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Coal Fly Ash and Polyacrylamide Influence Transport and Redistribution of Soil Nitrogen in a Sandy Sloping Land

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Abstract: Sandy soils are prone to nutrient losses, and consequently do not have as much as agricultural productivity as other soils. In this study, coal fly ash (CFA) and anionic polyacrylamide (PAM) granules were used as a sandy soil amendment. The two additives were incorporated to the sandy soil layer (depth of 0.2 m, slope gradient of 10°) at three CFA dosages and two PAM dosages. Urea was applied uniformly onto the low-nitrogen (N) soil surface prior to the simulated rainfall experiment (rainfall intensity of 1.5 mm/min). The results showed that compared with no addition of CFA and PAM, the addition of CFA and/or PAM caused some increases in the cumulative NO_3^--N and NH_4^+-N losses with surface runoff; when the rainfall event ended, 15% CFA alone treatment and 0.01–0.02% PAM alone treatment resulted in small but significant increases in the cumulative runoff-associated NO_3^--N concentration ($p < 0.05$), meanwhile 10% CFA + 0.01% PAM treatment and 15% CFA alone treatment resulted in nonsignificant small increases in the cumulative runoff-associated NH_4^+-N concentration ($p > 0.05$). After the rainfall event, both CFA and PAM alone treatments increased the concentrations of NO_3^--N and NH_4^+-N retained in the sandy soil layer compared with the unamended soil. As the CFA and PAM co-application rates increased, the additive effect of CFA and PAM on improving the nutrient retention of sandy soil increased.

Keywords: fly ash; polyacrylamide; sandy soil; nitrate nitrogen; ammonia nitrogen

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1. Introduction

Coal fly ash (CFA), an inevitable byproduct of thermal electricity generation from coal, accounts for about 85% of the total ash produced and consists of fine and glass-like particles (≤100 μm) seized from flue gas [1,2]. The particles are predominantly spherical in shape, either solid or hollow, and mostly glossy (amorphous) in nature [1,3]. Today coal still plays a crucial role in power generation in many countries (e.g., China and India), with estimated over 750 million tons of coal ash produced by coal-based electricity generation per year globally [4]. With increasing accumulation of large amounts of CFA, improper disposal of CFA has become a worldwide environmental concern. Due to the shortage of available land for disposal of CFA at ash ponds, lagoons, and landfills, growing attempts have been made to recycle and reutilize CFA mainly as soil amendment or construction additive [1–3,5].

With respect to recycling of CFA for soil amelioration, previous studies have shown that CFA incorporation in sandy soil, which is prone to water drainage and nutrient leaching, can improve the capacity of sandy soil to retain water and nutrients, because fine CFA particles alter the coarse soil texture [6–9]. A recent study of Yang et al. [10] applied high-calcium FA to a sandy sloping land and found that the storage of infiltrating water originated from the artificial rainfall in the sandy soil was increased by FA. FA has also been co-applied with other materials for soil amelioration [1–3,11]. Polyacrylamide (PAM) is often applied to prevent soil erosion mainly due to its effect on binding soil particles to form stable aggregates [12–18]. Several studies have shown that co-application of CFA and PAM caused an additive effect on improving some properties of sandy soil, including increased threshold wind speed and resistance to wind erosion [19–21] and enhanced water retention capacity [10]. Other studies also noted that excessive amounts of CFA could affect the structural stability of sandy soil, consequently reducing its resistance to wind erosion [19] and antiwater erosion ability [10]. Nevertheless, little information is available on the interaction effect of CFA and PAM on retaining nutrients in sandy soil on sloping land or hilly regions where there is usually a significant tendency to lose water, nutrients, and soil [10,16,22,23].

Soil NO_3^--N and NH_4^+-N, two key nutrient elements of plant growth [14,24], were selected as indicators for nutrient loss from a sandy slope under simulated rainfall in this study. It was found that both concentrations of NO_3^--N and NH_4^+-N in runoff exhibited strong power relationships with runoff rate, decreasing with the increase of runoff rate, and NO_3^--N is the dominant form of dissolved nitrogen lost with surface runoff in sandy land [18]. We hypothesized that co-application of CFA and PAM holds the potential to enhance the NO_3^--N and NH_4^+-N retention capacity of sandy soil compared to CFA or PAM alone. In addition, we hypothesized that PAM may mitigate runoff-associated losses of the two nitrogen ions caused by high CFA dosage. Our objectives were (1) to investigate the influence of CFA and PAM on runoff-associated nutrient loss from the sandy slope, and (2) to examine the effect of CFA and PAM on nutrient retention in the sandy soil. The findings will deepen our understanding of co-application of CFA and PAM for sandy soil amelioration.

2. Material and Methods

2.1. Model CFA, PAM, and Sandy Soil

An infertile alluvial sandy soil (air-dried and 2 mm sieved) was used as the model soil, and a dry high-calcium coal fly ash (2 mm sieved) was used as the model CFA. The physicochemical properties of the sandy soil and CFA were shown in Table S1. The model PAM was water-soluble, dry anionic granules with a molecular weight of 3 Mg/mol.

2.2. Simulated Rainfall Experiment

The simulated rainfall experiment was conducted on a test platform with an area of 2 m $\times$ 2.25 m and a gradient of 10°. The gradient indicates relatively less steep landforms. The experimental plot was divided into nine subplots (with an area of 2 m $\times$ 0.25 m for each plot) for CFA and PAM treatments. The CFA and PAM treatments consisted of 0% CFA + 0% PAM (control group), 10% CFA + 0% PAM, 15% CFA + 0% PAM, 0% CFA + 0.01% PAM, 0% CFA + 0.02% PAM, 10% CFA + 0.01% PAM, 10% CFA + 0.02% PAM, 15% CFA + 0.01% PAM, and 15% CFA + 0.02% PAM. The dosages of FA and PAM were expressed as percentages of the dry sandy soil weight. The sandy soil was amended with CFA and PAM in the above dosages prior to being packed onto each subplot to form a 0.2 m soil layer. The diagram of experimental apparatus and treatment plots was displayed in Figure 1. The detailed procedures for packing the soil onto the subplot can be found in our previous study [10]. Then, urea (analytical grade) was applied to the soil surface at a dosage of 80 g/m^2 (approx. 36 N g/m^2) as N source in accordance with local fertilization practice in depleted sandy land. To be specific, an appropriate amount of urea was mixed thoroughly with 1 kg sandy soil or the above soil mixture, and then scattered uniformly on the surface of each subplot. Once urea is incorporated into the soil, urea granules will dissolve in the soil water within a short time. Urease, a widespread enzyme in soils quickly hydrolyzes the dissolved urea into NH_4^+-N. NH_4^+-N in the soil can be subsequently oxidized to NO_3^--N [25].

