored how the TP R_L varied with increases in the ADP. There was no significant change in the TP R_L of column G as the ADP duration increased ($p > 0.05$), and the ADP duration had little influence on the TP R_L of columns without a submerged zone. This might reflect P removal by sorption, and it has been reported elsewhere that the ADP duration had no clear effect on the sorption of the media in the submerged zone (Skorobogatov et al., 2020). In column GW, which contained WTR but had no submerged zone, the TP removal efficiency improved because of the WTR, but the TP R_L did not vary significantly as the ADP duration increased ($p > 0.05$).

In column GS, which had a submerged zone, the TP R_L decreased as the ADP duration increased. As the ADP duration increased, the HRT increased, and the moisture content of the media was high when there was a submerged zone. Therefore, during the intervals between rainfall, the adsorbed P was desorbed, and the TP removal efficiency gradually decreased as the ADP duration increased. For columns GWS, GIS, and GWI, the WTR provided amorphous aluminum (hydr)oxide with a large P sorption capacity (O'Neill & Davis, 2012), and the adsorbed phosphate would also precipitate out as a solid with ferric ion in zero-valent iron (Yoshino & Kawase, 2013). Therefore, the WTR and zero-valent iron probably mitigated P desorption during the ADP, thus ensuring P removal was maintained through relatively long ADPs. Therefore, the TP R_L of columns GWS, GIS, and GWI did not differ significantly for ADP durations from 1 to 10 days ($p > 0.05$).

3.2 Influence of ADP on N Removal

The R_L values for TN and NH_4^+-N for the six bioretention columns with ADPs of different durations are shown in Fig. 3. For ADP durations of 1, 3, 5, and 10 days, the TN R_L of column GS was higher than that of column G, while the NH_4^+-N removal efficiency of column GS was lower than that of column G. When there was a submerged zone and the environment was beneficial for denitrification, the TN removal significantly improved. However, because the submerged zone occupied part of the media space, the NH_4^+-N removal by sorption might be affected

(Li & Davis, 2014; Wang et al., 2018a, 2018b). Since the removal of NH_4^+-N was a highly variable process with many uncontrollable factors, further experiments were needed to verify this interpretation. The TN and NH_4^+-N concentrations in the outflow during the semi-synthetic runoff experiment are shown in Fig. 4. The patterns in the NH_4^+-N outflow concentrations were similar in the columns with a submerged zone, and the mean values were higher in the columns with a submerged zone than in those without a submerged zone. This indicates that the submerged zone adversely affected the NH_4^+-N removal efficiency.

The TN R_L of column GW was lower than that of column G for ADP durations from 1 to 10 days, but the NH_4^+-N R_L values of these columns did not differ significantly ($p > 0.05$). The TN concentrations in the outflow from column GW (3.31–4.26 mg/L) were significantly higher than those in other columns, and the NH_4^+-N concentrations were similar to those in other columns, indicating that the WTR affected the TN removal, but not the NH_4^+-N removal. This might have been caused by the media characteristics. The available N in the media in column GW (with 10% WTR) was 65.29 mg/kg, which was significantly higher than that in column G, where the main media was garden soil (44.89 mg/kg, $p < 0.05$). The high available N might promote TN leaching, and may explain the reduction in the TN R_L when there was WTR in the media. The TN R_L of column GWS, which had WTR, a submerged zone, and a carbon source (wood chips), was significantly higher than that of column GW for ADP durations from 1 to 10 days ($p < 0.05$), and the NH_4^+-N removal efficiency of these columns did not differ significantly. Meanwhile, for the same ADP duration, the R_L values for TN and NH_4^+-N of column GWS were not significantly different from those of column GS, which had a submerged zone but no WTR ($p > 0.05$). These results suggest that the enhanced N removal from the submerged zone could effectively counterbalance the N leaching caused by the WTR. When there is a submerged zone, N leached from the media may be removed by denitrification, and so the submerged zone may effectively mitigate the negative effect of WTR on TN removal. Indeed, N conversion is a complex process, and N removal is associated with multiple factors. In addition, leaching characteristics of materials would help understanding of real mechanisms within the columns (Ding et al., 2023). This problem needs to be further explored in future research.

