

THE IMPACT OF APPLYING BIOCHAR ON NITROGEN AND PHOSPHORUS LEACHING FROM SOIL UNDER SIMULATED RAINFALL CONDITIONS

ZHAO, Y.^{1,2} – QI, S. W.³ – LU, M.^{1,2} – MA, B. G.^{1,2*}

¹*School of Water Conservancy and Hydroelectric Power, Hebei University of Engineering,
Handan 056038, China
(e-mail: zym3506020@126.com; phone: +86-150-7503-2464)*

²*Hebei Key Laboratory of Intelligent Water Conservancy, Hebei University of Engineering,
Handan 056038, China*

³*Zhejiang Provincial Water Resources and Hydropower Survey and Design Institute,
Hangzhou 310000, China*

**Corresponding author
e-mail: mabghd@aliyun.com; phone: +86-135-1310-5026*

(Received 28th Apr 2025; accepted 26th Jun 2025)

Abstract. The leaching of nitrogen and phosphorus is the main cause of groundwater pollution. To study the characteristics of nitrogen and phosphorus leaching in southern Hebei, this article analyzes the effects of different rainfall intensities and fertilization on the leaching of dissolved nitrogen (DN) and available phosphorus (AP), as well as the vertical distribution of soil moisture and nutrients, using simulated rainfall experiments under equal total rainfall. The results show that compared with conventional fertilization (CF), both the biochar group (CFB) and the zeolite group (CFZ) can reduce the leaching of soil moisture and nutrients, especially in the topsoil. Under the same fertilization treatment, there is a positive correlation between rainfall intensity and the cumulative leaching loss of AN, NN, DN, and AP, specifically: $L30\text{mm}\cdot\text{h}^{-1} > L20\text{mm}\cdot\text{h}^{-1} > L10\text{mm}\cdot\text{h}^{-1}$. Nitrogen leaching is predominantly in the form of nitrate nitrogen, accounting for 96.16% to 97.72% of the total. Compared with CF, the application of biochar reduced the leaching volume by 6.09% to 8.31%, DN leaching by 50.21% to 67.92%, and AP leaching by 27.62% to 41.35%. The application of zeolite can reduce the leaching volume by 3.57% to 6.94%, DN leaching by 43.50% to 65.51%, and AP leaching by 20.95% to 36.60%. Pearson correlation analysis shows that leaching volume is the main factor affecting nitrogen and phosphorus leaching. Rainfall intensity and fertilization are important factors influencing nitrogen and phosphorus leaching, while biochar and zeolite are effective in controlling it. There is a highly significant linear positive correlation between leaching volume and the leaching amounts of DN and AP ($y=ax+b$, $r^2>0.91$, $p<0.0001$). The research results indicate that in agricultural production, controlling leaching volume is key to reducing nitrogen and phosphorus loss from farmland. Reducing seepage generation, improving soil water and nutrient retention, and decreasing fertilizer application are important strategies for effectively controlling groundwater pollution.

Keywords: *biochar, zeolite, agriculture non-point source pollution, nitrogen and phosphorus leaching loss, correlation analysis*

Introduction

Fertilizer loss from farmlands, livestock and poultry farming, and rural life is considered one of the main sources of agricultural non-point source pollution (Tao et al., 2020; Zhu et al., 2021; Bai et al., 2021). Nutrient loss from farmlands is an important component of agricultural pollution (Hou et al., 2008). In the process of agricultural production, farmers continuously increase fertilizer use to achieve higher agricultural yields (Wang et al., 2017). The average fertilizer usage in China is significantly higher than the global average, while its fertilizer utilization rate remains relatively low (Zhang

et al., 2015). The utilization rate of nitrogen fertilizer is only 27% to 35% (Wen et al., 2021), and that of phosphate fertilizer is only 10% to 15% (Guo et al., 2021). The average fertilizer usage in China is approximately 400 kilograms per hectare, while the globally recognized safety threshold for fertilizer is 225 kilograms per hectare. China's usage exceeds the safety threshold by more than 1.8 times and is more than four times the global average. The accumulation of large amounts of nitrogen and phosphorus in the soil can lead to soil degradation (Cai et al., 2021). China's arable land accounts for less than 10% of the world's total. In 2019, middle-to-low grade arable land reached 9.27 million ha, representing 69% of the total, which poses severe challenges to both the quantity and quality of farmland (Xu et al., 2020). Additionally, nitrogen and phosphorus entering water bodies can contaminate drinking water, with nitrate concentrations exceeding standards in many regions both in China and abroad (Dana et al., 2017; Erostate et al., 2018; Jiang et al., 2020; Wang et al., 2021). High nitrate content in drinking water has already caused health problems, including human methemoglobinemia (blue baby syndrome) and animal poisoning (Ahmed et al., 2019; Yin et al., 2019).

Nitrogen and phosphorus leaching is an important pathway for agricultural non-point source pollution. With the development of agricultural intensification, farmland in plain areas tends to become fragmented, and ridges exist between fields. Under conditions of light to moderate rainfall, it is difficult to generate runoff, and most accumulated nutrients are lost through leaching in the form of seepage. Therefore, controlling nitrogen and phosphorus leaching is a crucial step in reducing agricultural non-point source pollution.

In recent years, the application of soil amendments (biochar, zeolite) has effectively controlled nitrogen and phosphorus leaching and has become a popular method in agricultural sectors worldwide (Yin et al., 2019). Numerous studies have demonstrated that applying biochar and zeolite to soil can improve fertilizer efficiency, enhance water utilization efficiency, and reduce potential nutrient losses (Liu et al., 2014; Li et al., 2000, 2020). For instance, Rasheed Ahmed and others conducted a study on soil improvement in vegetable fields in Beijing using biochar and found that biochar treatment reduced mineral nitrogen leaching by 35% and decreased leachate flux by 7.63%. In trials conducted in northern Greece using zeolite to improve vegetable soil (Tzanakakis et al., 2021), Tzanakakis and colleagues discovered that the addition of zeolite to the soil can regulate the availability of NH_4^+ , promote nitrification, enhance the crop's nitrogen absorption, and reduce nitrogen losses.