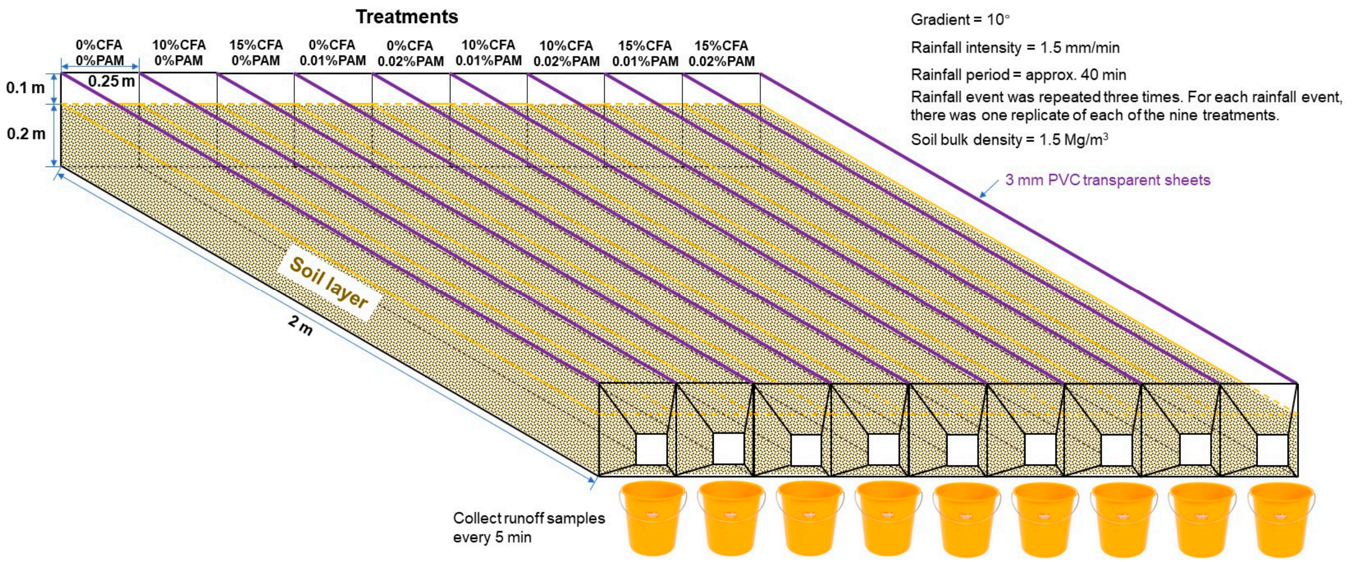

Figure 1. Diagram of the experimental apparatus and treatment plots.

The rainfall intensity was adjusted to 1.5 mm/min in this study, representing heavy storms. The rainfall period for all plots lasted approx. 40 min. The rainfall experiment was repeated in triplicates, with three replicates of each treatment. The detailed procedures of the rainfall simulation as well as runoff and soil profile sampling can be found in our previous study [10]. An aliquot of each runoff sample collected regularly during the rainfall event was taken for N concentration measurement. The 0–0.04, 0.04–0.08, 0.08–0.12, 0.12–0.16, and 0.16–0.2 m soil samples collected 4 h after the end of the rainfall event were analyzed for N concentration.

2.3. Sample Analysis

The volume of runoff samples was measured using a measuring cylinder [10]. For N concentration measurement, the NO_3^--N and NH_4^+-N concentrations in the runoff samples were determined using the ultraviolet spectrophotometric method. The NO_3^--N concentration in the soil samples was determined by the phenoldisulfonic acid colorimetric procedure [26]. The NH_4^+-N concentration in the soil samples was determined by the 2 mol/L KCl extraction-indophenol blue colorimetric procedure [26]. All absorbance was measured on an ultraviolet spectrophotometer (UV-1800, Mapada, Shanghai, China).

2.4. Calculation of N Loss with Runoff

Nutrient loss with runoff from sloping land can be influenced by soil initial nutrient content, bulk density, initial water content, texture, and rainfall and underlying surface conditions. When the above variables are consistent, nutrient loss with runoff depended exclusively on nutrient concentration in the runoff and runoff yield. Therefore, the NO_3^--N or NH_4^+-N loss rate was calculated using the following equation [14]:

$$m(t) = c(t) \times r(t) \tag{1}$$

where $m(t)$ is instantaneous nutrient loss rate at time t (mg/min), $c(t)$ is nutrient concentration in the runoff sample collected at time t (mg/L), and $r(t)$ is instantaneous runoff yield at time t (L/min).

Cumulative nutrient loss was calculated using the following equation [14]:

$$M = \int_0^T m(t)\mathrm{d}t = \int_0^T c(t)r(t)\mathrm{d}t \tag{2}$$

where M is cumulative nutrient loss (mg) and T is runoff duration (min).

2.5. Statistical Analysis

Data in the tables and figures are the averages of the triplicates, and the error bars represent one standard deviation of the triplicates. The differences between treatments were analyzed by one-way ANOVA in IBM SPSS Statistics 20, and the least significant difference (LSD) test was used for mean comparisons. The regression analysis was performed in Microsoft Excel 2016. The scatter plots were created using Microsoft Excel 2016. The contours of soil nitrogen distribution were drawn with OriginPro 9.

3. Results

3.1. Instantaneous N Concentration in Runoff

Figures 2 and 3 show NO_3^--N and NH_4^+-N concentrations in runoff sampled from different treatments at different sampling times, respectively. In the control, CFA alone treatments (Figures 2a and 3a with the exception for 15% CFA treatment), PAM alone treatments (Figures 2b and 3b), and 10% CFA + 0.01–0.02% PAM treatments (Figures 2c and 3c), both NO_3^--N and NH_4^+-N concentrations in the runoff decreased sharply at the early stage of the runoff and remained generally stable over the following stage. To be specific, for the single use of CFA, during the entire rainfall event the NO_3^--N concentration in the runoff in 10% CFA treatment was consistently higher than the control, while that in 15% CFA treatment was consistently lower than the control (Figure 2a), whereas the NH_4^+-N concentration in runoff in CFA treatments remained lower than the control except for a peak in the value noted around the 40th minute (Figure 3a). Moreover, CFA had a more obvious effect on reducing the NH_4^+-N concentration in runoff at a dosage of 15% than 10% at the latter stage of the rainfall (Figure 3a). In contrast, the single use of PAM resulted in a significant reduction in the NO_3^--N and NH_4^+-N concentrations in the runoff compared with the control at the early stage of the runoff, and the higher PAM application rate had a more obvious reducing effect (Figures 2b and 3b). During the latter stage of the rainfall, the NO_3^--N and NH_4^+-N concentrations in the runoff in PAM treatments were generally close to the control (Figures 2b and 3b).