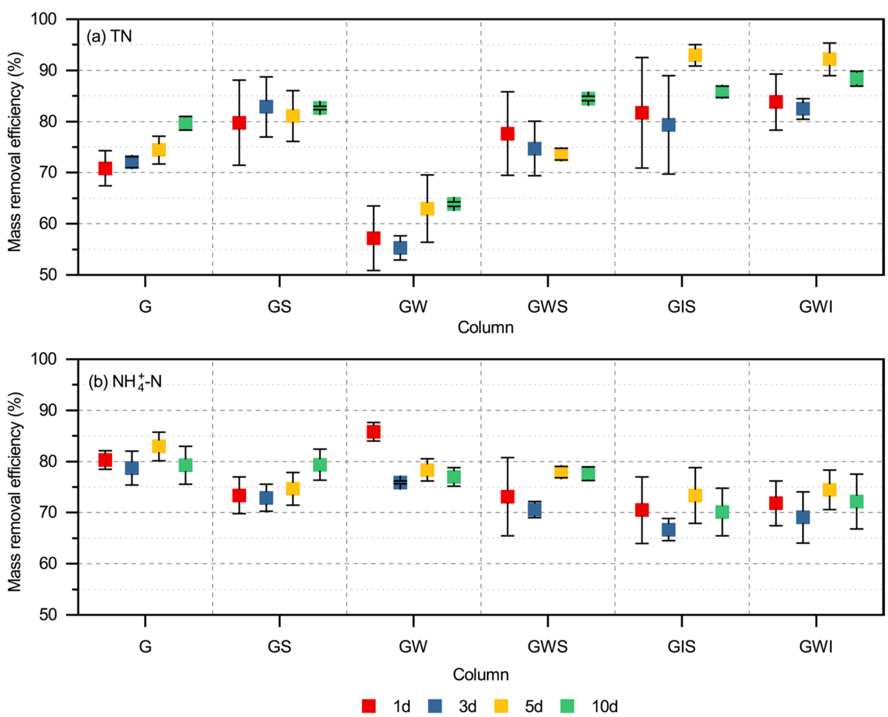

Fig. 3 Mean TN and NH_4^+-N mass removal efficiencies (R_L) of bioretention columns for ADPs of different durations

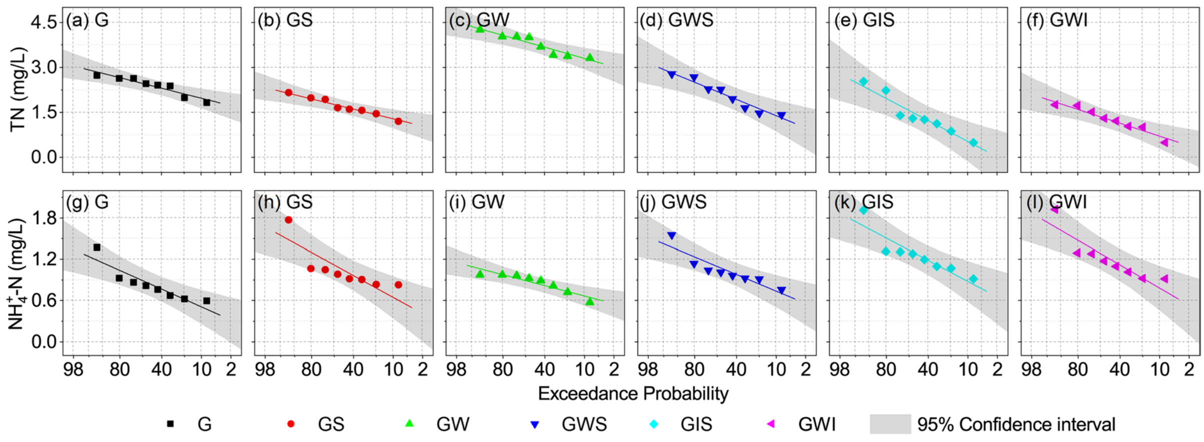

Fig. 4 Outflow TN and NH_4^+-N concentrations during the semi-synthetic runoff experimental stage

The TN R_L of column GWI (with zero-valent iron) was higher than that of column GWS (without zero-valent iron) for ADP durations of 1 to 10 days. Meanwhile, the TN R_L of column GIS (with zero-valent iron) was generally higher than that of column GS (without zero-valent iron) for the same ADP durations. This indicates that zero-valent iron additions to a bioretention filter could enhance the TN removal. Early studies reported that zero-valent iron promoted denitrification (Till et al., 1998) by providing suitable electron donors for denitrifying bacteria. Tian et al. (2019) added zero-valent iron into the submerged zone of a bioretention filter and found that the NO_3^--N removal efficiency was significantly higher than in the control group. Their results confirmed that the TN removal was enhanced in the presence of zero-valent iron.

