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Simultaneous removal of phosphate and ammonium nitrogen from agricultural runoff by amending soil in lakeside zone of Karst area, Southern China

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ABSTRACT

The loss of phosphorus(P) and nitrogen from agricultural non-point source(ANPS) is one of the main causes of eutrophication in rivers, lakes and reservoirs in the Karst region, southern China. The lakeside buffer zone has proven to be effective in reducing the input of ANPS pollutants. However, the interception efficiency of natural soil for P and ammonia nitrogen is insufficient to control ANPS pollution. In this study, natural zeolite(NZ), aluminium modified clay(AMC) and lanthanum modified bentonite(LaMB) were used to amend the natural soil collected in the lakeside zone of Kelan Reservoir, Guangxi, China. An experimental study was conducted to examine the dissolved inorganic P(DIP) and ammonia nitrogen removal efficiency and fixation mechanism of three amended soils under simulation conditions. The results showed that natural soil had a high fraction of clay and silt (particle size < 20μm; 75.2 %), and had a high removal rate of > 95 % for the DIP at the beginning of the experiment. With the intermittent input of farmland drainage, the P removal rate of natural soil from runoff decreased gradually. Compared with the control group, P removal rates of AMC- and LaMB amended soils remained at a high level within 46 days, with means of 93.6 % and 93.9 %. However, NZ amended soil has a weak interception capacity of runoff P pollutant. The chemical sequential extraction showed that AMC increased soil P capacity by forming NaOH-P and $NaHCO_3$-P, while LaMB by forming NaOH-P, $NaHCO_3$-P and Residual-P. In addition, LaMB amended soil can simultaneously remove ammonia from farmland runoff, with the removal rate of 89.3 %. AMC- and LaMB amended soils are proved to be potential and effective technologies for ANPS pollution control. This study provide an important basis for the treatment of ANPS pollutants and the construction of lakeside buffer zone in eutrophic watershed.

1. Introduction

Water eutrophication is a serious worldwide environmental problem (Qin et al., 2019). Nitrogen(N) and phosphorus(P) are the main elements contributing to eutrophication and limiting the primary productivity of water bodies (Conley et al., 2009). Therefore, the key to controlling eutrophication is controlling P and N pollution in the watershed. For surface water, sources of N and P nutrient pollution can be divided into point sources (such as industrial wastewater and domestic sewage) and non-point sources (mainly agricultural non-point sources, ANPSs). Globally, 30–50% of the earth's surface is affected by agricultural non-point source pollution (Bernhardt et al., 2005; Wang et al., 2019). Since the mid-2000s, agriculture has surpassed industry as the largest polluter of the water system in China (Ministry of environmental protection(MEP, 2010).

China's annual fertilizer production accounts for approximately one third of the world's total production, and its consumption accounts for approximately 35 % of the world's total consumption (Ju et al., 2019). China has become the largest fertilizer producer and consumer in the world. The results of simulations and field observations under different soil conditions, tillage systems, and management levels have demonstrated a significant positive correlation between soil fertilization and N and P pollutant concentrations in farmland runoff (Pote et al., 1999; Eghball, 2000). Point source pollution is becoming effectively controlled from sources such as industrial and biological sewage. As such, ANPS N and P pollution have become a focus for eutrophication control

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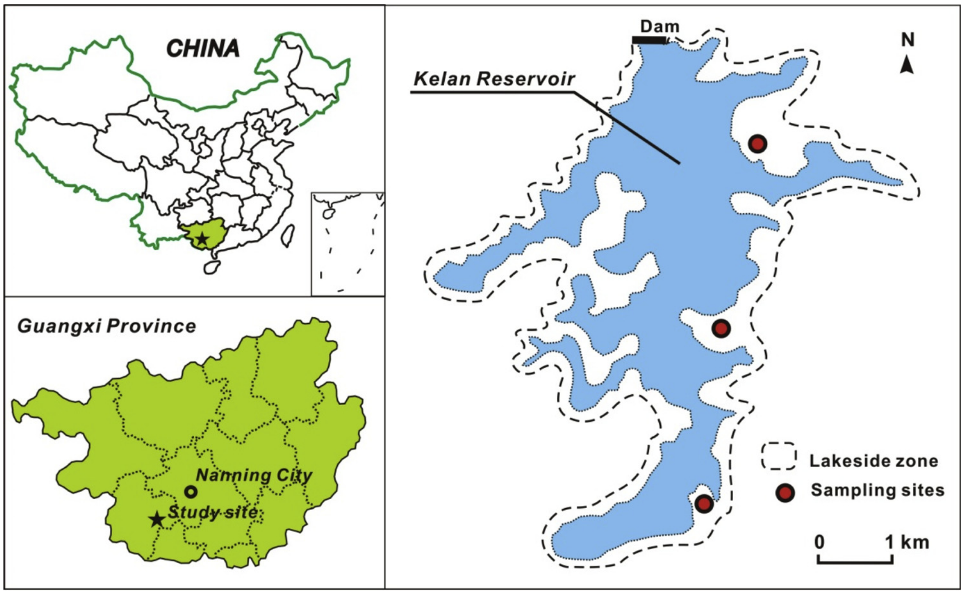

Fig. 1. Soil sampling sites in the lakeside zone of the Kelan Reservoir in Guangxi, China.

in China's lakes and reservoirs.

The dynamics of agricultural ecosystem significantly affect the quality of surface water. El-Khoury et al. (2015) studied the impact of land use on N and P in river water in a Canadian river basin, and found that the change of nutrient concentration in rivers was due to alteration in land-use. The application of livestock manure on farmland can increase the yield of crops, however, crops on farmland cannot absorb all the fertilizer because they cannot absorb N according to the nutrient demand of crops (Clark and Tilman, 2017). At the same time, excessive fertilizer in the farmland will lead to the accumulation of P and the loss of nitrate and nitrite in the soil (Long et al., 2018). Therefore, it is of great significance to study the variations of N and P on the scale of farmland and small watershed for the control of ANPS pollution.