There are many factors affecting nitrogen and phosphorus leaching, including rainfall, fertilization, soil texture, and the addition of soil amendments. The leaching of nitrogen and phosphorus is a very complex process, and all factors influencing seepage generation and nitrogen and phosphorus concentrations will affect their leaching. Due to regional differences, conclusions from studies in other areas cannot be directly applied to the southern Hebei region. This study conducted indoor controlled simulated rainfall experiments. Indoor simulation experiments provide highly controllable and repeatable conditions, enabling the exclusion of external interferences, precise manipulation of variables, and detailed observation of the leaching process, thereby revealing the inherent mechanisms of nitrogen and phosphorus leaching. The article analyzes the combined effects of different rainfall intensities and fertilization practices on nitrogen (N) and phosphorus (P) leaching in agricultural fields of Southern Hebei (a region in North China) under identical rainfall amounts. The main research objectives include: (1)

Comparative analysis of the impact of different fertilization treatments on the vertical distribution of soil moisture and nutrients; (2) Investigation of the effects of varying rainfall intensities and fertilization on the leaching of ammonium nitrogen ($\text{NH}_4^+\text{-N}$), nitrate nitrogen ($\text{NO}_3^-\text{-N}$), dissolved nitrogen, and available phosphorus; (3) Exploration of the relationships between external factors (rainfall intensity, percolation volume, fertilization) and nitrogen and phosphorus leaching. The study aims to provide a theoretical basis and reference for the prevention and control of agricultural non-point source pollution in the Southern Hebei region.

Materials and methods

Overview of the study area

This experiment was conducted on December 15, 2020, in the simulated rainfall laboratory at Hebei University of Engineering in Handan City, Hebei Province ($36^\circ39'\text{N}$, $114^\circ35'\text{E}$). Handan is situated in the southern area of the North China Plain and in the Haihe River Basin (Figure 1). The terrain is higher in the west and lower in the east, with the highest elevation at 1898.7 meters and the lowest at 32.7 meters. The western region is mostly mountainous, while the eastern region is flat. The area experiences a warm temperate continental monsoon climate, with distinct seasons and favorable conditions for rain, heat, and sunlight, an average annual rainfall of 537.6 mm, a frost-free period of 200 days per year, and an annual sunshine duration of 2557 hours, which is an important agricultural production area in Hebei Province.

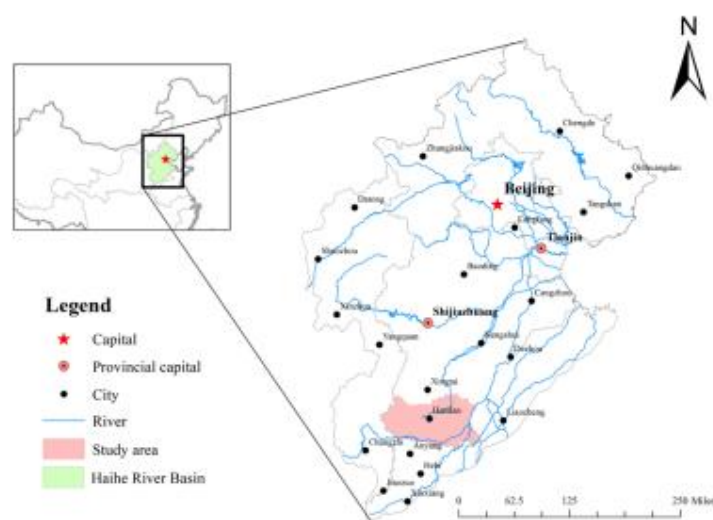


Figure 1. Schematic diagram of the study area

The soil used in this experiment was collected from farmland in the southern Hebei region of the Haihe River Basin, specifically at the coordinates $36^\circ39'30''\text{N}$ and $114^\circ35'43''\text{E}$. In October 2020, the test soil was sampled from local farmland using a five-point random sampling method. A standard measuring stick was used to collect soil samples at three vertical depths: 0-30 cm for the surface layer, 30-60 cm for the middle layer, and 60-100 cm for the deep layer. The physico-chemical properties of the test soil are presented in Table 1.

Table 1. Physical and chemical properties of tested foundation soil

Soil depth /cm	Mechanical composition			pH	EC	Avail-N / (mg·kg ⁻¹)	Avail-P/ (mg·kg ⁻¹)	Avail-K/ (mg·kg ⁻¹)	O.M./ (g·kg ⁻¹)
	Sand	Silt	Clay particles						
0-30	79.08%	12.24%	8.67%	7.47	162.5	28.11	5.53	340	4.17
30-60	82.32%	9.90%	7.78%	7.37	159.9	21.23	8.95	240	3.93
60-100	86.36%	9.09%	4.55%	7.67	198.3	15.75	7.24	220	3.08

Note: Particle size distribution (mechanical composition) was determined using a Malvern laser granulometer; Alkali-hydrolyzable nitrogen was measured by the alkali diffusion method; Available phosphorus was analyzed with an ultraviolet-visible spectrophotometer; Available potassium was quantified by flame photometry (FP); Organic matter content was determined via the potassium dichromate volumetric method

Experimental design

This experiment controls three rainfall intensities and four fertilization treatments, conducting three batches of combined experiments, resulting in a total of 12 groups. Based on local rainfall characteristics, three moderate rainfall intensities are set: 10 mm·h⁻¹(R₁), 20 mm·h⁻¹(R₂), 30 mm·h⁻¹(R₃), with a total rainfall amount of 100 mm, which qualifies as heavy rainfall. The four fertilization treatments are: no fertilization (Control check, CK), conventional fertilization (Conventional fertilization, CF), conventional fertilization + biochar (Conventional fertilization + biochar, CFB), and conventional fertilization + zeolite (Conventional fertilization + zeolite, CFZ). The experiments will be carried out in three batches according to different rainfall intensities, with an interval of one week between each batch. The specific plan is shown in *Table 2* below.

Table 2. Fertilization scheme and rainfall intensity test design

Batch	Soil column number	N /(kg·hm ⁻²)	P ₂ O ₅ /(kg·hm ⁻²)	K ₂ O /(kg·hm ⁻²)	biochar /(kg·hm ⁻²)	zeolite /(kg·hm ⁻²)	rainfall intensity /(mm·h ⁻¹)
1	1	0	0	0	0	0	10
	2	135	105	70	0	0	10
	3	135	105	70	855	0	10
	4	135	105	70	0	1500	10
2	5	0	0	0	0	0	20
	6	135	105	70	0	0	20
	7	135	105	70	855	0	20
	8	135	105	70	0	1500	20
3	9	0	0	0	0	0	30
	10	135	105	70	0	0	30
	11	135	105	70	855	0	30
	12	135	105	70	0	1500	30

A layer of 3 cm thick dry quartz sand washed with deionized water is laid at the bottom of the soil column. The test soil is placed in the test soil column according to the soil depth of 0-30 cm, 30-60 cm, and 60-100 cm, and each 20 cm is compacted. The test soil column has an outer diameter of 20 cm and an inner diameter of 18 cm. After

compaction, the surface soil needs to be deliberately turned over to avoid errors caused by soil stratification. The soil is filled to a height of 1 m. The test soil needs to be naturally dried and sieved, and the soil is evenly packed according to the field soil bulk density (the bulk densities of topsoil, middle soil, and deep soil are $1.38 \text{ g}\cdot\text{cm}^{-3}$, $1.40 \text{ g}\cdot\text{cm}^{-3}$, and $1.42 \text{ g}\cdot\text{cm}^{-3}$, respectively) to ensure uniform soil (try to maintain the original soil state). The soil is filled into the simulated test soil column. When fertilizing, the fertilizer is fully mixed with the top 10cm of the surface layer, and the soil is fully moistened. It should then stand for a week to allow the nutrients to fully dissolve and transform. The rainfall experiment can only begin once the soil bulk density approaches that of the farmland soil.