We explored how the R_L for N pollutants varied with changes in the ADP duration, and found that the TN R_L values of columns G and GW generally increased with increases in the ADP, but with some exceptions. Bioretentions without the submerged zone also had the possibility of denitrification, thereby removing N pollutants. Because the bioretentions might contain local denitrification processes due to microbial action and microenvironment (Huang et al., 2022). Therefore, this problem needs to be further explored in the future research. Plant root exudates provide a carbon source, and the available carbon accumulates as the ADP duration increases, promoting TN removal (Barron et al., 2020; Dagenais et al., 2018; Skorobogatov et al., 2020). Other studies of bioretention filters have shown that, in the absence of a submerged zone setting, plant uptake became the main route for N removal (Osman et al., 2019; Skorobogatov et al., 2020), and that more N was absorbed by plants as the ADP duration increased, resulting in higher TN removal efficiency. The TN removal varied, but not significantly, with ADP durations from 1 to 10 days, which shows that the local micro-environment denitrification and plant action had a minimal influence on the TN removal.

The TN R_L values of columns GS and GWS, which had a submerged zone, reached $82.64 \pm 0.24\%$ and $84.50 \pm 0.28\%$, respectively, for an ADP of 10 days, showing that the denitrification effect of the submerged zone and the carbon source increased as the ADP duration increased. The TN removal efficiencies were high in columns GIS and GWI for all the ADP durations, and the TN R_L of these two columns reached maximum values of $92.95 \pm 1.50\%$ and $92.16 \pm 2.28\%$ for an ADP of 5 days. The zero-valent iron in the submerged zone further enhanced the denitrification, the denitrification peaked when the ADP was 5 days.

3.3 Nitrogen Transformation in the Submerged Zone

The TN and NH_4^+-N concentrations in the submerged zone of columns GS, GWS, GIS, and GWI are shown in Fig. 5. The TN concentration in the submerged zone of column GS decreased rapidly in the initial 3 days of the ADP, and then were relatively stable (Fig. 5a) and did not change significantly from 4 to 14 days ($p > 0.05$). The TN concentration in the submerged zone of column GWS showed a similar pattern, but decreased in the initial 5 days, and then continued to decrease between 5 and 14 days, which reflected the ongoing leaching of N compounds promoted by the WTR in the column.

The initial TN concentrations in the submerged zone of columns GIS and GWI with zero-valent iron added (0.90 ± 0.03 mg/L and 0.95 ± 0.03 mg/L, respectively) were lower than those of columns GS and GWS (1.84 ± 0.03 mg/L and 1.52 ± 0.14 mg/L, respectively). This difference reflects the N removal by the zero-valent iron. From 0 to 14 days, the TN concentrations in columns GIS and GWI first decreased and then stabilized. Notably, the TN concentrations did not change significantly ($p > 0.05$) after 5 days, which coincides with the peak TN R_L observed in columns GIS and GWI for an ADP duration of 5 days in the semi-synthetic runoff experiment.

The NH_4^+-N and TN concentrations in the submerged zone of the four columns generally followed a similar pattern. The NH_4^+-N concentrations in the submerged zone rapidly decreased to a low level within 5 days (Fig. 5), and then showed no significant change from 5 to 14 days ($p > 0.05$).

The variations in the TN and NH_4^+-N concentrations in the submerged zone reflect denitrification and N removal, and any consideration of how the submerged zone influences the TN and NH_4^+-N removal should also include the contributions of the submerged zone and infiltration zone, shown in Fig. 6. The percentage contribution of the submerged zone of different columns to the TN and NH_4^+-N removal increased as the ADP duration increased. However, when the ADP duration exceeded 5 days, the contribution rate of the submerged zone to the TN and NH_4^+-N removal remained stable, indicating that most of the TN and NH_4^+-N had been removed from the submerged zone. The contribution proportion did not change much as the ADP increased from 0.5 to 14 days, which indicates that the submerged zone setting was important for improving the TN removal but was not significantly affected by the ADP value. However, the scale of the submerged zone would affect the N removal in a bioretention filter. When the ADP is long enough to ensure the denitrification is complete, the proportion of the runoff that is stored in the submerged zone relative to the total runoff volume flowing into the bioretention filter will be important. In this study, the runoff stored