Farmland runoff carries many nutrients, such as N and P, into rivers, lakes, reservoirs, and other water bodies. This is the main process underlying ANPS pollution. Due to significant differences in the chemical properties of P and N, there are significant differences in their speciation, migration and transformation processes, and their controlling factors in farmland runoff (Moustafa, 1999). Firstly, N is a variable value element, which exists in the form of nitrate, nitrite and ammonia nitrogen, while P mainly exists in the form of pentavalent phosphate or hydrogen phosphate. Secondly, the migration and transformation of N are more complex affected by the nitrification and denitrification of microorganisms, while P mainly exists in the runoff in the form of particles, which is easily intercepted by the lakeside soil and vegetation. Simultaneously and efficiently reducing the input of ANPS P and N pollution, and decreasing their contribution to nutrients in lakes and reservoirs, is a technical challenge in controlling ANPS pollution.

A lakeside buffer zone is defined as the boundary area between water and land (width between 1 m and 100 m). The zone is the channel by which ANPS pollutants enter the water body (Lee et al., 2004). The zone is also the last barrier in which lakes and reservoirs can intercept ANPS pollutants. Soil and vegetation in the lakeside buffer zone can adsorb, precipitate, and absorb nutrients carried by the surface runoff from farmland. The soil and vegetation act as a buffer for purification and filtration before the pollutants enter the water body, and become a biological and physical barrier blocking pollutant entry into the water body (Hefting et al., 2005). Lowrance et al. (1988) studied the removal of N and P from farmland runoff by a lakeside buffer zone. They found that only one seventh of the total N and P remained in farmland surface runoff after passing through the lakeside buffer zone. The results of Delgado and Periago (1995) and Heathwaite (1998) showed that the lakeside buffer zone had a good controlling effect on ANPS pollution. The average removal rates of total N and total P were 70–95% and 70–98%, respectively. Therefore, constructing an artificial lakeside zone has become a potential and effective way to simultaneously remove N and P pollution from ANPS and control eutrophication (Borin et al., 2005; Young and Briggs, 2005).

Removing N and P from farmland runoff using a lakeside buffer zone has been shown to be feasible. The removal efficiency is controlled by complex factors, including the physical and chemical properties of soil, the width and slope of lakeside zone, and the decontamination ability of vegetation (Hefting et al., 2005). Of these factors, lakeside zone soil is a basic and key factor, and determines the removal efficiency of pollutants and vegetation growth conditions. However, the removal efficiency of N and P pollutants by natural soils is usually inadequate. Therefore, it is a potentially effective measure to improve the interception efficiency of N and P pollutants in the lakeside zone by artificially improving the soil.

Previous studies have confirmed that adding natural minerals, such as iron salt, aluminium salt, calcium salt, or zeolite, to lake sediments can significantly increase the ability of sediments to retain N and P pollutants (Lin et al., 2016; Yin et al., 2018; Wang et al., 2018). However, few studies have applied these modified materials to soil amendment in lakeside zone. In this study, reservoir lakeside zone soils in the Karst areas of southern China were collected and amended with natural zeolite (NZ), aluminium modified clay (AMC), and lanthanum modified bentonite (LaMB). These three materials were previously developed by our research team, and successfully applied to the in-situ control of P pollution in sediments of eutrophic lakes and reservoirs. An experimental study was conducted to simulate the process of removing pollutants from farmland runoff using theimproved soil. There were two goals forthis study. The first goal was to quantify the removal effects of DIP and ammonia from farmland runoff using NZ-, AMC-and LaMB-amended soils. The second goal was to describe the pollutant removal mechanism achieved through amended soil, and to providing technical guidance to support lakeside zone construction and eutrophication control in China's Karst area.

2. Materials and methods

2.1. Overview of Kelan Reservoir

The Kelan Reservoir, built in 1957, is located in the Karst area of

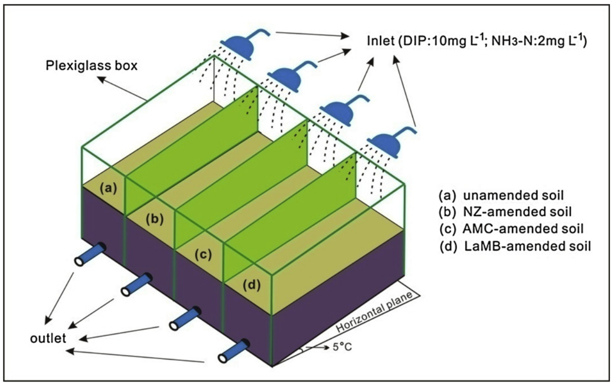

Fig. 2. Schematic diagram of the simulation experimental device.

southern China. It is one of the largest existing reservoirs in Guangxi Province and is an important urban water source (Fig. 1). The reservoir's drainage basin is 351 km^2 and the effective storage capacity is 46 million m^3. The main function of the reservoir is farmland irrigation, with a designed irrigation area of 34.9 km^2. The reservoir basin belongs to the subtropical monsoon climate zone, with an average annual temperature of 20.8–22.4 °C and an annual rainfall of approximately 1,400 mm. The humid and hot climate provides good natural conditions for agricultural development in the basin. The soil in the basin is lateritic red soil. Sugarcane is the main crop, accounting for 80 % of the planting area in the basin. Sugarcane growth requires significant amounts of chemical fertilizer; as a result, ANPS pollution is the main source of N and P pollution in the Kelan Reservoir.