Sample collection and analysis

In the preliminary experiment, it was found that signs of leaching only appeared 40 minutes after the rainfall began. Therefore, leachate collection started 40 minutes after the onset of rainfall. Water samples were collected at intervals of 20 minutes (six intervals), followed by 30 minutes (four intervals), and finally at 40 minutes (two intervals), 60 minutes (two intervals), and 180 minutes (one interval), using experimental plastic bottles as collection containers. A total of 15 water samples were collected for each treatment, resulting in a total of 180 water samples. On the second and seventh days after the rainfall ended, soil samples were taken from the soil column at 10 cm intervals. Each treatment had 20 soil samples, a total of 240 soil samples.

The collected leaching solution and soil samples were stored at low temperatures (4°C) and analyzed for nutrient content within 72 hours. Each sample was measured three times, and the average was calculated to reduce random error. The water sample tests included ammonium nitrogen (NH_4^+N , according to GB/T 8538-1995 using the phenol-sodium method) and nitrate nitrogen (NO_3^-N , according to GB/T8538-1995 using ultraviolet spectrophotometry). The total dissolved nitrogen content in this experiment was the sum of nitrate nitrogen and ammonium nitrogen. Available phosphorus was determined using potassium persulfate oxidation-molybdenum acid spectrophotometry (according to GB/T 11893-1989), filtered through a $0.45 \mu\text{m}$ membrane.

Soil sample analysis included alkaline nitrogen (using the alkaline hydrolysis diffusion method), available phosphorus (using spectrophotometry), available potassium (using flame photometry), and organic matter (using the potassium dichromate volumetric method). All methods referenced the "Soil Agricultural Chemistry Analysis" and "Water and Wastewater Monitoring Analysis Methods".

Data analysis

The calculation formula of nitrogen and phosphorus Leaching loss (L) during artificial simulated rainfall test is as follows:

$$L_i = \sum C_{ij}V_j \quad (\text{Eq.1})$$

where, L_i : leaching loss of DN, NN, AN, AP, mg; C_{ij} : i leaching concentration in the JTH water sample, $\text{mg}\cdot\text{L}^{-1}$; V_{ij} : Volume of leaching in water sample j, L.

The Leaching coefficient (LC) of nitrogen and phosphorus was used to evaluate the leaching degree of different rainfall intensity and fertilization treatment. The calculation formula is as follows:

$$LC = (L - L_0) / I \quad (\text{Eq.2})$$

where: LC: refers to leaching coefficient; L: nitrogen and phosphorus leaching loss, mg; L_0 , is CK nitrogen and phosphorus leaching loss, mg; I, nitrogen, phosphorus application amount, mg.

Data processing and analysis were conducted using Excel software for data organization, while IBM SPSS 17.0 software was used for least significant difference (LSD, $p < 0.05$) analysis and Pearson correlation testing. Origin 2019 professional graphing software was used to plot the variations of nitrogen and phosphorus leaching over time as well as the vertical distribution of soil nutrients and moisture content. The LSD test was applied to analyze the impact of different fertilization treatments on soil moisture and nutrient contents (alkaline nitrogen, available phosphorus, available potassium, and organic matter). The Pearson correlation coefficient method was used to analyze the correlation between nitrogen and phosphorus leaching and external factors (infiltration rate, rainfall intensity, fertilization, and addition of soil conditioners), while a regression model was applied to fit a linear equation between the cumulative nitrogen and phosphorus leaching amounts and the infiltration rate.

Result and analysis

Soil physical and chemical properties

Soil moisture content

According to *Figure 2*, the soil moisture content on the second and seventh days after the simulated rainfall experiment ranges from 15% to 23% and from 12.75% to 18.75%, respectively, with the soil moisture content on the second day being significantly higher than that on the seventh day. The results of the Mann-Kendall trend test indicate a significant increasing trend in soil moisture content with soil depth for all treatments ($z > 0$, $p < 0.01$). The soil moisture content in the topsoil layers of CFB and CFZ is higher than that of the CF group by 8.71% and 8.42%, respectively. On the second day, the average soil moisture content from 0 to 100 cm for CK, CF, CFB, and CFZ is 18.09%, 18.07%, 18.44%, and 18.31%, respectively, with no significant differences among the treatments. On the seventh day, the average soil moisture content from 0 to 100 cm is 15.59%, 15.71%, 16.31%, and 16.11%, respectively, with CFB and CFZ showing significant differences from CF ($p < 0.05$), while there are no significant differences between CK and CF.

Soil nutrients

Under simulated rainfall conditions, the overall content of soil nutrients (alkali-hydrolyzable nitrogen, available phosphorus, available potassium, and organic matter) shows a decreasing trend with depth (see *Figure 3*). The LSD test indicates significant differences in the contents of soil alkali-hydrolyzable nitrogen, available phosphorus, and available potassium between the fertilized and unfertilized treatments ($p < 0.05$).