When CFA and PAM were co-applied, the NO_3^--N and NH_4^+-N concentrations in the runoff in 10% CFA + 0.01–0.02% PAM treatments were lower than that in 10% CFA treatment during the entire rainfall event (Figures 2c and 3c). At the early stage of the runoff, a prominent reduction in the NO_3^--N and NH_4^+-N concentrations in the runoff in 10% CFA + 0.01–0.02% PAM treatments was noted in comparison with that in 10% CFA treatment. When CFA was co-applied at a dosage of 15% with PAM, the NO_3^--N concentration in the runoff in 15% CFA + 0.01–0.02% PAM treatments was generally constant and higher than that in 15% CFA treatment during the entire rainfall event (Figure 2d), meanwhile small but prominent fluctuations were noted in the NH_4^+-N concentration in the runoff in 15% CFA alone treatment and 15% CFA + 0.01–0.02% PAM treatments (Figure 3d). Moreover, there was generally no significant difference in the NO_3^--N and NH_4^+-N concentrations, respectively, in the runoff between 10% CFA + 0.01–0.02% PAM treatments (Figures 2c and 3c) and between 15% CFA + 0.01–0.02% PAM treatments (Figures 2d and 3d) ($p > 0.05$).

3.2. Relationship between N Concentration in Runoff and Runoff Rate

The variations in the runoff rate in different treatments during the rainfall event were presented in our previous study [10]. As displayed in Figure 4, the NO_3^--N concentration in the runoff had a strong negative relationship with runoff rate, except for those in 0.02% PAM alone treatment (Figure 4b) and a higher CFA dosage of 15% along with 0.01–0.02% PAM treatments (Figure 4d). As displayed in Figure 5, there was a strong negative relationship between NH_4^+-N concentration in the runoff and runoff rate in the control (Figure 5a), 0.01% PAM alone treatment (Figure 5b), 10% CFA + 0.01–0.02% PAM treatments (Figure 5c), and 15% CFA + 0.02% PAM treatment (Figure 5d), respectively.

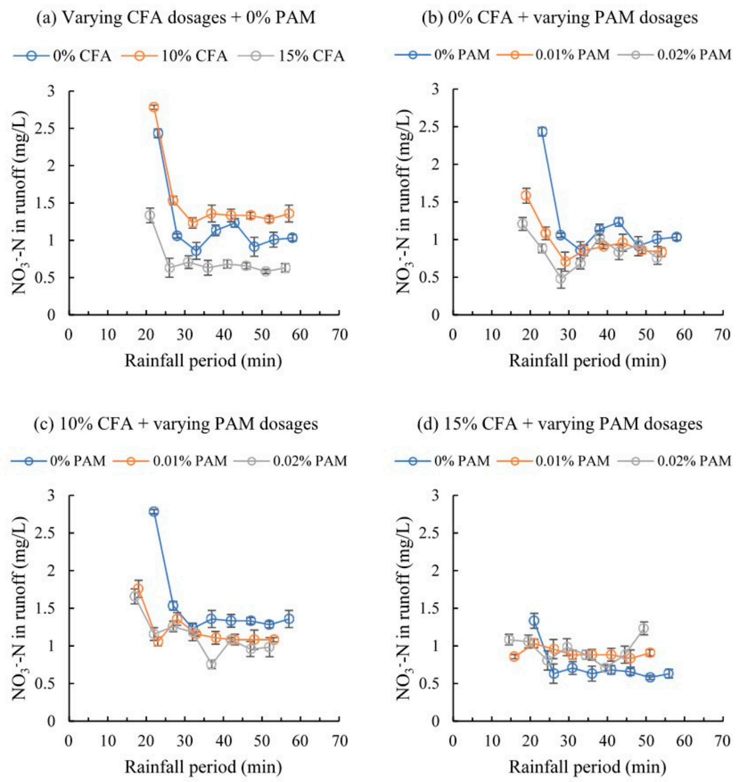

Figure 2. Variations in instantaneous NO_3^--N concentration in runoff with rainfall period for varying CFA dosages + 0% PAM (**a**), 0% CFA + varying PAM dosages (**b**), 10% CFA + varying PAM dosages (**c**), 15% CFA + varying PAM dosages (**d**).

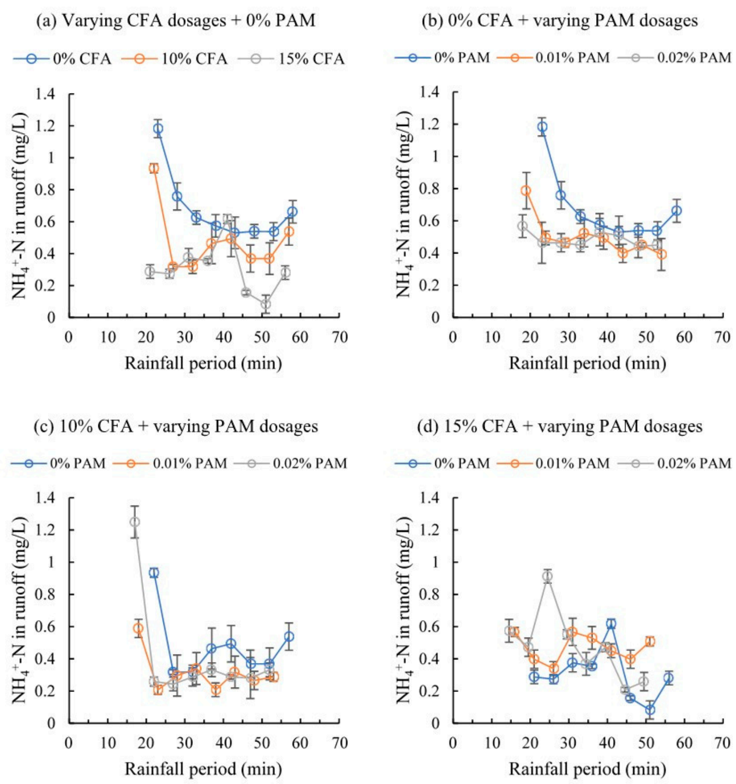

Figure 3. Variations in instantaneous NH_4^+-N concentration in runoff with rainfall period for varying CFA dosages + 0% PAM (**a**), 0% CFA + varying PAM dosages (**b**), 10% CFA + varying PAM dosages (**c**), 15% CFA + varying PAM dosages (**d**).