2.2. Simulation experiment and sampling

Soil samples were collected at three sites along the lakeside zone of the Kelan Reservoir (Fig. 1). The three soils were air-dried, crushed, sieved through 10 meshes, and mixed evenly. A simulation device was constructed to test the removal efficiency of N and P pollutants from the agricultural return flow using natural soil and amended soil (Fig. 2). The mixed soil samples were divided into four parts, which wereplaced into four pieces of plexiglass boxes (numbered *a*, *b*, *c*, and *d*) with the same specifications. Each box was 75 cm long, 20 cm wide, and 30 cm high. The soil layer in the plexiglass box was approximately 20 cm thick. The soil in box *a* was not amended, and the soils in boxes *b*, *c*, and *d* were completely mixed with NZ(from Xinyang, Henan, China), AMC(developed by our group with China Patent No. ZL201510823659.1) and LaMB(commercially known as Phoslock® with US Patent No. 6350383), respectively, at a 3 % mass ratio. To better simulate the actual situation of the lakeside zone in the Kelan Reservoir, the horizontal slope of the simulator box was set to 5 degrees.

Before the experiment, a small amount of deionized water was added to the mixed soil to simulate the field water holding capacity. Simulated runoff was manually allocated, and the concentrations of DIP and ammonia were set to 10 mg/L and 2 mg/L, respectively. The simulated runoff velocity was set to 30 L/h. On Days 5, 10, 20, 30, 33, 39, 42, 44, and 46, runoff effluent was collected through the outlet pipe. Water samples were stored at 4 °C before chemical analysis.

2.3. Chemical analysis

A laser particle size analyzer(Mastersizer 2000, Malvine Corporation, UK) was used to determine soil granularity. Soil pH was determined using apotentiometry and pH meter(pH SJ-3C, Leici, China). Soil for chemical analysis was freeze-dried and ground to less than 200-mesh. Soil organic matter (OM) was determined using the potassium dichromate volume etric method. Total N (TN) and orgniac carbon contents in soil were determined using a elemental analyzer (Elementar-Vario MACRO cube, Elementar, Germany). The C/N ratio was obtained by dividing the organic carbon content by the Total N content, then this ratio is converted to a molar ratio. All chemical data were measured by dry weight.

Soil P fractionation was extracted using the chemical continuous extraction method(Hendly et al., 1982), which divided the fractions into H_2O-P, $NaHCO_3$-P, NaOH-P, HCl-P, and Residual-P. In short, 3.3 g soil samples were placed in 250 mL centrifugal bottles, and 200 mL extractants (H_2O, 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1 M HCl) were subsequently added. The materials were then centrifuged. After 16 h of oscillation, the supernatant was filtered through a0.45 μm glass fiber membrane. Soil residues used to support the Residual-P content analysis were heated to ash (500°C) and extracted for 16 h using oscillation with a 1 M HCl solution. The supernatant was filtered through a0.45 μm glass fiber membrane. The P concentration in all extracts was measured using the molybdenum-blue method (Murphy and Riley, 1962). Soil available P content was determined using sodium bicarbonate extraction-molybdenum antimony anti-spectrophotometry.

The DIP concentration in the effluent of the simulator was determined using the molybdenum-blue method (Murphy and Riley, 1962). Ammonia N in the effluent was determined using Nessler's reagent spectrophotometry. In addition, the principal components of NZ, AMC, and LaMB were analyzed using X-ray fluorescence spectrometer (Axios-PW4400, Panaco Corporation, Netherlands).

2.4. Calculation of pollutant removal rate

To quantify the N and P pollutant removal rates from natural and amended soils, the variations of DIP and ammonia concentrations in the effluent from the simulator overtime were analyzed. The pollutant removal rate (RE) from these soils was calculated using the following formula:

$$RE = \left(1 - \frac{C_{inlet} \times V_{inlet} - C_{outlet} \times V_{outlet}}{C_{inlet} \times V_{inlet}}\right) \times 100\%$$

In this expression, RE denotes the removal rate of DIP or ammonia pollutants in %; C_{inlet} denotes the concentration of DIP or ammonia in the influent in mg L^{-1}; C_{outlet} denotes the concentration of DIP or ammonia in the outlet water in mg L^{-1}; V_{inlet} and V_{outlet} denote the volume of inlet and outlet water in L.

Table 1

Basic physical and chemical properties of the soil in the lakeside zone of Kelan Reservoir in Guangxi, China.

Parallel samples	pH –	Moisture %	Bulk density g cm^{-3}	Organic matter %	Total N %	C/N ratios –	Available P mg kg^{-1}
Sample-1	4.01	31.2	1.33	2.52	0.135	7.9	11.9
Sample-2	3.75	40.0	1.27	1.74	0.122	8.6	13.1
Sample-3	3.89	27.8	1.54	2.08	0.129	8.1	14.5
Avgrage	3.88 ± 0.13	33.0 ± 6.3	1.38 ± 0.14	2.11 ± 0.39	0.129 ± 0.007	8.2 ± 0.4	13.2 ± 1.3

Table 2
Grain size distribution of soil in the lakeshore zone used in simulation experiments.

Samples	Average grain diameter				Percentage of each grain size				
	D [3, 2] μm	d (0.1) μm	d (0.5) μm	d (0.9) μm	Clay < 2μm	Silt 2-20 μm	fine sand 20-200μm	coarse sand 200-2000μm	Gravel > 2000μm
Soil-a	3.28	1.3	6.5	56.3	18.7	55.9	23.2	2.2	0
Soil-b	3.54	1.4	7.5	58.6	16.5	55.5	25.9	2.1	0
Soil-c	3.23	1.3	6.3	44.7	18.5	58.9	20.8	1.8	0
Soil-d	3.33	1.3	6.5	49.1	17.7	58.8	21.5	2.0	0
Avgrage	3.35	1.3	6.7	52.2	17.9	57.3	22.9	2.0	0

3. Results

3.1. Physical and chemical properties of soil in lakeside zone of Kelan Reservoir

Table 1 provides the physical and chemical parameters of the three natural soils collected from the lakeside zone of the Kelan Reservoir. The soil in the lakeside zone was acidic, with a mean pH of 3.88 ± 0.13. Soil water content ranged from 27.8 to 40.0%, with an average value of 33.0 ± 6.3 %. Soil organic matter and TN content were relatively low, with average values of 2.11 ± 0.39 % and 0.129 ± 0.007 %, respectively. The average C/N molar ratio of the soil was 8.2 ± 0.4. The soil available P content ranged from 11.9–14.5 mg L^{-1}, with the average value of 13.2 ± 1.3 mg kg^{-1}. The physical and chemical parameters of the soil at the three sites were approximated based on these parameters.