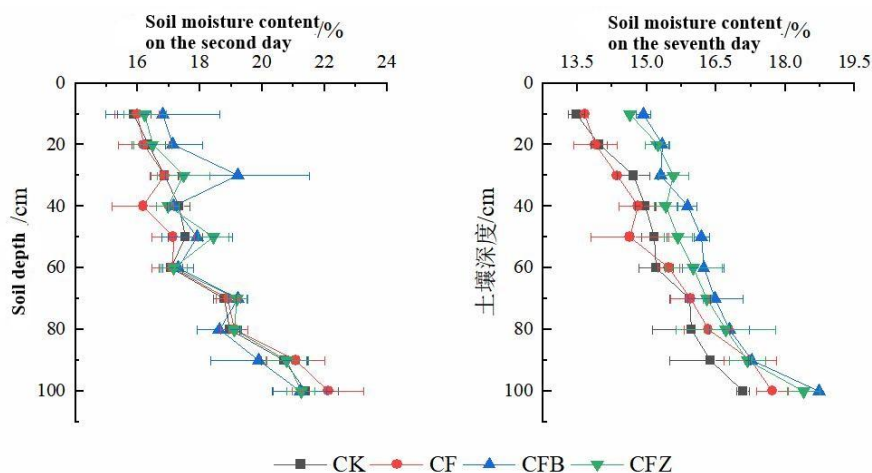


Figure 2. Soil moisture content on the 2nd and 7th days after rainfall

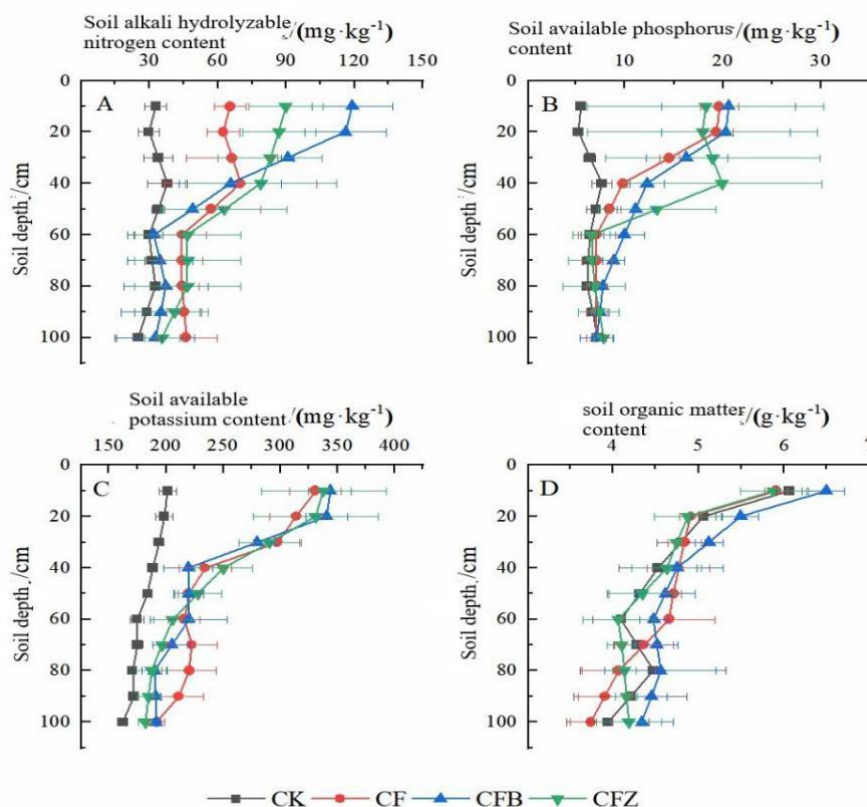


Figure 3. Vertical distribution of soil alkali hydrolyzable nitrogen (A), available phosphorus (B), available potassium (C) and organic matter (D)

Additionally, the CFB group significantly increased soil organic matter content after the addition of biochar ($p < 0.05$). Compared to the CK group, the contents of soil alkali-hydrolyzable nitrogen, available phosphorus, and available potassium in the CF group increased by 72.79% to 93.73%, 66.36% to 91.33%, and 31.45% to 34.95%, respectively, particularly in the topsoil layer, but there was no significant impact on soil

organic matter (see *Table 3*). Compared to the CF group, the average contents of soil alkali-hydrolyzable nitrogen, available phosphorus, available potassium, and organic matter in the CFB group with biochar addition increased by 12.11%, 5.08%, 2.35%, and 6.32%, respectively, while the average contents in the CFZ group with zeolite addition increased by 8.41%, 13.13%, and 2.60%, respectively. Under conventional fertilization conditions, the addition of biochar and zeolite to the soil can improve the soil environment, enhance nutrient retention, and increase fertilizer utilization efficiency.

Table 3. LSD test of soil nutrients under different fertilization treatments

nutrients	Fertilization plan		Mean difference (I-J)	standard error	significance	95% confidence interval	
	I	J				lower limit	upper limit
Avail-N	CF		-22.9833*	8.0670	0.022	-41.5859	-4.3807
	CK	CFB	-29.5955**	8.0670	0.006	-48.1981	-10.9929
		CFZ	-27.5718**	8.0670	0.009	-46.1744	-8.9692
	CF	CFB	-6.6122	8.0670	0.436	-25.2148	11.9904
		CFZ	-4.5885	8.0670	0.585	-23.1911	14.0141
	CFB	CFZ	2.0237	8.0670	0.808	-16.5789	20.6263
Avail-P	CF		-4.2767***	0.3321	0.000	-5.0425	-3.5109
	CK	CFB	-5.9033***	0.3321	0.000	-6.6691	-5.1375
		CFZ	-5.6933***	0.3321	0.000	-6.4591	-4.9275
	CF	CFB	-1.6267**	0.3321	0.001	-2.3925	-0.8609
		CFZ	-1.4167**	0.3321	0.003	-2.1825	-0.6509
	CFB	CFZ	0.2100	0.3321	0.545	-0.5558	0.9758
Avail-K	CF		-63.7000***	5.9115	0.000	-77.3318	-50.0682
	CK	CFB	-57.9167***	5.9115	0.000	-71.5485	-44.2848
		CFZ	-57.3167***	5.9115	0.000	-70.9485	-43.6848
	CF	CFB	-5.7833	5.9115	0.357	-19.4152	-7.8485
		CFZ	-6.3833	5.9115	0.312	-20.0152	-7.2485
	CFB	CFZ	0.6000	5.9115	0.922	-13.0318	14.2318
O.M.	CF		-0.0118	0.0944	0.904	-0.2294	0.2059
	CK	CFB	-0.3063*	0.0944	0.012	-0.5239	-0.0886
		CFZ	0.0632	0.0944	0.522	-0.1545	0.2809
	CF	CFB	-0.2945*	0.0944	0.014	-0.5121	-0.0768
		CFZ	0.0750	0.0944	0.450	-0.1427	0.2926
	CFB	CFZ	0.3694**	0.0944	0.004	0.1518	0.5871

Note: $p < 0.05$, Significant difference, *, $p < 0.01$, **, $p < 0.001$, Extremely significant difference, ***

Nitrogen leaching under different rainfall intensities

During the simulated rainfall testing process, noticeable seepage occurred at different rainfall intensities after 40 minutes. This was primarily due to the fact that, in the initial stage of the rainfall, the rainwater was mainly used to fill depressions, replenish soil moisture, and infiltrate. There is a significant lag between the onset of rainfall and the emergence of seepage, referred to as the initial loss duration. *Table 4* presents the seepage rate in the early stage (with a rainfall duration of 60 minutes) and the total seepage collected over 11 hours. From the table, it can be concluded that SC9 had the highest initial seepage rate and total seepage over 11 hours, while SC3 had the lowest. The observed trend for initial seepage rates and total seepage over 11 hours is: $V_{30\text{mm}} \cdot \text{h}^{-1} > V_{20\text{mm}} \cdot \text{h}^{-1} > V_{10\text{mm}} \cdot \text{h}^{-1}$.