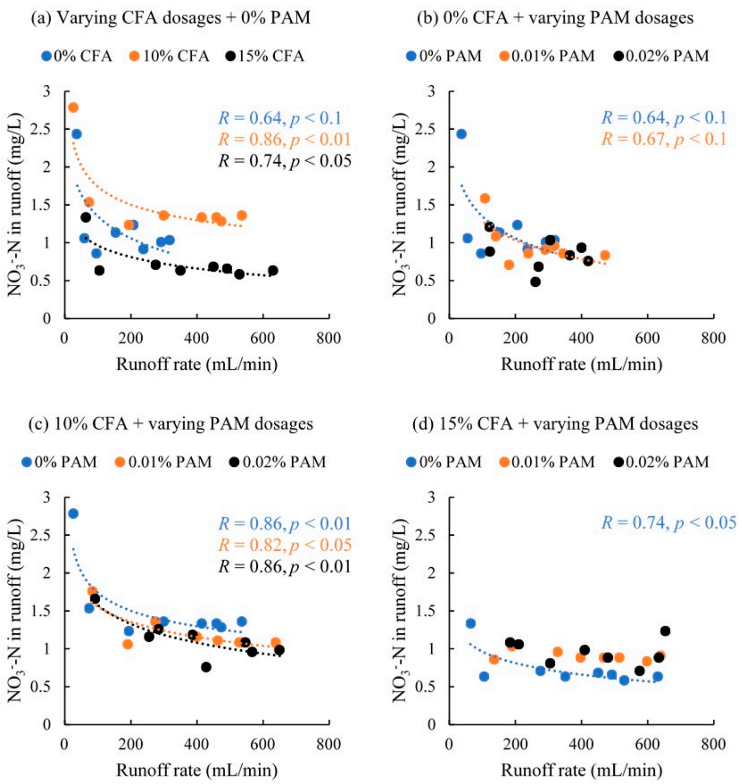

Figure 4. Correlation between NO_3^--N concentration in runoff and runoff rate for varying CFA dosages + 0% PAM (**a**), 0% CFA + varying PAM dosages (**b**), 10% CFA + varying PAM dosages (**c**), 15% CFA + varying PAM dosages (**d**).

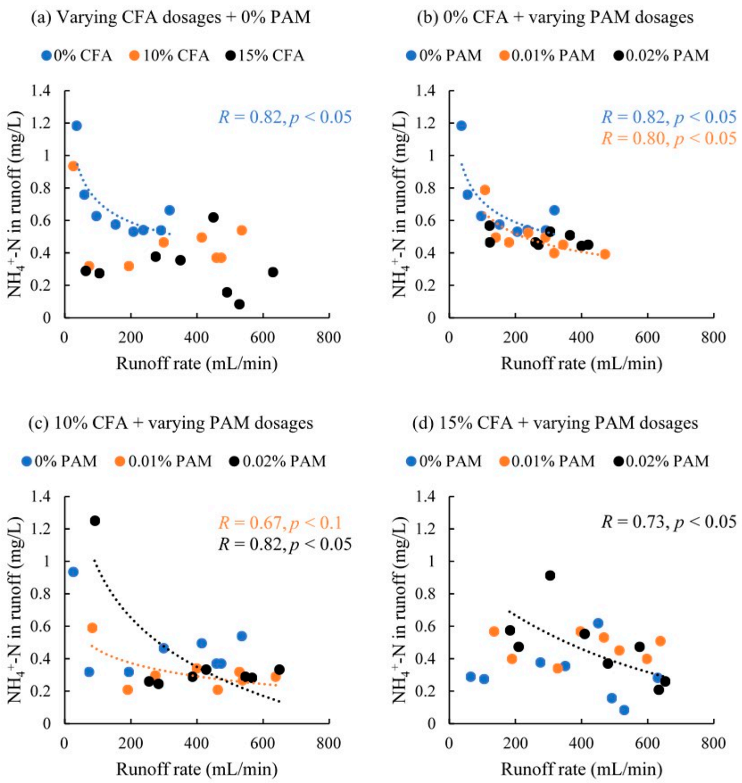

Figure 5. Correlation between NH_4^+-N concentrations in runoff and runoff rate for varying CFA dosages + 0% PAM (**a**), 0% CFA + varying PAM dosages (**b**), 10% CFA + varying PAM dosages (**c**), 15% CFA + varying PAM dosages (**d**).

3.3. Relationship between N Concentration in Runoff and Sediment Rate

The variations in the sediment rate in different treatments during the rainfall event were presented in our previous study [10]. There was a strong negative relationship between NO_3^--N concentration in the runoff and sediment rate in CFA alone treatments (Figure 6a) and 10% CFA + 0.01% PAM treatment (Figure 6c), respectively, whereas a strong negative relationship between the NH_4^+-N concentration in the runoff and sediment rate was only noted in 10% CFA + 0.01% PAM treatment (Figure 7c) and 15% CFA + 0.02% PAM treatment (Figure 7d).

3.4. Cumulative NO_3^--N and NH_4^+-N Losses with Runoff

The changes in cumulative NO_3^--N and NH_4^+-N losses with runoff for different treatments are shown in Figure 8a,b, respectively. For all treatments, the cumulative NO_3^--N and NH_4^+-N losses increased obviously with rainfall period. Compared with the control, both CFA and PAM increased the cumulative NO_3^--N and NH_4^+-N losses to different extent. To be specific, with respect to NO_3^--N (Figure 8a), there was an obvious increase in the cumulative NO_3^--N loss in 10% CFA + 0–0.02% PAM treatments and 15% CFA + 0.01–0.02% PAM treatments. In contrast, there was only a very small increase in the cumulative NO_3^--N loss in the remaining FA and/or PAM treatments. When the rainfall event ended, a higher CFA dosage alone resulted in a lower cumulative NO_3^--N loss, and the lowest value among all CFA and/or PAM treatment was observed in 15% CFA alone treatment, which was 1.3-times higher than the control ($p < 0.05$) (Table 1). The co-application of CFA and PAM increased the cumulative NO_3^--N loss. At the same PAM rate, the addition of CFA increased the cumulative NO_3^--N loss conspicuously; When the rainfall event ended, the highest cumulative NO_3^--N loss was found in 10% CFA + 0.01% PAM treatment, which was 2.4-times higher than the control ($p < 0.05$) (Table 1).

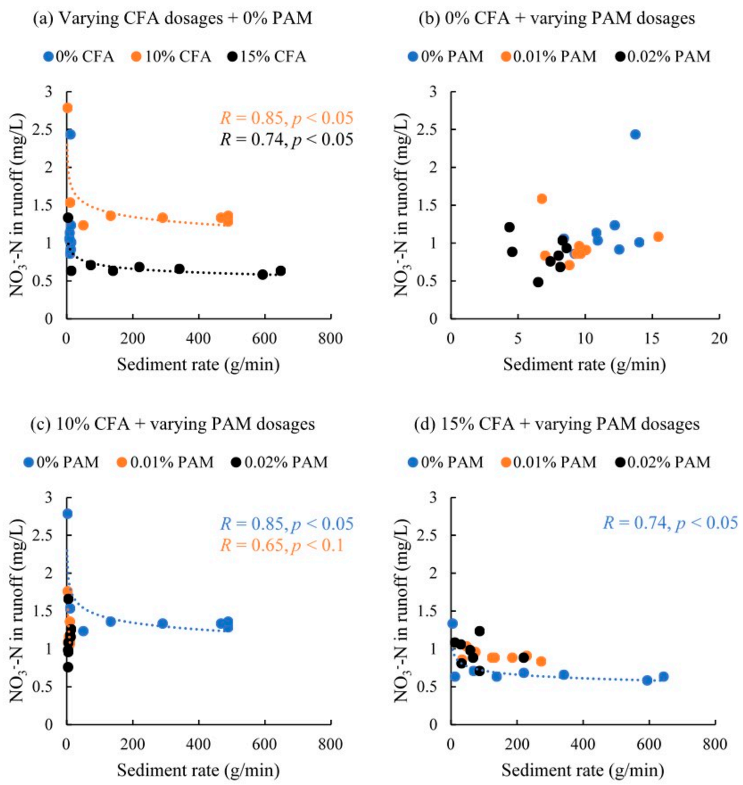

Figure 6. Correlation between NO_3^--N concentration in runoff and sediment rate for varying CFA dosages + 0% PAM (**a**), 0% CFA + varying PAM dosages (**b**), 10% CFA + varying PAM dosages (**c**), 15% CFA + varying PAM dosages (**d**).

