

Article

Causes of the Aging Effect of Polyacrylamide Addition in Sandy Loam Soil Under Alternating Drying and Wetting Conditions: Column Infiltration

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Abstract

Polyacrylamide (PAM), as a widely used effective soil conditioner, can decrease sandy soil infiltration, but its function may decline significantly in a short time. Previous study results showed that the annual degradation rate of PAM in soil is about 10%, and the migration ability of PAM in soil is fairly weak; thus we hypothesized that the functional group of PAM is prone to aging caused by physical and biological factors, which is different from degradation caused by the breaking of long main chains into short ones. The sandy loam soil was selected to conduct column infiltration experiments to (1) determine the effects of PAM application and drying and wetting intensity on infiltration and (2) identify the causes of the aging effect. Soil samples were treated with three doses of PAM (0, 1, and 2 g·kg⁻¹) and incubated in three soil water conditions (constant wetting, moderate and strong drying/wetting cycles). Under constant wetting condition, the stable infiltration rates of soils were decreased by PAM. However, after two strong drying and wetting cycles, the decrement of infiltration rates of PAM-treated soils was reversed. The results of FTIR suggested that drying and wetting cycles led to the hydrolysis of amide groups in PAM, resulting in the weakening of PAM's function on soil infiltration characteristics. The leaching amounts of NH₄⁺-N generated by the amide group hydrolysis increased through the drying/wetting alternation and the application of PAM. Therefore, based on the findings of this column study using a specific sandy loam soil under controlled intense drying–wetting cycles, reapplication of polyacrylamide (PAM) after two cycles may facilitate the sustained lowering of infiltration. However, this recommendation should be confined to analogous experimental conditions and necessitates further validation under field scenarios or for alternative soil types.

Keywords: drying and wetting alternation; sandy loam; FTIR analysis; amide groups hydrolysis



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1. Introduction

Polyacrylamide (PAM), polymerized from acrylamide monomers, primarily functions as a flocculant and has been widely applied in petroleum and wastewater industries [1,2] and in agricultural practices [3–7]. In soils, PAM can bind soil particles to form aggregates, improving soil structure and soil moisture status, reducing soil erosion [8–12].

It can also be used to effectively control the transport of pollutants, nutrients, and pesticides in soil runoff [5,13,14]. Moreover, PAM increases soil available water content and provides a nitrogen source for microorganisms, so as to promote crop yield and quality [6,7]. Specifically, sandy soils, characterized by high permeability, exhibit a limited capacity to retain water and nutrients. The application of polyacrylamide (PAM) effectively enhances water and fertilizer use efficiency, thereby improving crop yields.

Previous studies have demonstrated that the annual degradation rate of PAM in soils is only 10% [15,16]. Kang et al. [17] used experiments and a dual-porosity model to show that PAM exhibits low mobility within soils, which suggests that PAM undergoes strong adsorption onto soil particle surfaces rather than migrating into deeper soil layers. If this is the case, PAM should maintain long-term influences on soil properties. However, many studies demonstrated that PAM has remarkable effects initially but the effects are significantly weakened after one or several irrigation/rain events. Kornecki et al. [18] observed that PAM plays a prominent role in reducing soil erosion (88%) during the first three rainfall events after application to soils, but the effects are weakened significantly in the subsequent rainfall events. Investigations on the role of PAM in soil erosion control have discovered that the amount of soil runoff is not affected by PAM after the third irrigation [19]. Sepaskhah and Shahabizad [20] found that after the addition of PAM, irrigation with ordinary water and waste water reduces surface runoff by 28% and 25% in the first irrigation event, respectively. However, the effects of PAM decrease significantly during the second irrigation. Other studies have also shown the relatively short duration of PAM's effect in soil [21,22]. The effectiveness of PAM as a soil amendment is based on its flocculation of amide groups with soil particles by direct or indirect adsorption via exchangeable cation bridges [5,8,23]. Although various types of PAM with different structures and molecular types have been introduced to agriculture [8,21], the basic mechanisms of soil amendment are the same as mentioned above, which are the formation of soil aggregates due to the adsorption between amide groups and soil particles [8,13,23,24].