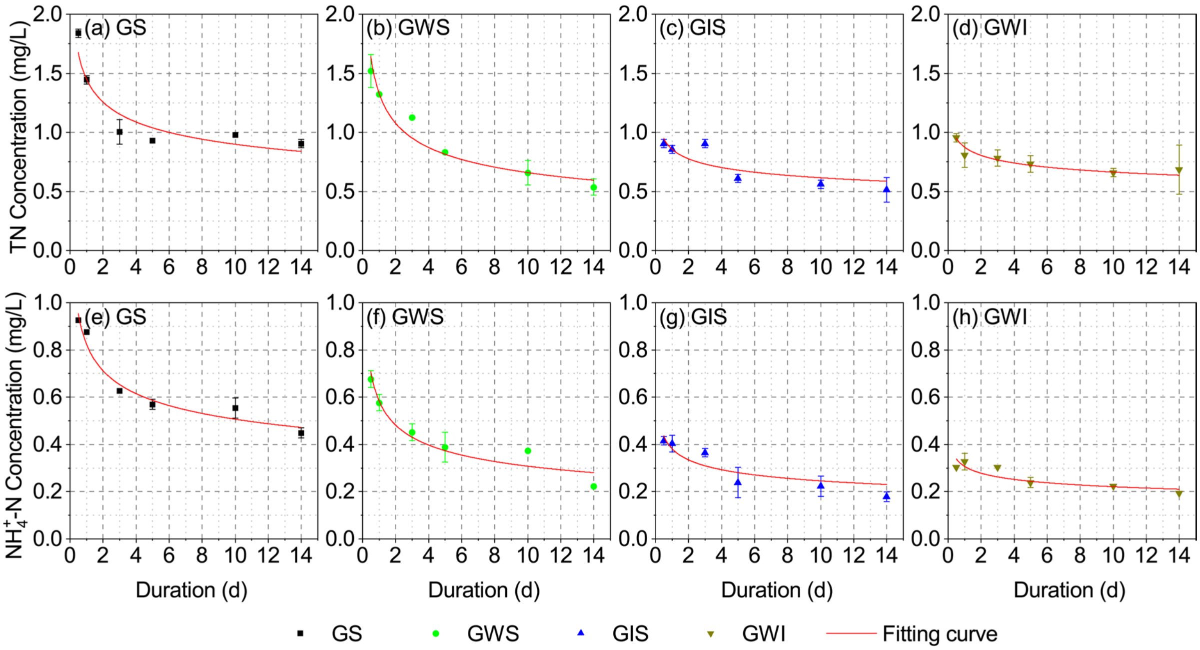

Fig. 5 TN and NH_4^+-N concentrations in the submerged zone in the bioretention columns