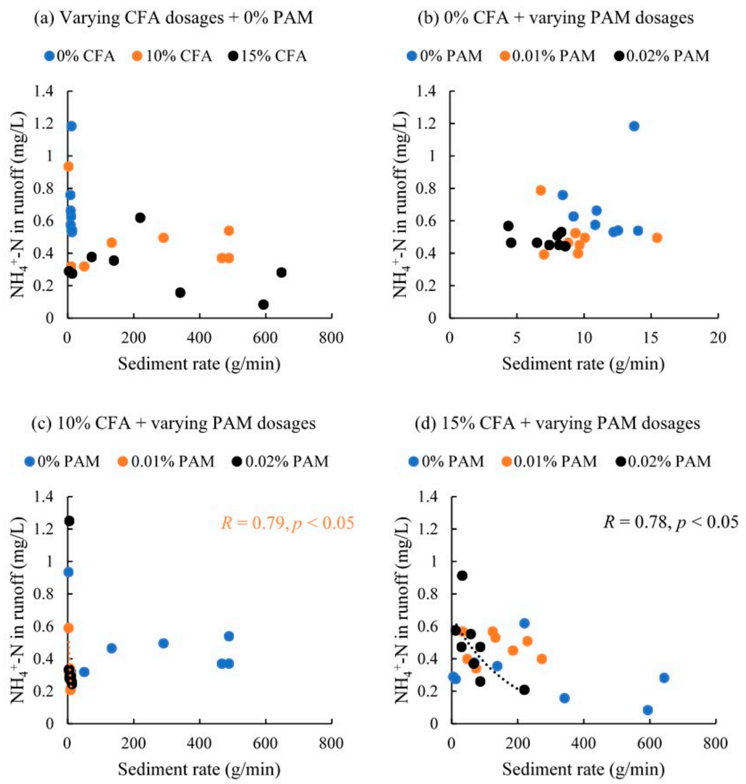

Figure 7. Correlation between NH_4^+-N concentrations in runoff and sediment rate for varying CFA dosages + 0% PAM (**a**), 0% CFA + varying PAM dosages (**b**), 10% CFA + varying PAM dosages (**c**), 15% CFA + varying PAM dosages (**d**).

In the case of NH_4^+-N (Figure 8b), the cumulative NH_4^+-N loss increased significantly in 15% CFA + 0.01–0.02% PAM treatments compared with the remaining treatments ($p < 0.05$). Similar to the effect of CFA on the cumulative NO_3^--N loss, a higher CFA dosage alone also resulted in a lower cumulative NH_4^+-N loss when the rainfall event ended, and the lowest value among all CFA and/or PAM treatment was found in 15% CFA alone treatment. This value was slightly higher than the control ($p > 0.05$) (Table 1). Different from the trend in the cumulative NO_3^--N loss as affected by CFA and PAM, at the same PAM rate, the addition of 10% CFA resulted in a lower cumulative NH_4^+-N loss, while the addition of 15% CFA led to a much higher cumulative NH_4^+-N loss. When the rainfall event ended, the highest cumulative NH_4^+-N loss was observed in 15% CFA + 0.01–0.02% PAM treatments, which was about 1.8-times higher than the control ($p < 0.05$) (Table 1).

Table 1. Effect of CFA and PAM on runoff-associated cumulative NO_3^--N and NH_4^+-N losses at the end of the rainfall event.

Treatment	Cumulative NO_3^--N Loss with Runoff (mg) $^{\$}$	Cumulative NH_4^+-N Loss with Runoff (mg)
0% CFA, 0% PAM (Control)	6.45 ± 0.13 ^{f}	3.56 ± 0.08 ^{f}
0% CFA, 0.01% PAM	8.18 ± 0.12 ^{e}	4.20 ± 0.17 ^{cde}
0% CFA, 0.02% PAM	8.20 ± 0.37 ^{e}	4.75 ± 0.24 ^{b}
10% CFA, 0% PAM	14.65 ± 0.20 ^{b}	4.65 ± 0.19 ^{bc}
10% CFA, 0.01% PAM	15.63 ± 0.15 ^{a}	3.91 ± 0.06 ^{def}
10% CFA, 0.02% PAM	14.83 ± 0.57 ^{b}	4.35 ± 0.37 ^{bcd}
15% CFA, 0% PAM	8.29 ± 0.30 ^{e}	3.76 ± 0.14 ^{ef}
15% CFA, 0.01% PAM	12.90 ± 0.12 ^{d}	6.66 ± 0.32 ^{a}
15% CFA, 0.02% PAM	13.82 ± 0.49 ^{c}	6.60 ± 0.11 ^{a}

$^{\$}$—The values in the table are expressed as mean ± standard deviation (n = 3). The different lower-case letters in the same column indicate significant difference between treatments ($p < 0.05$).