We assumed that alterations to PAM's primary functional groups, induced by the complex physicochemical properties of soil, result in the weakening or loss of its efficacy—a process defined as “aging”. Unlike degradation, the stable long-chain structures of PAM are not degraded into shorter chains during an aging process. However, once applied to soil, PAM becomes difficult to extract, making it challenging to study how soil affects its transformation. For that reason, studies have paid little attention to the issue before. A convenient analytical method for solving this problem without the need to separate the polymer–soil complexes is established by Fourier Transform Infrared Spectroscopy (FTIR) [5]. Determining the optimal timing for PAM application is advantageous, as it can reduce the economic costs of soil conservation and mitigate the potential risks associated with overuse. Furthermore, previous studies have demonstrated that PAM-treated soils exhibit higher levels of soil amidase and urease—enzymes involved in nitrogen cycling [25,26]. Additionally, bacterial enrichment cultures from agricultural soil can utilize PAM as a sole nitrogen source [25,26]. This represents another biological aspect of PAM aging effects, which needs further investigation into how PAM contributes to nitrogen production in soil.

The effects of PAM in soil are also influenced by soil water status [19,21,24,27,28]. Soil moisture, particularly the cycles of drying and wetting, also affects PAM's performances. Soil drying reduces the distance between the main chain of PAM and soil particle surfaces, promoting the formation of irreversible adsorption [29,30]. Irrigation techniques and precipitation cause significant fluctuations in soil water content [2]. Alternating drying and wetting in soil exerts complex effects on soil structure and aggregates [31]. Ma et al. [32] showed that this process reduces the stability and tensile strength of water-stable

aggregates in undisturbed soils. Additionally, drying and wetting cycles cause variation in soil redox potential [33,34], which would affect the efficacy of PAM. Furthermore, after a drying and wetting cycle, the cohesive force between PAM and soil particles becomes stronger [13].

Given the short duration of PAM's effectiveness in soil, we propose the following two hypotheses: (1) after application, hydrolysis of PAM's functional groups alters its efficacy; (2) soil drying and wetting cycles affect the durability of PAM's effects. Accordingly, the present study examined how drying–wetting cycles and PAM application rates affect water infiltration in sandy loam soil, and investigated changes in PAM's functional group structures using infrared spectroscopy.

2. Materials and Methods

2.1. Soil Samples

Soil samples were collected from the Red Soil Ecological Experiment Station of the Chinese Academy of Sciences, located in Yingtan City, Jiangxi Province, China (28°14' N, 116°53' E), at an average elevation of 45 m. The site has a typical subtropical monsoon climate, and the annual average temperature and precipitation are 17.7 °C and 1750 mm, respectively. Approximately 50% of the annual precipitation occurs from March to July in each year. The frost-free season lasts 262 days. The soil, developed from red sand shales, is classified as Inceptisols [35]. The primary crop is peanut, and the main clay mineral is kaolinite, and each chemical and physical property of soil was measured three times, with samples collected from different points at a depth of 0.15 m from the surface (Table 1). Soil samples were collected from the surface to a depth of 0.15 m in 2015, then air-dried, crushed, and passed through a 1 mm sieve. Sundries, such as plant roots, were removed from the samples. The processed soils were stored prior to analysis.

Table 1. The chemical and physical properties of tested soil.

Soil	Bulk Density (g/cm ³)	Field Capacity (v/v)	pH	Particle Size (%)			Soil Organic Matter (g/kg Soil)
				Sand	Silt	Clay	
Sandy loam	1.20	21.1%	4.9	69.5	12.3	18.2	2.13

2.2. Preparation of Soil Columns and Incubation Experiment

The prepared soils were thoroughly mixed with anionic PAM at three application rates: 0, 1, and 2 g·kg^{−1} (designated as P0, P1, and P2, respectively). The anionic PAM used had an average molecular weight exceeding 5×10^6 . The soils were filled into the 15 cm high organic glass columns according to their natural density. The glass columns, which had an inner diameter of 4 cm, had drain holes on the bottom. The 200-mesh filter cloth were placed at the bottom of the glass columns to prevent the leakage of soil particles. The side walls of the organic glass columns were painted with Vaseline in order to prevent the generation of preferential flow. The soil that was filled into the column had a height of 8 cm, and 1 cm quartz sands were placed on the top and bottom of the soil, respectively. Deionized water was slowly added to the soil column in accordance with the soil field capacity. It was important to ensure that the water contents of all soil samples were uniform and no leakage occurred during the wetting process.