Table 4. Initial seepage flow (First 60min) and total seepage volume in 11h of each soil column

Soil column	Initial seepage flow /mL	Total seepage volume /mL
1	73	2329
2	71	2349
3	63	2206
4	66	2265
5	113	2562
6	115	2588
7	92	2397
8	81	2432
9	126	2738
10	125	2695
11	104	2471
12	94	2508

Figure 4 shows the variations in leaching concentrations of ammonia nitrogen (AN), nitrate nitrogen (NN), dissolved nitrogen (DN), and available phosphorus (AP) from the 12 soil columns over time. In the early stages of seepage, SC6 exhibited the highest AN leaching concentration ($2.58 \text{ mg} \cdot \text{L}^{-1}$), while SC1 had the lowest ($0.52 \text{ mg} \cdot \text{L}^{-1}$). The changes in DN leaching concentration were consistent with those of NN, both reaching their maximum in the early seepage stage and stabilizing after 320 minutes of rainfall duration. In the initial seepage phase, there was a significant positive correlation between NN leaching concentration and rainfall intensity, specifically expressed as $\text{C30mm} \cdot \text{h}^{-1} > \text{C20mm} \cdot \text{h}^{-1} > \text{C10mm} \cdot \text{h}^{-1}$. The variation in AP leaching concentration was relatively small, with most concentrations remaining below $0.1 \text{ mg} \cdot \text{L}^{-1}$. In the early seepage stage, SC10 had the highest AP leaching concentration ($0.46 \text{ mg} \cdot \text{L}^{-1}$), while SC1 had the lowest ($0.05 \text{ mg} \cdot \text{L}^{-1}$). Under the same fertilization treatment, there was a positive correlation between rainfall intensity and the cumulative leaching of AN, NN, DN, and AP, following the trend $\text{L30mm} \cdot \text{h}^{-1} > \text{L20mm} \cdot \text{h}^{-1} > \text{L10mm} \cdot \text{h}^{-1}$. SC10 had the largest cumulative leaching amounts of DN and AP, at 126.82 mg and 2.73 mg , respectively, while SC1 had the smallest cumulative amounts, at 36.68 mg and 0.86 mg , respectively.

Nitrogen leaching under different fertilization treatments

Table 5 shows that compared to the control treatment (CK), fertilization treatments (CF, CFB, CFZ) can increase the cumulative leaching amounts of dissolved nitrogen (DN) and available phosphorus (AP), with the most significant increase observed at a rainfall intensity of $20 \text{ mm} \cdot \text{h}^{-1}$. In SC6, the cumulative leaching amounts of DN and AP were higher than CK by 96.64% and 138.54%, respectively. Nitrate nitrogen (NN) is the main leaching form of DN, accounting for 96.16% to 97.72%, with the highest proportion (97.72%) in SC9. This is mainly because NN, being negatively charged, easily dissolves in water and leaches out, while ammonia nitrogen (AN), being positively charged, tends to combine with soil colloids, making it less mobile (Guan et al., 2020).

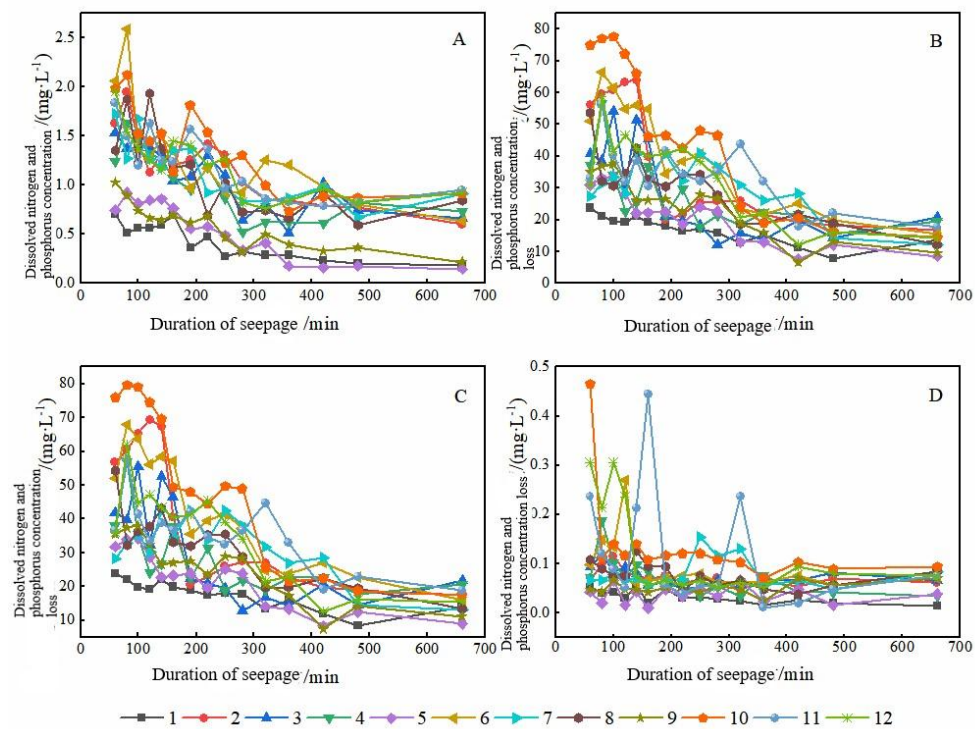


Figure 4. Dynamic change of leaching concentration of ammonia nitrogen, nitrate nitrogen, dissolved nitrogen and available phosphorus with seepage time

Table 5. Leaching amount and leaching coefficient of nitrogen and phosphorus and the proportion of different forms of nitrogen

Soil column	Leaching loss /mg				Proportion /%		Leaching coefficient /%	
	AN	NN	DN	AP	P _{AN}	P _{NN}	LC _N	LC _P
1	0.84	35.84	36.68	0.86	2.29	97.71	—*	—*
2	2.42	69.34	71.76	1.91	3.37	96.63	1.9065	0.0148
3	2.06	51.58	53.64	1.62	3.84	96.16	0.9217	0.0107
4	2.02	54.48	56.49	1.69	3.57	96.43	1.0766	0.0117
5	1.28	51.49	52.78	0.96	2.43	97.57	—*	—*
6	3.11	100.67	103.79	2.29	3.00	97.00	2.7723	0.0188
7	2.58	75.59	78.17	1.74	3.30	96.70	1.3799	0.0110
8	2.48	68.38	70.86	2.01	3.50	96.50	0.9826	0.0149
9	1.53	65.62	67.15	1.20	2.28	97.72	—*	—*
10	3.60	123.22	126.82	2.73	2.84	97.16	3.2429	0.0216
11	2.87	83.42	86.29	2.16	3.32	96.68	1.0402	0.0136
12	2.91	84.82	87.73	2.17	3.31	96.69	1.1185	0.0138