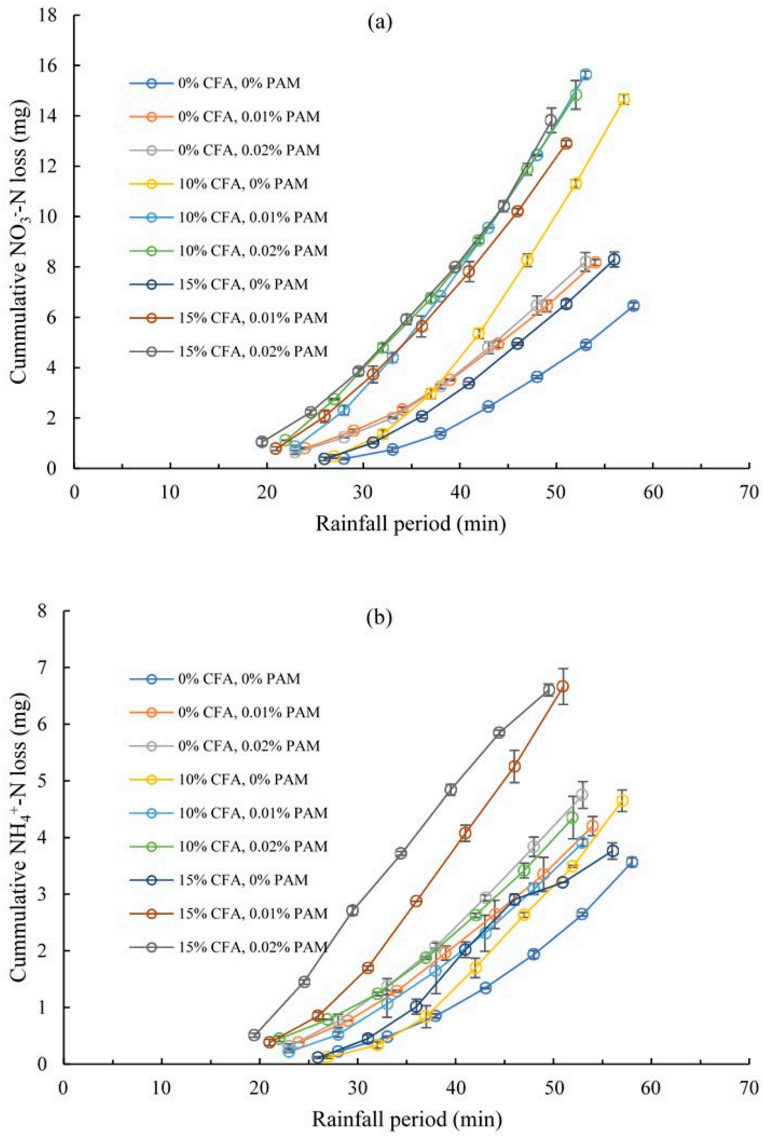

Figure 8. Variations in cumulative NO_3^--N loss (**a**) and cumulative NH_4^+-N loss (**b**) with runoff for different CFA and PAM treatments.

3.5. NO_3^--N and NH_4^+-N Concentrations in Soil after Rainfall

Figure 9 displays two-dimensional distribution of NO_3^--N concentrations in soil profiles amended with different CFA and PAM dosages. Regarding the single application of CFA (Figure 9d,g), the NO_3^--N leaching loss was obviously reduced in the soil profile amended with CFA in comparison with the control (Figure 9a). The mean NO_3^--N concentration in the control and 10% and 15% CFA amended soil profiles was 7.6, 8.5, and 12.8 mg/kg, respectively. The coefficient variation (CV) value of NO_3^--N concentration in the control was 0.47. In contrast, the CV value of NO_3^--N concentration in the 10% and 15% CFA amended soil profiles was 1.08 and 0.14, respectively, suggesting a conspicuous spatial variation in NO_3^--N concentration in the soil profile amended with 10% CFA. With respect to the single application of PAM (Figure 9b,c), the NO_3^--N concentrations which remained in the soil profile after the rainfall event increased with PAM dosage, from a mean value of 7.6 mg/kg in the control to 8.1 and 9.2 mg/kg in the 0.01% and 0.02% PAM amended soil profiles, respectively. In addition, there was a small variation in the CV values (0.47–0.57) of NO_3^--N concentration in the soil profile among different PAM treatments. For the co-application of CFA and PAM (Figure 9e,f,h,i), the effect on reducing soil NO_3^--N leaching loss was significantly enhanced compared with the single use of CFA or PAM. To be specific, the mean NO_3^--N concentrations in the soil profiles amended with 10–15% CFA together with 0.01–0.02% PAM ranged from 10.0 to 26.1 mg/kg. There was an increasing trend in soil NO_3^--N concentration with increasing CFA and PAM dosages. Moreover, the CV values of NO_3^--N concentration in the 10% CFA + 0.01–0.02% PAM amended soil profiles was in the range of 1.28–1.39, while the values in 15% CFA + 0.01–0.02% PAM amended soil profiles was around 0.5. The above difference indicated a smaller spatial variation in NO_3^--N concentration in the soil profile and a more prominent effect on reducing soil NO_3^--N leaching loss at a higher FA dosage along with different PAM dosages.

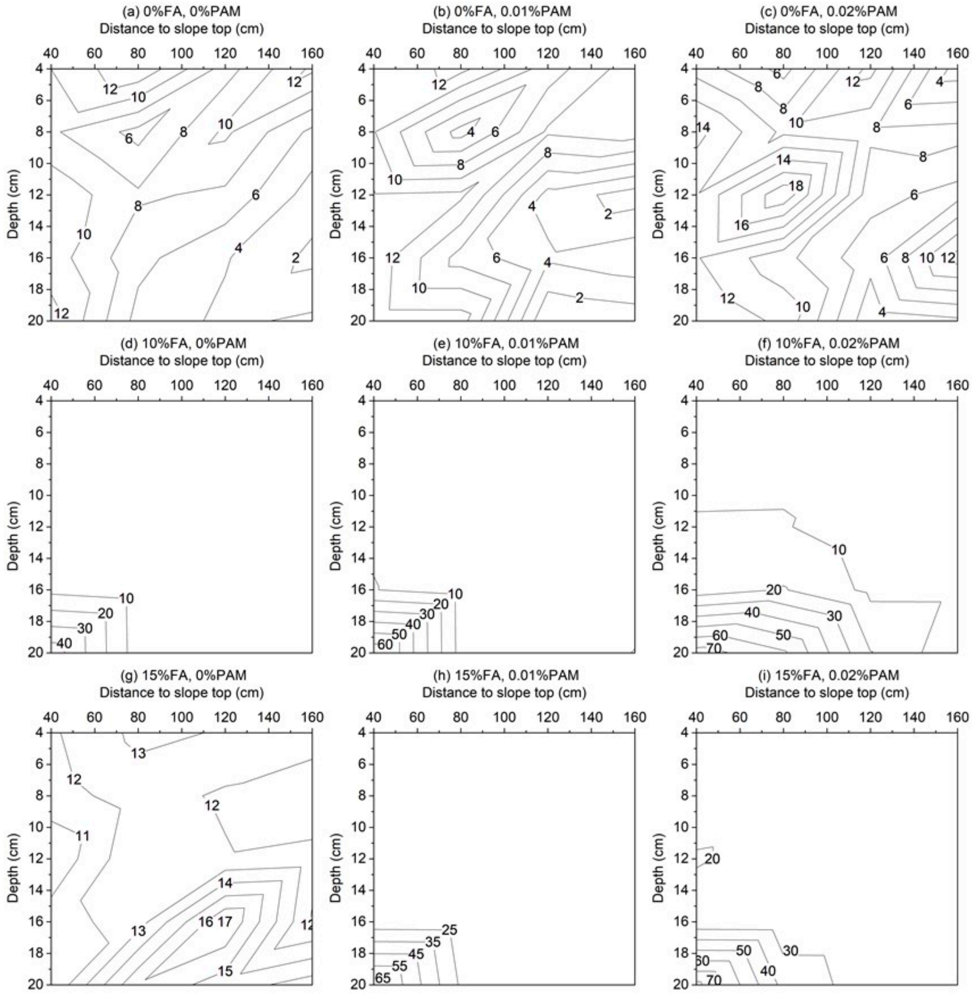

Figure 9. Contour plot displaying redistribution of NO_3^--N (Unit: mg/kg) in soil profiles amended with different CFA and PAM dosages (i.e., 0% CFA + 0% PAM (**a**), 0% CFA + 0.01% PAM (**b**), 0% CFA + 0.02% PAM (**c**), 10% CFA + 0% PAM (**d**), 10% CFA + 0.01% PAM (**e**), 10% CFA + 0.02% PAM (**f**), 15% CFA + 0% PAM (**g**), 15% CFA + 0.01% PAM (**h**), 15% CFA + 0.02% PAM (**i**)) after rainfall.