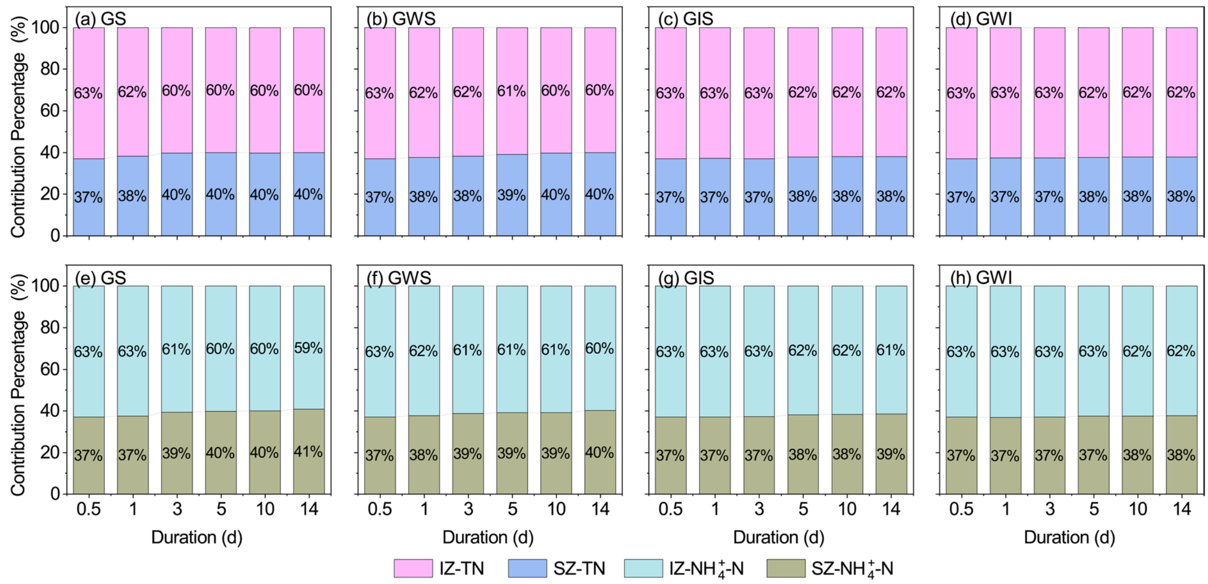

Fig. 6 Contribution of the submerged zone and the infiltration zone to TN and NH_4^+-N removal in the bioretention filters. IZ-TN and SZ-TN represent the contributions of the infiltration zone and the submerged zone to the TN removal, respectively, and IZ-NH_4^+-N and SZ-NH_4^+-N represent the contributions of the infiltration zone and the submerged zone to the NH_4^+-N removal, respectively

in the submerged zone represented approximately 30% of the total runoff volume (4.3 L). Given the volume reduction of bioretention, this indicates that 25%–30% of the outflow volume was made up of runoff stored in the submerged zone, and it affected the N removal performance. If the stored volume could be increased, and if the submerged zone volume could be enlarged by increasing the submerged zone depth or increasing the media porosity in the submerged zone, it could give further improvements in the TN removal of the bioretention filter.

The initial TN and NH_4^+-N concentrations in the submerged zone of column GWS were significantly higher than those of columns GIS and GWI that contained zero-valent iron ($p < 0.05$). However, after an ADP of 14 days, the TN and NH_4^+-N concentrations in the submerged zone of column GWS were at almost the same level as those of columns GIS and GWI. In column GS, which did not have WTR, the TN and NH_4^+-N concentrations were always higher than those of columns GIS and GWI from 0 to 14 days. These results suggest that the effects of WTR and zero-valent iron on denitrification and N removal deserve further research.

4 Conclusions

The influence of the ADP duration on the pollutant removal efficiency of bioretention filters was assessed in a laboratory-scale experiment. The main findings were as follows.

- For a bioretention filter without a submerged zone, the TN removal increased, the COD removal decreased, and there were no clear trends in TP, DP, and PP as the ADP duration increased.
- When the bioretention filter had a submerged zone, the TN removal peaked (82.64 ± 0.24% and 84.50 ± 0.28%) when the ADP duration was 10 days. The denitrification and TN removal efficiency benefitted from a long ADP, a submerged zone, and a carbon source.
- The denitrification improved significantly, the COD and TP removal efficiencies improved, and the TN removal peaked (92.95 ± 1.50% and 92.16 ± 2.28%) within an ADP of 5 days when zero-valent iron was added. The zero-valent iron was not significantly related to the ADP duration.

- The concentrations of TN and NH_4^+-N in the submerged zone decreased significantly for an ADP of 3 days, and stabilized after 5 days, which matched the peak TN R_L observed for an ADP of 5 days.

The ADP duration had a strong influence on the nutrient removal of the bioretention filters, and had a particularly strong influence on the TN removal when the bioretention filter had a submerged zone. By adding zero-valent iron, the denitrification improved significantly, and the COD and TP removals improved. While the relationships between zero-valent iron and denitrification and N removal deserve further research, the results from this study provide useful information about the effectiveness of the submerged zone in bioretention filters.

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Author Contribution Wei Zhang proposed the research idea; Wei Zhang and Wu Che designed the experiment; Juan Li and Wei Zhang carried out the experiment; Wei Zhang, Juan Li, and Huichao Sun analyzed the data; Juan Li and Zimeng Zhuang wrote the manuscript draft; Wei Zhang, Zimeng Zhuang, and Huichao Sun revised the manuscript; Huichao Sun, Wu Che, and Zimeng Zhuang edited the manuscript.

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Data Availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics Approval and Consent to Participate Not applicable.

Consent for Publication Not applicable.

Competing Interests The authors declare no competing interests.

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