Table 2 shows the soil granularity composition. The size of natural soil in the lakeside zone was small, with a median size (D[3,2]) of only 3.35 μm. Silt and clay components of the soil accounted for 57.3 % and 17.9 %, respectively, making up total of 75.2 % in the soil. The soil also contained some coarse sand and fine sand, accounting for 2.0 % and 22.9 % of the total, respectively. The soil granularity compositions of the four soil segments *(a–d)* were similar.

Table 3 shows the main chemical constituents of the amendment used to treat the soil. The P contents of the three amendment materials (NZ, AMC, and LaMB) were lower than 0.05 %. NZ was mainly composed of SiO_2 and Al_2O_3, with these two compounds comprising 84.3 % of the total. AMC was mainly composed of SiO_2 and CaO; the two compounds made up 53.3 % of the total. AMC also contained 8.4 % Al_2O_3. The main components of LaMB were SiO_2, AlO_3, FeO_3, and MgO, making up 84.2 % of the total mass. The loss on ignition(LOI) of AMC was significantly higher than that of NZ and LaMB, which was 33.0 %.

3.2. Removal rate of DIP from agricultural return flow by amended soil

Fig. 3 shows the variation in the DIP concentration and removal rate of DIP in effluent overtime. In the control group, the concentration of DIP in effluent was very low on the first day (0.1 mg L^{-1}), and increased to 2.0 mg L^{-1} as time passed. This indicated that unamended soil initially had a strong ability to fix DIP, and the removal rate exceeded 95 %. However, its DIP interception efficiency decreased significantly overtime, and the removal rate dropped to 73.5 % on Day46 day.

The three amended soils had different DIP interception abilities. In the NZ-amended soil group, the DIP concentration in effluent gradually increased from 2.0–5.7 mg L^{-1}, which was significantly higher compared to the amendments. The DIP removal rate of NZ-amended soil decreased from 78.3–37.8%, with an average drop of 52.9 %. The DIP removal rates of AMC-amended soil and LaMB-amended soil were high, at 93.6 % and 93.9 % respectively. The effluent DIP concentration with the two amended soils remained low for 46 days, with an average value of approximately 0.6 mg L^{-1}.

3.3. Removal of ammonia from agricultural return flow by amended soil

Fig. 4 shows the variation in ammonia concentration and ammonia removal rate in effluent overtime. In the control group, the ammonia concentration in effluent was 1.4 mg L^{-1} on the first day, then decreased to 0.5 mg L^{-1}, and finally increased slowly to 0.7 mg L^{-1} on Day 46. The average removal rate of ammonia by the unamended soil was 69.6 %, which indicated the unamended soil had a strong ability to remove ammonia.

The three amended soils *(b–d)* showed different ammonia interception abilities. Compared with unamended soil, the NZ-amended soil had a significantly lower ammonia removal rate, at an average of 45.9 %. The ammonia concentration in the effluent consistently exceeded 1.0 mg L^{-1}, which was higher than that of control group *(a)*. Of the three amended soils, the ammonia removal rate was lowest with the AMC-amended soil, ranging from 5.7%–58.6%, with an average of 37.6 %. The ammonia removal rate of the LaMB-amended soil was the highest. In the first five days, its ammonia concentration in effluent was the highest, which was close to the other two amended soils. The ammonia removal rate of LaMB-amended soil maintained very high from Day 10–46, at an average of 89.3 %.

3.4. Variation of P contents in soils before and after the simulation experiment

Fig. 5 shows the different forms of P in natural soils and amended soils before and after the experiment. The total-P content ranged from 248.4–308.0 mg L^{-1}, with the average concentration of 271.1 mg L^{-1}. In these soils, the main forms of P were NaOH-P, Residual-P, and $NaHCO_3$-P, accounting for 45.3 ± 2.8 %, 43.2 ± 3.7 %, and 9.8 ± 1.4 % of

Table 3
Main chemical composition of soil amendments for this study.

	Chemical composition (%)										
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	LOI
NZ[a]	80.6	13.7	0.75	0.13	0.2	0.61	2.67	0.03	0.02	0.06	1.2
AMC[b]	26.4	8.4	0.89	1.64	26.9	1.82	0.77	0.01	0.04	0.10	33.0
LaMB[c]	63.0	14.9	3.18	3.16	3.1	0.91	1.29	0.01	0.05	0.30	10.1

[a] NZ-natural zeolite.
[b] AMC-aluminium modified clay.
[c] LaMB-Lanthanum modified bentonite.