Figure 10 displays two-dimensional distribution of NH_4^+-N concentrations in soil profiles amended with different CFA and PAM dosages. For CFA application alone (Figure 10d,g), there was a prominent increase in NH_4^+-N concentration remained in CFA amended soil profiles after the rainfall event. The mean soil NH_4^+-N concentration in the control was 13.4 mg/kg (Figure 10a), while the mean value in the 10% and 15% FA amended soil profiles was 18.2 and 29.4 mg/kg, respectively (Figure 10d,g). Similar to the spatial distribution of NO_3^--N in the soil profiles amended with CFA alone, a more significant spatial variation was observed in NH_4^+-N concentration in the soil profile amended with 10% CFA, as indicated by a larger CV value of 1.09 than the other two treatments (CV range 0.68–0.73). When PAM was applied solely (Figure 10b,c), the mean soil NH_4^+-N concentration increased from 13.4 mg/kg in the control to 26.4 mg/kg in both 0.01% and 0.02% PAM amended soil profiles, and the CV value of NH_4^+-N concentration decreased from 0.73 in the control to 0.46–0.57 in the PAM amended soil profiles. Likewise, an enhanced effect on reducing soil NH_4^+-N leaching loss was observed when CFA and PAM were applied together (Figure 10e,f,h,i). The mean NH_4^+-N concentration in CFA and PAM amended soil profile increased with increasing CFA and PAM dosages, from 28.4 mg/kg in 10% CFA and 0.01% PAM amended soil profile to 43.7 mg/kg in 15% CFA and 0.02% PAM amended soil profile. Moreover, the CV values of NH_4^+-N concentration in CFA and PAM amended soil profiles ranged from 0.87 to 1.29.

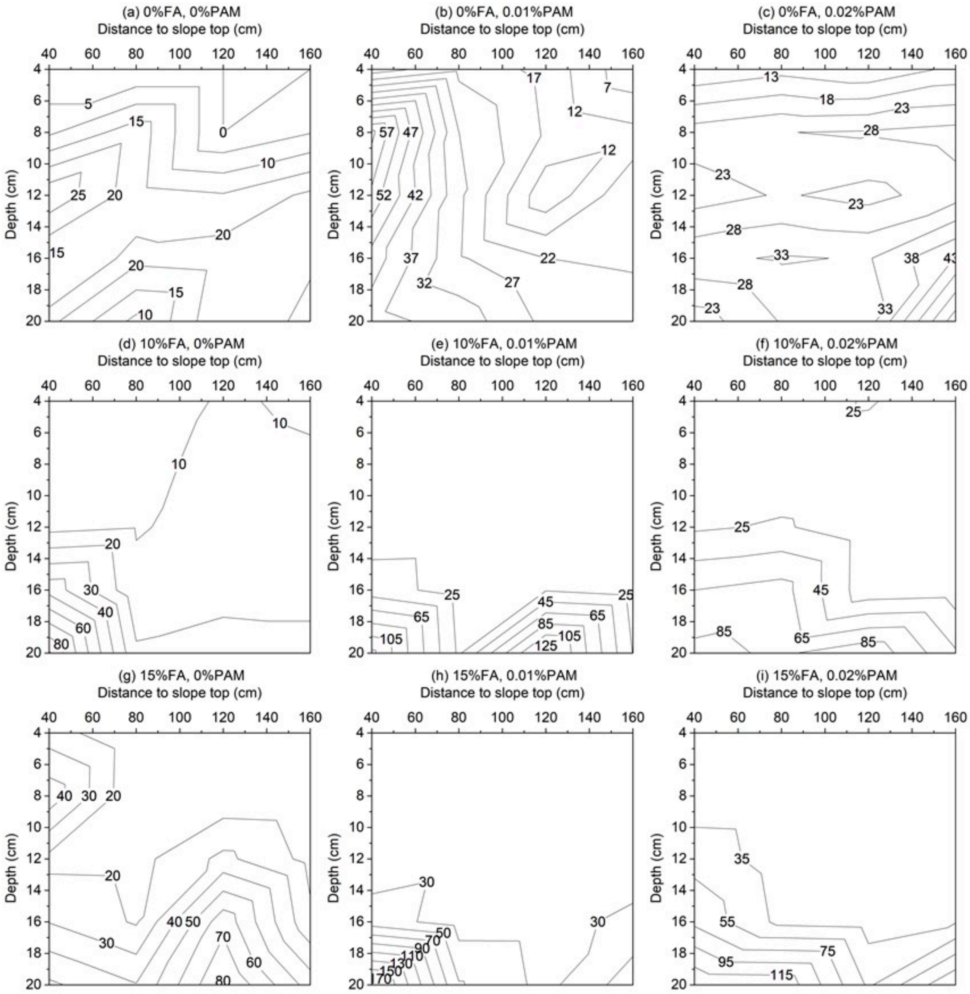

Figure 10. Contour plot displaying redistribution of NH_4^+-N (Unit: mg/kg) in soil profiles amended with different CFA and PAM dosages (i.e., 0% CFA + 0% PAM (**a**), 0% CFA + 0.01% PAM (**b**), 0% CFA + 0.02% PAM (**c**), 10% CFA + 0% PAM (**d**), 10% CFA + 0.01% PAM (**e**), 10% CFA + 0.02% PAM (**f**), 15% CFA + 0% PAM (**g**), 15% CFA + 0.01% PAM (**h**), 15% CFA + 0.02% PAM (**i**)) after rainfall.