The prepared soil columns were divided into two groups: (1) a constant moisture (W0) group and (2) drying and wetting cycle groups. The samples undergoing drying and wetting alternation were further divided into two subgroups: a moderate drying intensity group (W1), in which soil water content decreased from field capacity to 70% of field capacity during drying, and a strong drying intensity group (W2), in which soil

water content decreased from field capacity to 40% of field capacity during drying (Table 2). Consequently, the experiment consisted of nine treatment combinations (W0P0, W0P1, W0P2, W1P0, W1P1, W1P2, W2P0, W2P1, and W2P2), each with three replicates.

Table 2. Experimental design.

Soil	Drying and Wetting Intensity	PAM Application Rates (g/kg Soil)		
		0	1	2
Sandy loam	Constant moisture	W0P0	W0P1	W0P2
	Moderate drying and wetting	W1P0	W1P1	W1P2
	Strong drying and wetting	W2P0	W2P1	W2P2

Note: Constant moisture means that the soil water content was always equal to the field capacity; moderate drying and wetting mean that soil water content decreased from the field capacity to 70% of field capacity during drying; strong drying and wetting means that soil water content decreased from the field capacity to 40% of field capacity during drying.

For the constant moisture group (W0), soil columns were weighed periodically, and the water lost was added back to maintain the soil at field capacity. The drying–wetting treatments involved three complete cycles. In each cycle, the drying process lasted 14 days, and the rewetting process lasted 2 days. During the drying process, all soil samples of the same treatment were placed in one sealed plastic box. The drying time was controlled by drying agent so that the samples subjected to different drying intensities would simultaneously reach their target lower moisture limits (70% or 40% of field capacity). During the rewetting process, the lost water of different treatments was slowly added back into soil columns. After adding deionized water, the soil columns were placed in a constant-temperature (25 °C) incubator for 2 days in order to achieve uniform distribution of soil water; the soil column tops were sealed with plastic film to minimize evaporation.

2.3. Measurement Methods

Parameters were measured after the initial wetting and every re-watering, resulting in four measurement time points: on the 3rd, 19th, 35th, and 51st days of incubation. On these days, all soil columns were maintained at field capacity prior to measurement. Soil water infiltration characteristics were determined using a constant-head vertical infiltration method. A constant infiltration head of 3 cm was maintained using a Mariotte bottle (inner diameter: 4 cm; height: 30 cm). Infiltration rates were calculated according to the infiltration volume and time, the stable infiltration rate was determined when the infiltration rate stabilized. Leachate was collected during infiltration, and its $\text{NH}_4^+\text{-N}$ concentration was analyzed by the indophenol blue colorimetry method at 625 nm using an ultraviolet spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan). For each treatment, infiltration measurements and $\text{NH}_4^+\text{-N}$ concentration measurements in the leachate were performed for every replicate. After the infiltration tests, soil was removed from the organic glass columns, air-dried, crushed, and passed through a 100 μm sieve for Fourier transform infrared spectrum analysis by a spectrometer (VERTEX 70, Bruker, Bremen, Germany). Fourier transform infrared (FTIR) spectroscopy analysis identified the antisymmetric stretching peak of amide groups ($-\text{NH}_2$) [36,37] and the absorption peaks corresponding to $-\text{CH}_2$ and $-\text{CH}$ [38–40] in the main chain of polyacrylamide (PAM).

2.4. Data Analysis

A two-way mixed-design repeated-measure ANOVA was conducted with time as the within-subject factor and different PAM application rates as the between-subject factor. Tukey tests were used to assess the differences among means; the significant differences were based on $p < 0.05$. All the statistical analyses were performed using SPSS 16.0 software.

3. Results

3.1. Soil Stable Infiltration Rate

The soil infiltration characteristic was decreased by the application of PAM under constant soil moisture. On the 3rd day of incubation experiment, the stable infiltration rates of W0P1 and W0P2 were lower than those of W0P0 (Table 3), and this phenomenon persisted throughout the whole incubation period. On the 35th day of the incubation experiment (corresponding to two drying and wetting cycles), the stable infiltration rates of W0P1 and W0P2 were 21% and 57% lower than those of W0P0, respectively; on the 51st day of the incubation experiment, the stable infiltration rates of W0P1 and W0P2 were 66% and 45% lower than those of W0P0, respectively.