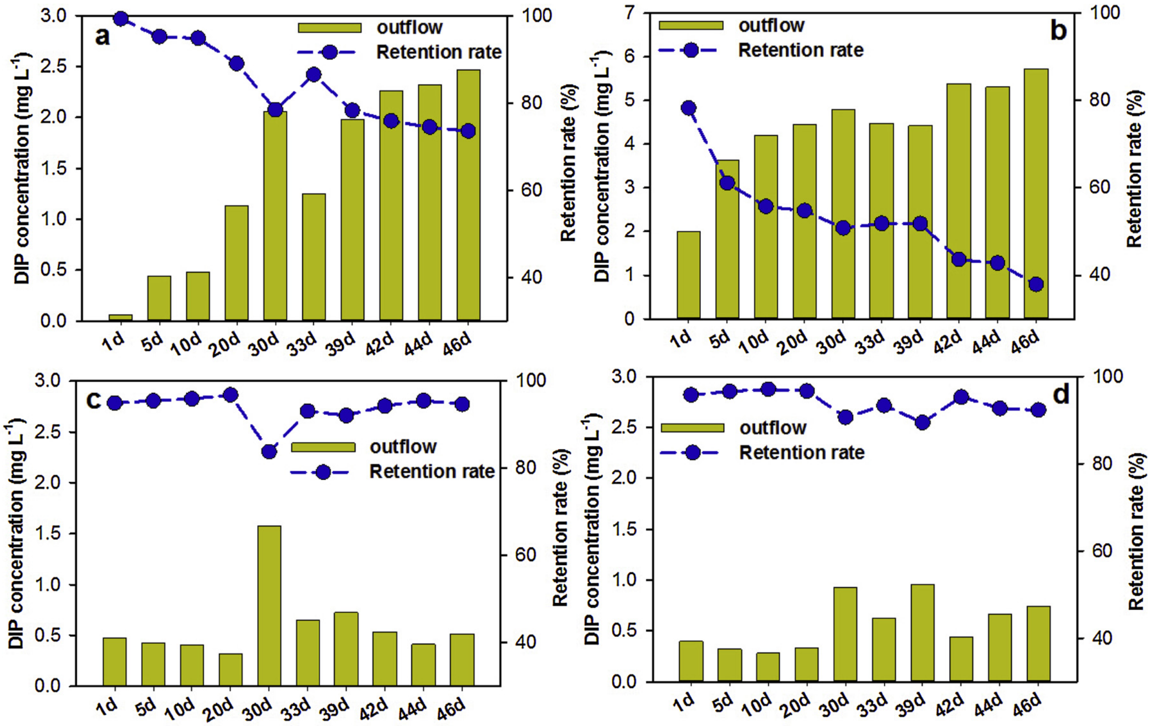

Fig. 3. Variation in DIP concentration in the effluent and the removal rate of DIP using unamended-(a), NZ-(b), AMC-(c), and LaMB-amended(d) soils over time.

total-P, respectively. The HCl-P and H_2O-P levels were very low, totaling only approximately 2 % of total-P.

At the end of the experiment, the total-P content in the unamended soil increased from 259.4–354.4 mg L^{-1}, an increase of 36.6 %. The total-P of NZ amended soil, AMC-amended soil, and LaMB-amended soil increased by 21.8 %, 34.8 % and 51.9 %, respectively. In the unamended soil, the increase of $NaHCO_3$-P, NaOH-P, and Residual-P accounted for 24.6 %, 38.7 % and 24.0 % of total-P increase, respectively. These three compounds were the three main P forms of transformation. In the NZ-amended soil, the increase of NaOH-P and $NaHCO_3$-P accounted for 76.6 % and 10.4 %, respectively, of the total-P increase. The changes of P forms of the AMC-amended soil was similar to the NZ-amended soil. The increase of NaOH-P and $NaHCO_3$-P accounted for 65.4 % and 19.9 % of the total-P increase, respectively. For LaMB-amended soil, the residual-P increased by 30.1 mg L^{-1} and accounted for 21.4 % of the total-P increase. This differed from the residual-P contents

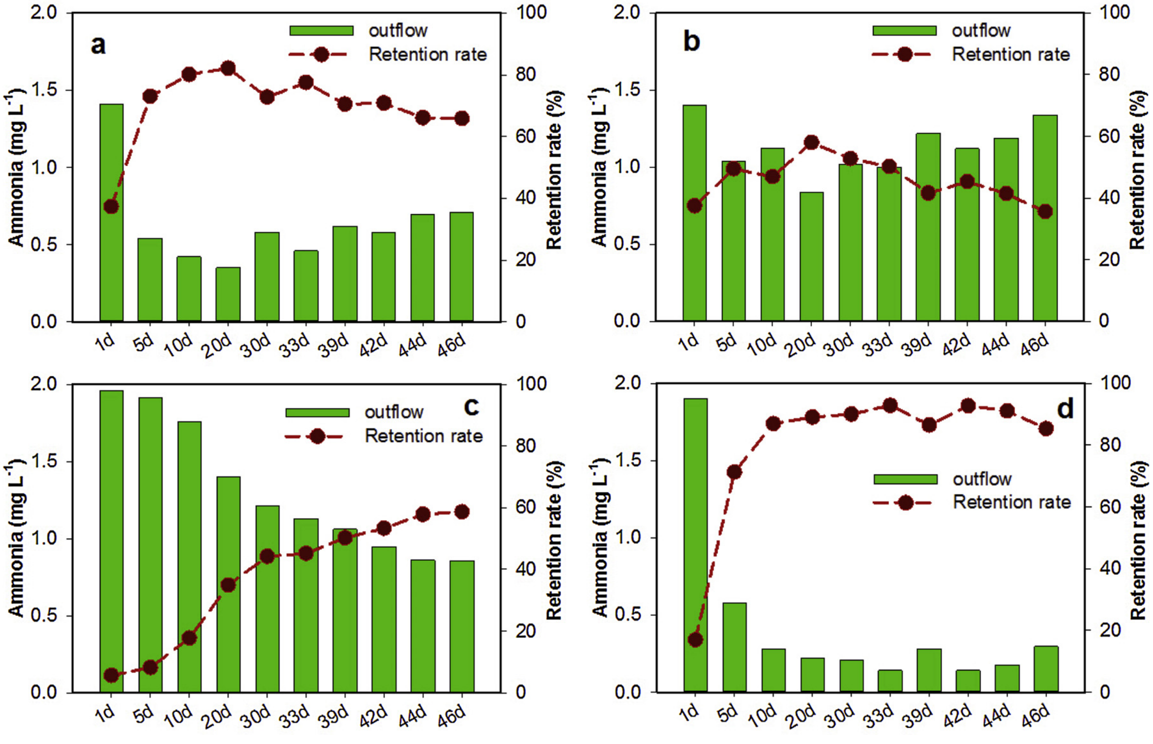

Fig. 4. Time variation of ammonia nitrogen concentrations in the outflow and retention rates for unamended-(a), NZ-(b), AMC-(c), and LaMB-amended(d) soils.