4. Discussion

The sharp decline in the instantaneous NO_3^--N and NH_4^+-N concentrations in the runoff at the early stage of the runoff and much less obvious fluctuations over the following stage of the rainfall in most treatments in this study agrees with some previous studies on using PAM to control N loss from sandy sloping land [16–18,27]. For example, Ao et al. [18] performed artificial rainfall experiments and found that the concentrations of NO_3^--N and NH_4^+-N in the runoff in the untreated sandy soil and sandy soil treated with surface-applied PAM granules (PAM ratio $\leq$ 2 g/m^2) were relatively high at the beginning of the runoff and decreased sharply thereafter to a nearly steady state with increasing rainfall period. Moreover, Ao et al. [18] noted that PAM reduced both instantaneous NO_3^--N and NH_4^+-N concentrations in the runoff during the entire rainfall event, and it stabilized the loss of NO_3^--N earlier than the loss of NH_4^+-N in the runoff. In this study, the single use of PAM also had a reducing effect on the NO_3^--N and NH_4^+-N concentrations in the runoff. In contrast to Ao et al. [18], PAM reduced the NO_3^--N concentration in the runoff during the first approx. 30 min (Figure 2b) and the NH_4^+-N concentrations in the runoff during the first approx. 20 min of the rainfall event (Figure 3b). A similar decreasing trend in the concentrations of K^+, NO_3^--N, and NH_4^+-N in the runoff in the untreated loam and loam treated with surface-applied PAM solution (PAM ratio $\leq$ 2 g/m^2) with increasing simulated rainfall period was reported by Li and Wang [17]. Additionally, Li and Wang [17] found that the addition of PAM solution to the loam surface generally reduced the concentrations of nutrients in the runoff, except at a higher ratio of 2 g/m^2, which resulted in increased NO_3^--N concentration in the runoff during the entire rainfall event. The decreased NO_3^--N and NH_4^+-N concentrations in the runoff by the single use of PAM in this study may be attributed to the following two factors: (1) Mixing PAM granules with the soil improved the resistance of sandy soil to interrill erosion [10]. With increasing rainfall period, the unamended soil was subjected to interrill erosion. The surface soil nutrients were lost first with runoff. After the destruction and transport of surface soil aggregates, the subsurface soil nutrients were exposed to the interrill erosion and consequently lost with runoff. In contrast, the long chains of dissolved PAM adsorbed on the surface soil aggregates could bind them together and increase their resistance to detachment by runoff, and consequently reduce the amount of soil nutrients ejected into the runoff [10,18]. (2) The anionic charges on PAM can adsorb the positively charged nutrient ions (e.g., NH_4^+-N) from soil and water, resulting in lower concentrations of some nutrients in the runoff [17,18]. This agrees with the more dramatical decline in the NO_3^--N concentration in the early runoff compared with NH_4^+-N in both unamended soil and PAM amended sandy soil in this study, as NO_3^--N is a very soluble anion and could be quickly removed by runoff, while either soil or PAM had a higher adsorption capacity of NH_4^+-N than that of NO_3^--N [18].

Previous studies demonstrated that CFA dominated by silt particles can fill the relatively large pores of coarse-textured sandy soil, and therefore significantly alter the soil texture [8,19]. Yang et al. [10] reported that CFA had a negative impact on the ability of sandy slope to resist rainfall erosion. This can be the possible reason for the increased NO_3^--N concentration in the runoff by the single use of 10% CFA in this study. However, the decreased NO_3^--N concentration in the runoff in the sandy soil amended with a higher CFA dosage of 15% in this study was inconsistent with the findings of Yang et al. [10], who demonstrated that the negative impact of CFA on the resistance of sandy soil to water erosion became more significant with increasing CFA dosage. A plausible explanation for the above phenomenon observed in this study can be owed to the stronger sorption of nutrients (e.g., NO_3^--N, NH_4^+-N, and P) by CFA at a higher CFA dosage [7]. This can also be the main reason for the decreased NH_4^+-N concentration in the runoff by the single use of CFA, which was generally more significant at a higher CFA dosage of 15%.

The NO_3^--N and NH_4^+-N concentrations in the runoff were influenced by both CFA and PAM when they were co-applied. The effect of PAM on reducing NO_3^--N and NH_4^+-N concentrations in the runoff was noted in 10% CFA + 0.01–0.02% PAM treatments compared with 10% CFA alone treatment, whereas the above reducing effect became less obvious in 15% CFA + 0.01–0.02% PAM treatments compared with 15% CFA alone treatment. The correlation analysis between N concentration in the runoff and runoff rate (Figures 4 and 5) or sediment rate (Figures 6 and 7) reflected that the loss of NO_3^--N and NH_4^+-N with runoff was more significantly associated with runoff rate in comparison with sediment rate. The strong negative relationship between runoff-associated NO_3^--N or NH_4^+-N concentration and runoff rate was resulted from the decreasing trend in the NO_3^--N or

NH_4^+-N concentration in the runoff and increasing trend in the runoff rate with increasing rainfall period.

When the rainfall event ended, the cumulative NO_3^--N loss with runoff was increased by the single use of CFA and PAM as well as co-application of CFA and PAM compared with the unamended soil. The lowest increase in the cumulative NO_3^--N loss with runoff was noted in 0.01–0.02% PAM alone treatments and 15% CFA alone treatment (Figure 8a). This is consistent with the above reducing effect of PAM and higher CFA dosage on the NO_3^--N concentration in the runoff. In addition, the cumulative nutrient loss with runoff in this study depended on both nutrient concentration in the runoff and runoff rate (Equation (2)). As the runoff rate was increased more greatly by CFA and PAM [10], the cumulative NO_3^--N loss with runoff was increased to different extent. Similarly, the addition of CFA and PAM also increased the cumulative NH_4^+-N loss with runoff except for the nonsignificant small increase in the value in 15% CFA alone treatment and 10% CFA + 0.01% PAM treatment compared with the unamended soil (Figure 8b). This can be ascribed to the effect of CFA and PAM on reducing the NH_4^+-N concentration in the runoff.

After the rainfall event, the NO_3^--N and NH_4^+-N concentrations retained in the soil profile were increased by the single use of CFA and PAM, and the retention of NO_3^--N and NH_4^+-N in the sandy soil layer was further enhanced by the co-application of CFA and PAM with increasing dosage (Figures 9 and 10). The improved nutrient storage capacity of sandy soil can be ascribed to three reasons: (1) Fine CFA particles can increase the sandy soil's capillary porosity and water holding capacity [6,8,10], and therefore hinder the leaching of nutrients within the soil layer. (2) After being dissolved in the infiltrating rainfall, the viscous PAM solution can contribute to the hindering of soil nutrient leaching with water seepage [10,28]. (3) Both CFA and PAM can adsorb nutrient ions [7,17,18], resulting in an increase in nutrient concentration retained in the soil mixture.

5. Conclusions

- Anionic PAM reduced runoff-associated NO_3^--N and NH_4^+-N concentrations originated from a sandy slope.
- The NO_3^--N concentration in the runoff was increased by the addition of 10% CFA while reduced by the addition of 15% CFA. Meanwhile, the NH_4^+-N concentration in the runoff in CFA amended sandy soil was reduced.
- When CFA and PAM were co-applied, the reducing effect of PAM on NO_3^--N and NH_4^+-N concentrations in the runoff was noted in a lower CFA dosage of 10% and 0.01–0.02% PAM treatments.
- CFA had a greater effect on increasing the concentrations of NO_3^--N and NH_4^+-N retained in the sandy soil layer compared with PAM.
- The co-application of CFA and PAM had an additive effect on improving the nutrient storage capacity of sandy soil, in particularly at higher CFA and PAM dosages.

Supplementary Materials: The following are available online at https://www.mdpi.com/2077-0472/11/1/47/s1, Table S1: Physicochemical properties of the model soil and CFA.

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