Table 3. The stable infiltration rate under constant wetting (W0).

PAM Application Rate (g·kg ^{−1})	Stable Infiltration Rate (mm/min)			
	Day 3	Day 19 (1 W/D Cycle)	Day 35 (2 W/D Cycles)	Day 51 (3 W/D Cycles)
P0	1.86 ± 0.14 a	0.92 ± 0.12 a	1.04 ± 0.07 a	1.18 ± 0.23 a
P1	1.02 ± 0.35 b	0.61 ± 0.07 a	0.82 ± 0.21 a	0.4 ± 0.20 b
P2	1.10 ± 0.26 b	0.76 ± 0.17 a	0.45 ± 0.05 b	0.64 ± 0.23 ab
Mauchly's W		χ^2		<i>p</i>
0.483		3.439		0.639
Repeated-measure ANOVA	F	<i>p</i>		η^2
Main effect of time	19.378	<0.001		0.764
Main effect of treatment	27.459	0.001		0.902
Interaction time × treatment	3.133	0.028		0.511

Note: Different lowercase letters in each column indicate significant differences ($p < 0.05$) among treatments with different PAM rates under the same incubation time.

However, this decline was attenuated by soil drying and wetting cycles (Tables 4 and 5). Moreover, the relationship between the stable infiltration rates of untreated and PAM-treated soils was reversed under intense drying–wetting alternations. After two and three intense drying–wetting cycles, higher stable infiltration rates were observed in PAM-treated soils compared to those without PAM. On the 35th day of the incubation experiment (corresponding to two drying–wetting cycles), the stable infiltration rates of W2P1 and W2P2 were 65% and 37% higher than those of W2P0, respectively; on the 51st day, the stable infiltration rates of W2P1 and W2P2 were 22% and 90% higher than those of W2P0, respectively. Notably, a significant difference was observed between W2P2 and W2P0 on the 51st incubation day.

Based on the results of the repeated-measure analysis of variance (ANOVA), under constant soil moisture conditions (Tables 3–5), the infiltration rates of soils amended with PAM were consistently lower than those of the control group. A significant time × treatment interaction indicated that the inhibitory effect of PAM on infiltration exhibited temporal variation. Under dry–wet cycling conditions, the efficacy of PAM in reducing soil infiltration rate gradually diminished over time. Although the main effect of treatment or its interaction with time reached significance during certain periods, the overall trend demonstrated that the initial suppression of infiltration by PAM weakened progressively with an increasing number of drying and wetting cycles. Collectively, the influence of PAM on soil infiltration rate is co-regulated by moisture conditions and application rate, and its effect varies dynamically over the course of soil drying and wetting cycles, showing a clear tendency to diminish under alternating dry–wet regimes.

Table 4. The stable infiltration rate under moderate drying and wetting cycle (W1).

PAM Application Rate (g·kg ⁻¹)	Stable Infiltration Rate (mm/min)			
	Day 3	Day 19 (1 W/D Cycle)	Day 35 (2 W/D Cycles)	Day 51 (3 W/D Cycles)
P0	1.86 ± 0.14 a	1.00 ± 0.20 a	1.05 ± 0.05 a	1.20 ± 0.10 a
P1	1.02 ± 0.35 b	0.77 ± 0.12 a	0.47 ± 0.05 b	1.09 ± 0.04 a
P2	1.10 ± 0.26 b	0.77 ± 0.15 a	1.05 ± 0.25 a	0.80 ± 0.44 a
Mauchly's W		χ^2		<i>p</i>
0.77		1.237		0.942
Repeated-measure ANOVA	F	<i>p</i>		η^2
Main effect of time	10.563	<0.001		0.638
Main effect of treatment	564.934	<0.001		0.989
Interaction time × treatment:	5.762	0.002		0.658

Note: Different lowercase letters in each column indicate significant differences ($p < 0.05$) among treatments with different PAM rates under the same incubation time.

Table 5. The stable infiltration rate under severe drying and wetting cycle (W2).