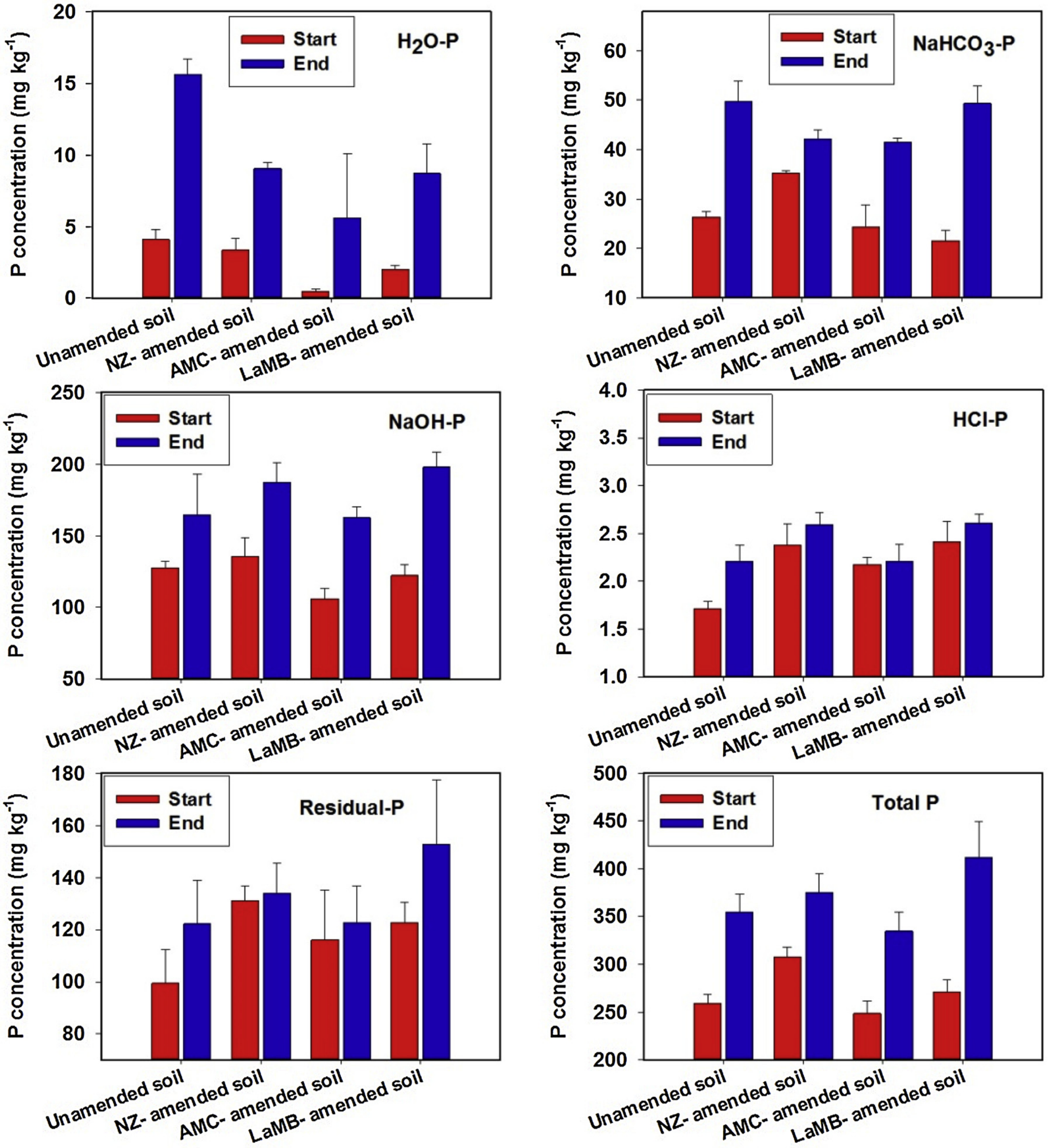

Fig. 5. Levels of different forms of P in unamended, NZ-, AMC-, and LaMB-amended soils before and after the experiment.

of the AMC-amended soil and NZ-amended soil, which remained constant.

4. Discussion

4.1. The mechanism of removing P and N pollutants from agricultural return flow by amended soil

Many scholars have focused on the transformation and migration mechanism of P and N in soil(Heathwaite et al., 1998; Pote et al., 1999). The process of removing P and N pollutants from lakeside zone soils occurs through the transformation and migration of P and N forms. Elemental P is usually less mobile in soil and is not easily leached by rainwater or irrigation water. However, when a large amount of P has accumulated in the soil, rainfall or irrigation will lead to P loss from farmland soil. This constitutes the main source of non-point source P pollution. Analyzing the changes in the different forms of P in soil reveals the migration and transformation mechanisms of ANPS P (Wright, 2009).

When using pure water as influent, the concentrations of DIP and ammonia in natural soil effluent remained low over time (DIP $< 0.05\,\mathrm{mg\,L^{-1}}$; ammonia $< 0.3\,\mathrm{mg\,L^{-1}}$). This indicated that the soils do not produce nutrient pollution (Fig. 6). When farmland runoff with high P concentrations passed through natural soil (Fig. 3a), the DIP concentration in effluent decreased significantly (Fig. 5). At the same time, the total P content of soil significantly increased. This indicates that the natural soil in lakeside zone had a high P removal capacity. This was closely related to the large amount of clay and silt in the soil, and its strong adsorption capacity (Table 2)(Zhang and Li, 2016). Ultimately, the adsorbed P may gradually be converted into $NaHCO_3$-P, NaOH-P, and Residual-P. This resulted in a significant increase in the content of these three P forms by the end of the experiment (Fig. 5). The NZ-amended soil removed DIP from farmland runoff mainly by forming new NaOH-P and a small amount of $NaHCO_3$-P.