*, CK is the control group, without fertilization. From equation 2, $i=0$, there is no leaching coefficient

Under the same rainfall conditions, the leaching concentrations of nitrogen (LCN) and phosphorus (LCP) from CF were both higher than from CFB and CFZ. At rainfall intensities of $10 \text{ mm} \cdot \text{h}^{-1}$ and $30 \text{ mm} \cdot \text{h}^{-1}$, LCN showed the order $\text{CF} > \text{CFZ} > \text{CFB}$; at a rainfall intensity of $20 \text{ mm} \cdot \text{h}^{-1}$, LCN was $\text{CF} > \text{CFB} > \text{CFZ}$. Similarly, LCP at all rainfall intensities followed the trend $\text{CF} > \text{CFB} > \text{CFZ}$. *Figure 5* indicates that at

different rainfall intensities, the net leaching amount of DN from CF was always the largest, with values of 35.08 mg ($10 \text{ mm} \cdot \text{h}^{-1}$), 51.01 mg ($20 \text{ mm} \cdot \text{h}^{-1}$), and 59.69 mg ($30 \text{ mm} \cdot \text{h}^{-1}$). The addition of biochar or zeolite during fertilization can reduce DN leaching, with the most significant reduction observed at a rainfall intensity of $30 \text{ mm} \cdot \text{h}^{-1}$. Compared to CF, the DN leaching amounts from CFB and CFZ were reduced by 67.92% and 65.51%, respectively. Similarly, the addition of biochar or zeolite during fertilization also resulted in reductions of 27.62% to 41.35% and 20.95% to 36.60% in AP leaching.

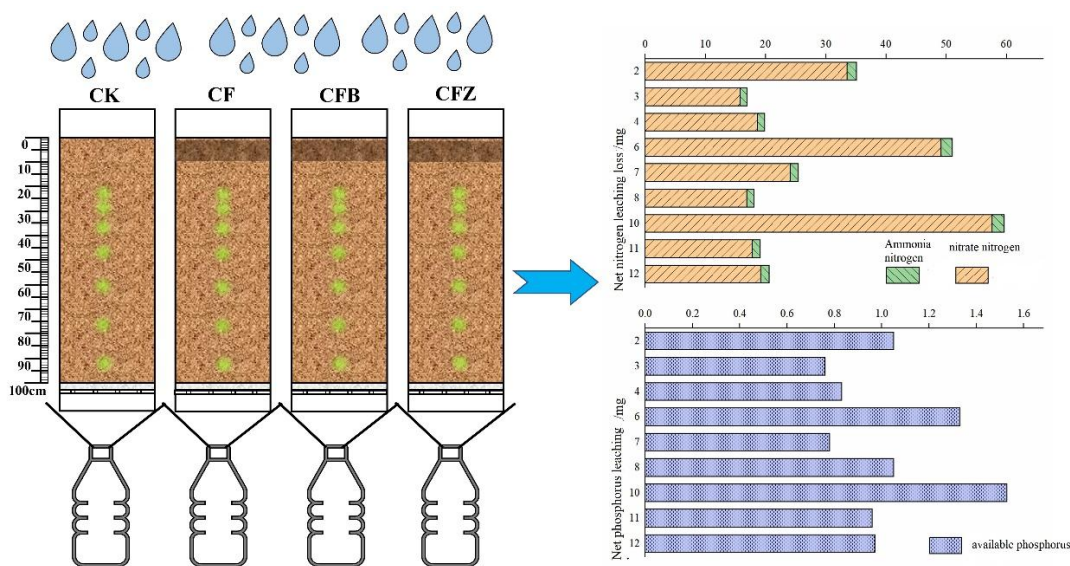


Figure 5. Net leaching loss of ammonia nitrogen, nitrate nitrogen and available phosphorus under each fertilization treatment

Seepage and nitrogen leaching

The leaching intensity of nitrogen and phosphorus is expressed as $\text{DN} > \text{NN} > \text{AN} > \text{AP}$, indicating that nitrogen leaches more easily than phosphorus. Table 6 presents the Pearson correlation test results of nitrogen and phosphorus leaching in the seepage with external factors (rainfall intensity, seepage volume, fertilization, biochar, and zeolite). From the table, it can be observed that there are significant positive correlations ($p < 0.05$) between rainfall intensity and seepage volume and the leaching amounts of AN, NN, DN, and AP. Fertilization shows a significant positive correlation with AN and AP ($p < 0.05$). However, there is a negative correlation between biochar and zeolite and the leaching amounts of AN, NN, DN, and AP, although this correlation is not significant. The correlation coefficients of DN and NN with external factors are basically the same because NN is the main form of DN. The external factors affecting the leaching amounts of nitrogen and phosphorus are ranked from largest to smallest as follows: seepage volume $>$ rainfall intensity $>$ fertilization $>$ addition of soil conditioners (biochar, zeolite). This indicates that seepage volume is the primary factor influencing nitrogen and phosphorus leaching, while rainfall intensity and fertilization are also significant factors. Adding biochar or zeolite during fertilization can reduce nitrogen and phosphorus leaching.

Table 6. Correlation test between leaching loss of an, NN, DN and AP and external factors

Influence factor	Seepage and leaching			
	AN	NN	DN	AP
rainfall intensity	0.803**	0.745*	0.741*	0.763*
seepage flow	0.973***	0.973***	0.972***	0.924***
spread manure	0.917*	0.795	0.794	0.930**
biochar	-0.547	-0.601	-0.602	-0.630
zeolite	-0.559	-0.623	-0.623	-0.534

Table 7 shows that the Under simulated rainfall conditions, the cumulative leaching amounts of AN, NN, DN, and AP exhibit a significant linear positive correlation with seepage volume ($y = ax + b$, $r^2 > 0.91$, $p < 0.0001$). Based on the goodness of fit indicated by r^2 , the average values of r^2 for AN, NN, DN, and AP are 0.9811, 0.9794, 0.9805, and 0.9610, respectively, demonstrating the order of $AN > DN > NN > AP$. Regarding the average values of the regression coefficient a in the equations, the average a values for AN, NN, DN, and AP are 0.91, 28.55, 29.77, and 0.07, respectively, indicating the order of $DN > NN > AN > AP$. This suggests that, compared to phosphorus, the leaching of nitrogen in seepage is more significantly influenced by the magnitude of the seepage volume.