PAM Application Rate (g·kg ⁻¹)	Stable Infiltration Rate (mm/min)			
	Day 3	Day 19 (1 W/D Cycle)	Day 35 (2 W/D Cycles)	Day 51 (3 W/D Cycles)
P0	1.86 ± 0.14 a	0.93 ± 0.51 a	1.10 ± 0.01 a	1.28 ± 0.08 b
P1	1.02 ± 0.35 b	0.63 ± 0.40 a	1.82 ± 0.27 b	1.56 ± 0.11 b
P2	1.10 ± 0.26 b	0.63 ± 0.12 a	1.51 ± 0.09 ab	2.43 ± 0.13 a
Mauchly's W		χ^2		<i>p</i>
0.384		4.514		0.486
Repeated-measure ANOVA	F	<i>p</i>		η^2
Main effect of time	30.150	<0.001		0.834
Main effect of treatment	0.943	0.44		0.239
Interaction time × treatment:	12.734	<0.001		0.809

Note: Different lowercase letters in each column indicate significant differences ($p < 0.05$) among treatments with different PAM rates under the same incubation time.

3.2. Soil FTIR Analysis

The antisymmetric stretching peak of amide groups ($-\text{NH}_2$) is observed at 3427 cm^{-1} , whereas the absorption peaks corresponding to $-\text{CH}_2$ and $-\text{CH}$ in the main chain of polyacrylamide (PAM) are located at 2925 and 2840 cm^{-1} , respectively. Following PAM application, the transmittance at 3427 cm^{-1} in PAM-treated soils exhibited a significant decrease (Figure 1), indicating an increase in amide groups due to PAM incorporation. In contrast, the absorption peaks at 2925 and 2840 cm^{-1} , which reflect the main chain content, showed no significant variation. However, after PAM application, the transmittance at 3427 cm^{-1} in soil samples subjected to drying–wetting cycles (W1P1, W1P2, W2P1, and W2P2) increased markedly. These results demonstrated that the content of amide groups decreased as a consequence of the drying–wetting process. The absorption at 2925 and 2840 cm^{-1} exhibited only minimal variation, implying that the main chain of PAM remained unaffected by the drying and wetting cycles.

3.3. Leaching of $\text{NH}_4^+\text{-N}$

Compared with untreated soils, the concentration of $\text{NH}_4^+\text{-N}$ in leachate from PAM-treated soils was relatively high and increased with the PAM application rate (Figure 2), except on the 3rd day of the incubation experiment. The same trend was observed in the total leaching amount of $\text{NH}_4^+\text{-N}$ (Figure 3). After the application of $2\text{ g}\cdot\text{kg}^{-1}$ PAM, the total leaching amount of $\text{NH}_4^+\text{-N}$ was significantly greater in samples subjected to drying

and wetting cycles than in those under constant moisture (Figure 3). This indicated that the drying and wetting cycles generally increased cumulative leaching of $\text{NH}_4^+\text{-N}$ from PAM-treated soils.