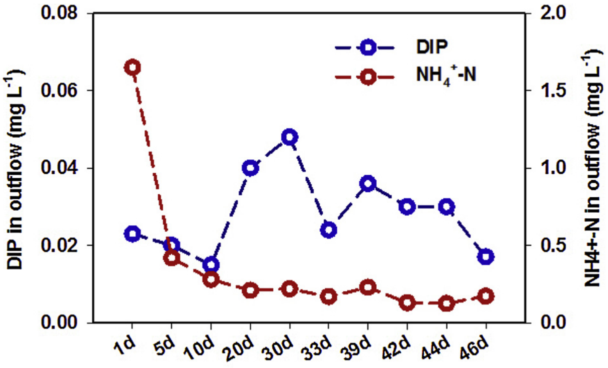

Fig. 6. Variation in DIP and ammonia concentrations in soil effluent using pure water as the influent over time.

$NaHCO_3$-P and NaOH-P were considered to be P encapsulated by iron-aluminium oxides and their hydrates. Their levels varied significantly with the redox state (Wright, 2009). In acidic soils, $NaHCO_3$-P and NaOH-P accounted for a large proportion of inorganic P. They represented potentially active P and served as the main carriers of P (especially water-soluble P) in soils (Pautler and Sims, 2000). The DIP removal rate of NZ-amended soil was lower compared to the unamended soil (Fig. 3b). This indicated that the NZ used in this experiment had a poor ability to adsorb phosphate. This may be related to the physical and chemical properties of the selected NZ, such as particle size and adsorption.

The AMC-amended soil and LaMB-amended soil both had high DIP removal rates (Fig. 3c,d); however, the removal mechanisms were different. Based on the calculation of mass balance relationship, AMC amended soil converted 65.4 % of the intercepted DIP into NaOH-P and 19.9 % into $NaHCO_3$-P, the sum of which accounts for 85.3 % of the total DIP removed. AMC-amended soil mainly removed DIP from farmland runoff by forming new NaOH-P and a small amount of $NaHCO_3$-P (Fig. 5). This was similar to the NZ-amended soil. In addition to forming NaOH-P and $NaHCO_3$-P, the LaMB-amended soil also formed a large amount of Residual-P (Ding et al., 2018). Mass balance calculation results indicated that LaBM amended soil transformed 53.9 % of the intercepted DIP into NaOH-P, 21.4 % into Residual-P, 19.8 % into $NaHCO_3$-P, and the sum of the three accounted for 95.2 % of the total DIP removed. This was consistent with previous studies (Krupa et al., 2011). Residual-P is usually considered as an inert P in the mineral lattice. Once formed, it is stable and no migration will occur. Therefore, DIP removal from farmland runoff using LaMB-amended soil was more complete.

The loss of ANPS P pollutants has two main forms: loss in particle state and loss in dissolved state. Most P migrates in surface runoff through adsorption on soil particles or organic matter. Therefore, removing suspended particulates in the lakeside zone is an important mechanism for removing ANPS P pollution (Narumalani et al., 1997). In general, the removal efficiency of total-P increases with the increase of buffer width. The removal efficiency of DIP is usually lower than total-P (Daniels and Gilliam, 1996; White et al., 1999). Uusi-Kämppä et al. (2000) tested the retention of P in eleven grass or vegetated buffer zones constructed in Finland, Norway, Sweden, and Denmark, and found that buffer zones mitigate in particular losses of particulate P and total P in agricultural runoff water by 27–97% (0.24-0.67 kg ha^{-1} yr^{-1}), whereas the retention of DIP was poor. After that, Uusi-Kämppä and Jauhiainen (2010) studied the retention capacity of buffer zones established in clay soil in Finland for total P and DIP, and showed that the total P removal efficiencies were 27–36% for the buffer zones as compared to the plots cultivated without a buffer; however, in the vegetated buffer zone plots, the DIP load was even 60 % greater than in the plots cultivated without a buffer, since the P from plant residues enriched the soil surface, enhancing the DIP losses in surface runoff. As compared with the efficiency of buffer zones to intercept DIP in the field studies, the interception efficiencies of amended soils in this study was remarkably high, suggesting that amending soil in lakeside buffer zones is an effective way to control the DIP output from the runoff of agricultural ecosystem.

In the surface runoff from the lakeside zone, N was intercepted mainly through physical processes, such as deposition and adsorption, and biochemical processes, such as plant uptake and denitrification (Lowrancer, 1992). In this study, the role of soil was discussed more than plants. The main components of the unamended soils were fine clay and silt (Table 2), which had a strong adsorption capacity. This led to a high ammonia removal rate, at an average value of 69.6 %. The ammonia removal rates of NZ-and AMC amended soils were significantly lower compared to unamended soils. This may be related to the coarsening of soil particle size and the decrease in adsorption capacity. The AMC-amended soil had the lowest ammonia removal effect, which may relate to its high water content, high calcium oxide, and other physical and chemical composition. The LaMB-amended soil had the largest ammonia removal capacity, atan average value of 89.3 %. In the agricultural ecosystems, the application of N fertilizer, causing high N concentrations in surface water in the fields, increases the amount of ammonia available toward catchment streams and thereby elevates the N concentration in stream water (Kim et al., 2006). For example, ammonia concentrations in the agriculture catchment streams (0.19–1.17 mg L^{-1} on average) were observed to be much higher than that in the forest catchment (0.09 mg L^{-1}) (Wang et al., 2014). On one hand, the increase in the concentration of ammonia in the runoff with increasing areal proportion of agriculture implies that agriculture ecosystems can hydrologically connect to the chemical composition of N in streams through fertilization and soil nutrient budgets (Wang et al., 2011, 2014). On the other hand, the high concentration of ammonia in the runoff of field farmlands indicated that it is necessary to establish buffer zones to reduce the N input of agricultural ecosystem to the surface water.