Table 7. Fitting equation between leaching loss of an, NN, DN and AP (y , mg) and seepage flow (x , L)

Soil column	AN fitting equation			NN fitting equation			DN fitting equation			AP fitting equation		
	a	b	r^2	a	b	r^2	a	b	r^2	a	b	r^2
1	0.3539	0.0967	0.9636	15.30	2.31	0.9869	16.14	2.21	0.9880	0.0362	0.0152	0.9204
2	1.0500	0.1801	0.9857	27.40	10.09	0.9613	28.62	10.56	0.9596	0.0774	0.0294	0.9395
3	0.9511	0.1540	0.9867	21.46	6.99	0.9569	22.48	7.12	0.9580	0.0729	0.0208	0.9740
4	0.8559	0.1888	0.9796	22.97	4.91	0.9886	24.06	4.92	0.9894	0.0677	0.0320	0.9102
5	0.4810	0.1933	0.9431	19.45	5.64	0.9773	20.43	5.59	0.9789	0.0385	-0.0018	0.9941
6	1.1270	0.3111	0.9930	37.94	10.47	0.9749	39.41	10.56	0.9764	0.0815	0.0280	0.9644
7	1.0280	0.1975	0.9904	33.22	0.01	0.9954	34.60	0.20	0.9950	0.0893	-0.0100	0.9893
8	0.9646	0.2585	0.9759	27.99	5.11	0.9843	29.20	5.48	0.9839	0.0690	0.0119	0.9844
9	0.5345	0.1683	0.9831	23.65	6.09	0.9817	24.68	5.79	0.9844	0.0400	-0.0083	0.9550
10	1.3090	0.2620	0.9904	43.97	16.23	0.9684	46.16	16.18	0.9760	0.0902	0.0105	0.9849
11	1.1360	0.1877	0.9901	34.42	2.38	0.9963	35.62	2.79	0.9963	0.0849	0.0115	0.9655
12	1.1330	0.1858	0.9919	34.83	5.14	0.9802	35.92	5.82	0.9803	0.0656	0.0347	0.9506

*The fitting equation is in the form of $y=ax+b$, r^2 .

Discussion

The effects of adding biochar or zeolite during fertilization on soil moisture and nutrients

Biochar can be defined as the solid byproduct obtained from the pyrolysis of biomass at temperatures between 300°C and 900°C. It is characterized by stable aromatic organic compounds, high specific surface area, variable charge, and functional groups (Guan et al., 2020). Research has demonstrated that biochar has great potential to enhance soil fertility and crop productivity by reducing soil acidity, increasing cation exchange capacity (CEC), enhancing soil organic matter and nutrient retention, and improving the availability of

nutrients to plants (Kookana et al., 2010; Joseph et al., 2010; Haque et al., 2019; Samuel et al., 2021; Kaur et al., 2021). During the period of 1789–1790, Lovitz was the first to report the use of charcoal to remove odors from water. Later, in 1900–1901, Swedish chemist von Ostroich developed the first commercial activated carbon. In recent years, biochar has been used as a soil conditioner in agricultural production, where it can reduce bulk density and improve soil texture, pore size distribution, and soil water permeability (Lin et al., 2016). Indian scholars Varinder Kaur and Praveen Sharma studied the effects of biochar on various physical and chemical parameters of sandy soil. The results showed that the application of biochar can reduce soil bulk density while increasing porosity, water retention capacity, and organic carbon content.

Zeolite is a widely distributed silicate mineral (Li et al., 1989), first discovered in the 1750s. Its crystal structure consists of a three-dimensional framework formed by silica tetrahedra and alumina tetrahedra, containing pores and channels of various sizes. Zeolite has three main properties: high water retention capacity, high cation exchange capacity, and high adsorption capacity, which are highly significant for agricultural applications (Cataldo et al., 2021). In the 1950s, Japanese researchers began to apply zeolites in agricultural production to enhance the nutrient retention capacity of soil, allowing crops to absorb nutrients better and increasing fertilizer efficiency. Iranian scholars (Kavoosi et al., 2007) believe that the combined application of zeolite and fertilizers has a significant positive effect. In experiments conducted in northern Greece to improve vegetable soils with added zeolite, Tzanakakis et al. (2021) found that zeolite could regulate the availability of NH_4^+ , promote nitrification, increase crop nitrogen absorption, and reduce nitrogen loss.

In the present experiment, compared with the control group (CF), the soil in the biochar treatment group (CFB) showed increases of 12.11%, 5.08%, 2.35%, 6.32%, and 8.71% in average alkali-hydrolyzed nitrogen, available phosphorus, available potassium, organic matter content, and surface moisture, respectively. The soil in the zeolite treatment group (CFZ) showed increases of 8.41%, 13.13%, 2.60%, and 8.42% in average alkali-hydrolyzed nitrogen, available phosphorus, available potassium content, and surface moisture, respectively.

The effects of rainfall intensity, fertilization, biochar, and zeolite on nitrogen and phosphorus leaching in farmland

Fertilizers are essentially inorganic salts (Chen et al., 2017), and only those that are absorbed can be called fertilizers; those that cannot be absorbed still belong to the category of salt substances. Excessive application of chemical fertilizers and low fertilizer utilization rates are the main factors causing nitrogen and phosphorus loss (Yang et al., 2019). According to the 2018 "China Statistical Yearbook," the total consumption of chemical fertilizers in China in 2017 was 58.594 million tons, ranking first in the world, and an increase of 47% compared to 1997. In this experiment, fertilization treatments significantly increased nitrogen and phosphorus leaching. *Table 5* shows that, compared with the control (CK), the chemical fertilizer (CF) treatment increased nitrogen (DN) leaching by 188.86% to 196.65% and phosphorus (AP) leaching by 222.09% to 238.54%. Similarly, *Table 6* indicates a significant positive correlation ($p < 0.05$) between the fertilization factor and nitrogen (AN) and phosphorus (AP) leaching (Liu et al., 2024). Liu et al. (2024) found a positive correlation between the amount of fertilizer applied and nitrogen leaching in their study of nitrogen leaching in rice paddies in red soil, suggesting

that reducing chemical fertilizer applications in agricultural production can effectively reduce nitrogen and phosphorus leaching.

Several factors influence nitrogen and phosphorus leaching, including rainfall, crop types, soil types, fertilizers, and soil conditioners. Among these, rainfall acts as the driving force behind nitrogen and phosphorus leaching; nutrients are lost through water transport, making rainfall a critical factor. Previous studies have found a positive correlation between nitrogen and phosphorus leaching and factors such as rainfall amount, rainfall intensity, and rainfall duration (Zhao et al., 2013; Shen et al., 2016). In this experiment, under the same fertilization treatment, *Table 6* shows a significant positive correlation between rainfall intensity and cumulative nitrogen and phosphorus leaching, specifically $L30\text{mm}\cdot\text{h}^{-1} > L20\text{mm}\cdot\text{h}^{-1} > L10\text{mm}\cdot\text{h}^{-1}$. *Table 4* indicates that the initial infiltration rate and total infiltration volume after 11 hours followed the order $V30\text{mm}\cdot\text{h}^{-1} > V20\text{mm}\cdot\text{h}^{-1} > V10\text{mm}\cdot\text{h}^{-1}$. This finding aligns yet contradicts the research by Jiao et al. (2021). on nitrogen and phosphorus leaching patterns under different rainfall conditions in the black soil region of Jilin Province, where it was found that every $10\text{ mm}\cdot\text{h}^{-1}$ increase in rainfall intensity resulted in a 1.81mm increase in leachate, and total nitrogen leaching showed a highly significant correlation with rainfall intensity, while total phosphorus leaching showed no obvious correlation. This discrepancy may stem from the differing soil types studied; in this experiment, the tested soil was sandy loam, which, compared to black soil, is more prone to nitrogen and phosphorus leaching.