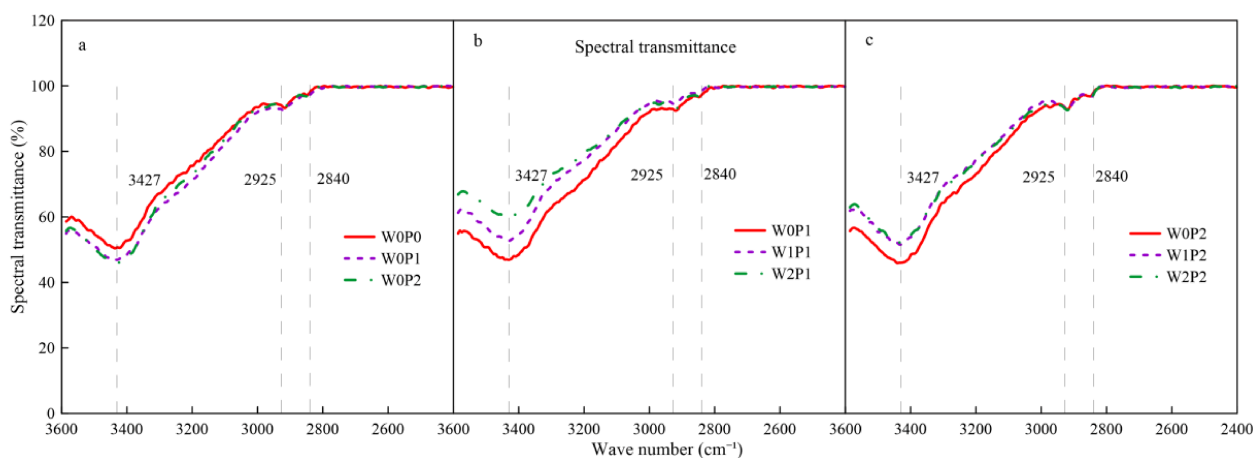


Figure 1. FTIR spectra of the soils with 0, 1, and 2 $\text{g}\cdot\text{kg}^{-1}$ PAM (P0, P1, and P2) under constant wetting (a); the soils with 1 $\text{g}\cdot\text{kg}^{-1}$ PAM under constant wetting (W0), moderate (W1) and strong (W2) drying and wetting cycles after three drying and wetting cycles (b); the soils with 2 $\text{g}\cdot\text{kg}^{-1}$ PAM under constant wetting (W0), moderate (W1) and strong (W2) drying and wetting cycles after three drying and wetting cycles (c).

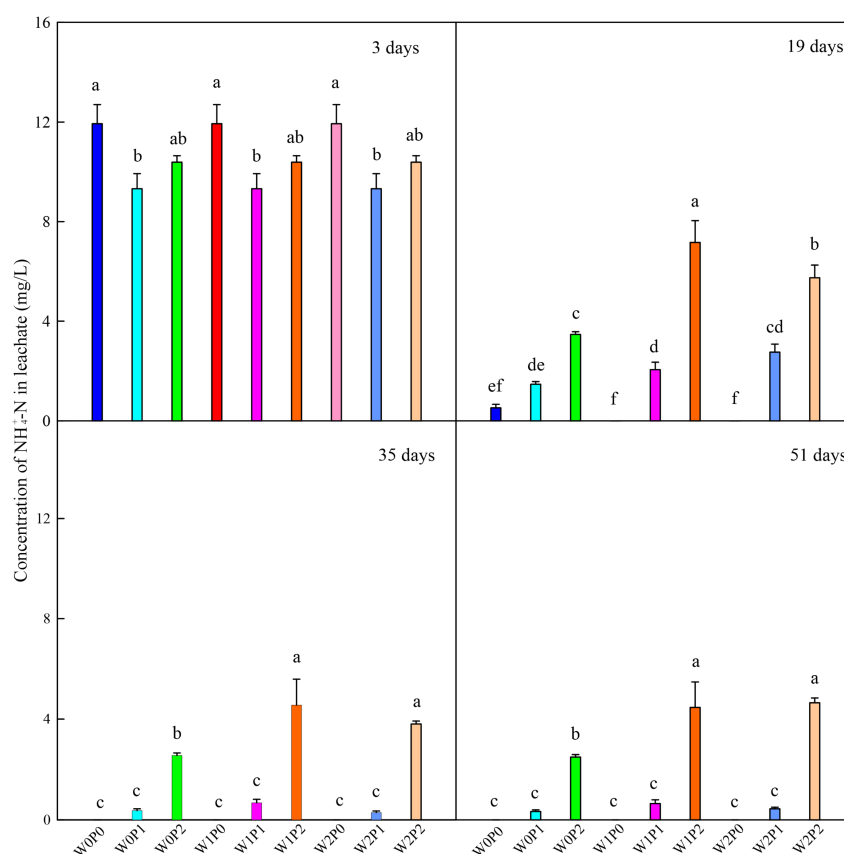


Figure 2. $\text{NH}_4^+\text{-N}$ concentration in the leachate from soils added with 0, 1, and 2 $\text{g}\cdot\text{kg}^{-1}$ PAM (P0, P1, and P2) under constant wetting (W0), moderate (W1), and strong drying and wetting (W2) during the incubation at days 3, 19, 35, and 51. Different lowercase letters over each column indicate significant differences ($p < 0.05$) among treatments with the same incubation time. Vertical bars indicate the standard deviation of the mean.