Only the amended soil could simultaneously and effectively reduce DIP and ammonia in the four studied soils. The mechanism for the efficient removal of ammonia by the LaMB-amended soil was unclear. This is an area that deserves further study. LaMB-amended soil clearly had broad application prospects in simultaneously reducing ANPS N and P pollutants in eutrophic water.

4.2. Key factors affecting the efficiency of ANPS pollution control in the artificial lakeside zone

The physical and chemical properties of soil determine soil nutrient dynamics in coastal zones (Djodjic et al., 2004). These soil properties decisively impact soil nutrient accumulation and output under specific vegetative conditions. The physical and chemical properties of lakeside zone soils drive the removal of N and P pollutants from farmland runoff (Brakerud, 2002). The soil properties also significantly impact the pollutant characteristics entering rivers. In constructing a lakeside buffer zone, it is vital to understand the nutrient composition, organic matter content, saturated water content, and soil bulk density. When soil conditions are poor, the lakeside zone soil can be amended to improve the decontamination efficiency of the buffer zone. In this study, the soil was better able to intercept pollutants when modified natural minerals (AMC and LaMB) were added to the soil. The results showed that AMC and LaMB were effective materials for amending soils and enhanced the removal rate of DIP and ammonia from contaminated soils (Figs. 4 and 5).

In addition to the physical and chemical properties of soil, factors affecting the removal of ANPS pollution in lakeside buffer zone also include vegetation, buffer zone width, and slope. Plants in lakeside buffer zones are usually composed of aquatic plants, hygrophyte, and terrestrial plants. The presence of these plants is another key factor driving the removal of ANPS pollutants by the buffer zone (DeSimone et al., 2010). The presence of vegetation can reduce runoff velocity, prolong the contact time between pollutants and soil, and maximize the opportunity for pollutants to be fully absorbed and fixed. Plant growth can consume the pollutants intercepted in the soil and can convert N and P from farmland runoff into plant biomass. This removes them completely (Woodward et al., 2009). Different species of plants have different habits and growth cycles; as such, they have different effects on lakeside zones (Hefting et al., 2005). When selecting vegetation in lakeside zones, the principles of natural rationality and low cost should be followed to maximize economic and environmental benefits.

The width and slope of lakeside buffer zones are important factors affecting pollutant interception in the buffer zone. Usually, pollutant removal is positively correlated with the width of the lakeside zone. Patty et al. (1997) found that buffer zone width increased by 1–2 times and the removal rate of N and P pollutants from farmland runoff increased by at least 38 % in three farms located in Brittany (France). However, increasing the buffer zone width requires more land. The optimum width of the lakeside zone should be studied and determined based on the actual situation. It is important to maintain a high efficiency of pollutant interception, while also decreasing social and economic interference. Slope is another variable affecting the environmental function of lakeside buffer zone. The smaller the slope, the longer it takes for pollutants to be intercepted and purified. This increases the pollutant removal efficiency. When designing a lakeside buffer zone, terrain conditions should be taken as the basis, and the slope should be changed slightly to meet the needs of the terrain conditions, with the goal of achieving a high removal efficiency.

As a complete ecological plant-water-soil system, the lakeside zone has specific advantages for preventing and controlling ANPS pollution. However, in the practice of treatment, different factors need to be thoroughly and meticulously analyzed to maximize the functions of water quality improvement, soil and water conservation, and landscape creation. These factors include soil physical and chemical properties, vegetation type selection and allocation, width of lakeside zone, and slope of buffer zone (Young and Briggs, 2005). Artificial lakeside buffer zones have the advantages of being low cost and convenient to manage. This makes these zones worth popularizing to treat ANPS pollution in large agricultural countries such as China.

The management of agricultural non-point source pollution from farmland to watershed scale is an ongoing challenge, which needs to consider the trade-off between environmental and economic objectives. The effect of improving water quality in different scales will be affected by many factors such as land use, soil types and river networks (Geng and Andrew, 2019), which needs to be taken into account. In addition, hydrological, meteorological and geomorphic factors at the scale of watershed are important factors affecting the pollution response of ANPS pollutants (Petit-Boix et al., 2017).

5. Conclusion

Simultaneously reducing P and N pollution input in farmland runoff is a challenge when controlling ANPS pollution. In this study, NZ, AMC, and LaMB were used to amend the soil in a lakeside zone in the Karst area of China. The study evaluated the removal efficiencies of DIP and ammonia from farmland runoff using amended soil. In the 46-day simulation experiment, the removal rates of DIP from farmland runoff by AMC-and LaMB-amended soils reached 93.6 % and 93.9 %, respectively. AMC-and LaMB-amended soils were effective technologies for controlling ANPS P pollution. In addition, LaMB amended soil simultaneously removed ammonia from farmland runoff, at a 89.3 % removal rate. Therefore, LaBM amended soil with 3 % mass ratio is recommended for ANPS N and P pollution control in lakeside zone. The matrix test of additive amount should be conducted in the future to determine a more precise addition under the effective and economic principles. Surface water pollution treatments are currently dominated by point source pollution treatment methods in China. There have been some studies on ANPS pollution, but the topic has not attracted much attention. To address the problem of water environmental pollution, point and non-point source pollution must be simultaneously treated. This is a potentially effective way to control ANPS pollution by using environmentally friendly materials for soil amendments. The goal is to establish efficient, low cost, and low risk lakeside zones between farmland and water bodies.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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