To control non-point source pollution and reduce nitrogen and phosphorus leaching, many researchers have added soil conditioners to conduct soil improvement experiments. Haider et al. (2017) conducted a four-year field trial, finding that woodchip biochar significantly reduced nitrate leaching and decreased infiltration volume. Sun (2019) studied the effect of zeolite on nitrogen leaching under alternating dry and wet irrigation, concluding that adding zeolite during fertilization can significantly reduce the leaching of ammonium nitrogen and nitrate nitrogen. In this study, *Table 3* shows that biochar and zeolite reduced infiltration volume by 6.09% to 8.31% and 3.57% to 6.94%, respectively. In the early stages of infiltration, biochar and zeolite were particularly effective in reducing infiltration by 11.26% to 20.00% and 7.04% to 29.56%, respectively. This is primarily because, at the initial stage of infiltration, the soil is unsaturated, and both biochar and zeolite have strong adsorption capacities to retain moisture; as the duration of rainfall increases, the soil gradually saturates, causing the adsorption capabilities of biochar and zeolite to diminish. *Figure 5* shows that the application of biochar can reduce nitrogen leaching (DN) by 50.21% to 67.92% and phosphorus leaching (AP) by 27.62% to 41.35%; the application of zeolite can reduce nitrogen leaching (DN) by 43.50% to 65.51% and phosphorus leaching (AP) by 20.95% to 36.60%. Therefore, in agricultural production, the use of biochar and zeolite can effectively retain soil nutrients and moisture, thereby improving fertilizer utilization efficiency.

The relationship between seepage flow and leaching loss of nitrogen and phosphorus

Nitrogen and phosphorus leaching are significant pathways for nutrient loss in farmland, with nitrate leaching accounting for 50% of the applied fertilizer annually (Xu et al., 2008). Numerous studies have shown a significant relationship between percolation output and rainfall intensity (Lan, 2011; Liu et al., 2021). *Table 6* indicates a significant positive correlation ($p < 0.05$) between DN (Dissolved Nitrogen) and AP (Available Phosphorus) leaching and rainfall intensity, and a highly significant positive correlation ($p < 0.001$) between DN and AP leaching and percolation volume. External factors (such as

rainfall intensity, percolation volume, fertilization, and soil amendments) have varying impacts on nitrogen and phosphorus leaching; in this study, percolation volume is the primary factor affecting nitrogen and phosphorus leaching. Rainfall intensity and fertilization are also important factors. Biochar and zeolite have a strong effect on controlling nitrogen and phosphorus leaching. In practice, controlling percolation volume is key to reducing nitrogen and phosphorus leaching in farmlands. Reducing fertilizer application can decrease the input of nitrogen and phosphorus, thereby reducing nutrient loss. Since it is impractical to alter rainfall intensity artificially, adding biochar and zeolite can effectively control percolation volume; therefore, their use is recommended in agricultural production. Other agricultural practices, such as straw return, increasing ground cover (Cameron et al., 1998), and implementing low-intensity, long-duration irrigation systems, can also mitigate the impact of rainfall (or irrigation) intensity on percolation, thus reducing nitrogen and phosphorus leaching.

Conclusion

The paper analyzes the impact of different rainfall intensities and fertilization on nitrogen and phosphorus leaching in farmland, as well as the vertical distribution of soil moisture and nutrients, through artificially simulated rainfall experiments. The following conclusions are drawn:

(1) Fertilization significantly increases the nutrient content (alkaline nitrogen, available phosphorus, and available potassium) in the soil, without significantly affecting soil organic matter content and moisture content. Compared to the control group (CF), the average soil levels of alkaline nitrogen, available phosphorus, available potassium, organic matter content, and surface moisture content in the biochar addition group (CFB) increased by 12.11%, 5.08%, 2.35%, 6.32%, and 8.71%, respectively. In the zeolite addition group (CFZ), the average soil levels of alkaline nitrogen, available phosphorus, available potassium, and surface moisture content increased by 8.41%, 13.13%, 2.60%, and 8.42%, respectively.

(2) Under the same fertilization treatment, there is a positive correlation between rainfall intensity and the cumulative leaching amounts of AN, NN, DN, and AP, specifically, $L30\text{mm}\cdot\text{h}^{-1} > L20\text{mm}\cdot\text{h}^{-1} > L10\text{mm}\cdot\text{h}^{-1}$. The initial seepage rates and the total seepage amount over 11 hours were also observed as $V30\text{mm}\cdot\text{h}^{-1} > V20\text{mm}\cdot\text{h}^{-1} > V10\text{mm}\cdot\text{h}^{-1}$. Under identical rainfall conditions, compared to the CK, the CF treatment increased DN leaching by 188.86% to 196.65% and AP leaching by 222.09% to 238.54%. Compared to CF, the application of biochar reduced DN leaching by 6.09% to 8.31% and AP leaching by 27.62% to 41.35%, while the application of zeolite reduced seepage rates by 3.57% to 6.94%, DN leaching by 43.50% to 65.51%, and AP leaching by 20.95% to 36.60%.

(3) The seepage rate is the primary factor affecting nitrogen and phosphorus leaching, while rainfall intensity and fertilization are crucial factors influencing nitrogen and phosphorus leaching. The application of biochar and zeolite significantly affect the control of nitrogen and phosphorus leaching. In practice, to reduce nitrogen and phosphorus leaching in farmland, controlling the seepage rate is critical. Reducing the generation of seepage, improving soil moisture and nutrient retention, and decreasing chemical fertilizer application are effective strategies for controlling non-point source pollution.

Acknowledgments. This research was funded by the National Natural Science Foundation (52209049), the Hebei Provincial Natural Science Foundation Project (E2024402128), Hebei Key Laboratory of Intelligent Water Conservancy, Hebei Collaborative Innovation Center for the Regulation and Comprehensive Management of Water Resources and Water Environment, Hebei Engineering Technology Research Center for Effective Utilization of Water Resource. The author sincerely thanks Researcher Liu Liang from Hebei University of Engineering for supporting this research.

Competing interests. All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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