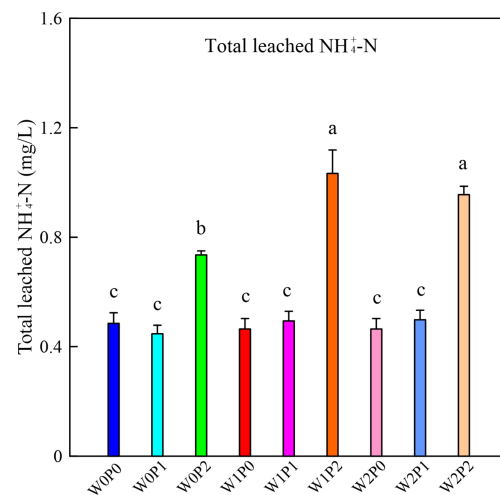


Figure 3. Total NH_4^+ -N leached from the columns of the soils added with 0, 1, and 2 $\text{g}\cdot\text{kg}^{-1}$ PAM (P0, P1, and P2) under constant wetting (W0), moderate (W1), and strong drying and wetting (W2). Different lowercase letters over each column indicate significant differences ($p < 0.05$) among treatments. Vertical bars indicate the standard deviation of the mean.

4. Discussion

4.1. Effects of PAM on Infiltration Rates of Soils Without Influences of Drying and Wetting

In sandy loam soil with high permeability—which was composed mainly of primary particles and lacked stable aggregates—PAM could reduce infiltration rates. This was because, in such soils, PAM’s ability to increase viscosity of the infiltrating water became the dominant phenomenon [5,13,41]. When PAM molecules adsorbed onto soil particles, some polymer segments extended away from the surfaces as loops and tails. These can cause steric interference with infiltrating water itself, thereby decreasing its flow rate through soil pores [41].

4.2. Aging Phenomenon of PAM in Sandy Loam Soil Caused by Drying and Wetting

After several drying and wetting cycles, the ability of PAM to affect soil infiltration rates was eliminated—a phenomenon previously defined as PAM aging. The results showed that after two strong drying and wetting cycles, the PAM-treated soils exhibited higher infiltration rates than untreated soils. Similar results were observed by Gardiner and Sun [42] and Sepaskhah and Shahabizad [20]. Inbar et al. [13] manually spread PAM granules on the soil surface and observed significantly lower infiltration rates during the first simulated rain storm, but not during subsequent storms. This observation suggested that the reverse of infiltration rate occurred because the PAM molecules were eventually washed away by runoff. But in our study, PAM was thoroughly mixed into the soil before the leaching process, indicating that removal by runoff was not the main cause of PAM aging. Shainberg et al. [30] considered that the eluent containing divalent cations could lead to tighter coiling and greater contraction of polymer chains, thereby reducing the viscosity of the PAM solution. In our research, however, the leachate was deionized water, which implied that changes in PAM molecules in soil occurred spontaneously under drying and wetting cycles.

Meanwhile, there were no significant differences in absorption at 2925 and 2840 cm^{-1} between the drying–wetting cycle treatments and the constant moisture treatment, indicating that the main chain of PAM was not affected by the drying and wetting. This indicated that the changes in soil infiltration rate were not affected by the main PAM chain.

4.3. Causing of Aging of PAM After Drying and Wetting Cycles

The spectral transmissivity at 3427 cm^{-1} (corresponding to amide groups) was significantly higher in PAM-treated soils subjected to drying and wetting cycles than in those under constant moisture. This implied that the obvious reduction in amide groups was observed after cycles of drying and wetting. Results from recent studies suggested that the $\text{NH}_4^+\text{-N}$ mainly comes from the hydrolysis of amid-N in PAM [25,26]. As compared with soils without PAM, the significantly higher amount of $\text{NH}_4^+\text{-N}$ leached (Figures 2 and 3) and reduction of amide groups in soils detected by FTIR in PAM-treated soils (Figure 1) together suggested that the $\text{NH}_4^+\text{-N}$ originated from the hydrolysis of amid-N in PAM. Moreover, PAM application to soils had also been correlated with increased activity of soil microbes and enzymes involved in nitrogen cycling, such as urease and amidase [25,26,43,44].

Changes in soil moisture significantly influence potential extracellular enzyme activities [45,46]. Soil drought alters microbial biomass, activity, and enzyme turnover, thereby suppressing extracellular enzyme activities by shifting microbial metabolism [46–48]. The results of Henry [45] also reported that the moisture decline in saturated soil can effectively increase the soil enzymes' activities, but the enzyme activity decreases with the continuous decline in soil water. The aforementioned conclusions implied that the optimal soil moisture is crucial for soil enzymes' activity. Therefore, the process of soil drying and wetting may periodically create conditions that promote enzymatic activity. Moreover, drought can promote the release of nutrients from enzymes and provide excess labile carbon sources, which stimulate the soil enzymes' activities in the subsequent rewetting process [49,50]. Consequently, the activities of urease and amidase for ammonia release from amides may be promoted by the soil drying and wetting [51–53]. Based on the findings of other studies mentioned above, enzymatic activity may be enhanced under drying and wetting cycles, and this enhancement could explain the accelerated hydrolysis of amide groups in PAM. The significantly higher total leaching amount of $\text{NH}_4^+\text{-N}$ from PAM-treated soils under drying and wetting cycles compared to constant moisture conditions may also be influenced by enzymatic activity (Figure 3).

Drying and wetting cycles slowed down the decrease in infiltration characteristics of sandy loam in the presence of PAM. After two cycles of strong drying and wetting, the sandy loam with added PAM exhibited higher infiltration rates compared to treatments without PAM. It has been suggested that hydrolysis of amide groups may modify the side chains of PAM, potentially altering its interaction with soil particles or its solution conformation [29,54]; however, no direct evidence of main-chain degradation was observed in our FTIR data. Previous studies have proposed an alternative mechanism: a drying cycle after PAM application allows shorter distance and closer interaction between dissolved PAM molecules and soil particles, leading to enhanced and more irreversible adsorption [13,55]. As a result, under drying and wetting cycles, greater soil porosity is formed compared to constant moisture conditions, which contributes to enhanced infiltration capacity. Therefore, after three moderate drying and wetting cycles, the steady infiltration rate of the soil approximated that observed under constant moisture conditions. Conversely, after three strong drying and wetting cycles, the soil exhibited a significant increase in its steady infiltration rate. This phenomenon is primarily attributed to the more tightly bound state of dissolved PAM molecules to soil particles induced by strong drying and wetting cycles, thereby creating larger soil pores and consequently enhancing the soil infiltration rate.

It should be noted that the FTIR spectra were collected only from 2400 to 3600 cm^{-1} , where the band at $\sim 3427\text{ cm}^{-1}$ may arise from both O–H and N–H stretching. Although the decrease after treatment is consistent with amide reduction, interference from water or mineral hydroxyls cannot be ruled out. The absence of a stable internal reference precludes quantitative analysis; therefore, this result serves only as qualitative supporting evidence.

5. Conclusions

When soil moisture was maintained at a constant level, the stable infiltration rates of sandy loam soils were reduced by PAM. However, the function of PAM in improving soil infiltration was weakened after drying and wetting cycles, which was defined as aging of PAM. In sandy loam soil, the opposite trend occurred after the second strong drying and wetting cycle, regardless of added PAM rates, leading to a rapid increase in soil infiltration rates. The results of FTIR revealed possible reasons for this aging. The FTIR analysis at 3427 cm^{-1} indicated that the contents of amide groups in soils treated with PAM were decreased by the drying and wetting alternations, resulting in the weakening of PAM's function on soil infiltration characteristics. The hydrolysis of PAM amide groups was supported by the increase in the amount of $\text{NH}_4^+\text{-N}$ leached. The leaching amounts of $\text{NH}_4^+\text{-N}$ from the soils were increased by the application of PAM and the drying/wetting alternation. This mechanistic understanding of PAM behavior in soils can explain the aforementioned inconsistent research findings, specifically that the loss of PAM's efficacy occurs much faster than its chemical degradation. Therefore, under the specific experimental conditions employing sandy loam soil in a column setup with controlled intense drying–wetting cycles, it is recommended that PAM be reapplied after two cycles to maintain lower infiltration rates. However, this recommendation should be confined to analogous experimental conditions and necessitates further validation under field scenarios or for alternative soil types.

Author Contributions: Conceptualization, Z.Z., D.X. and T.J.; methodology, Z.Z., D.X. and T.J.; formal analysis, Z.Z. and Q.Y.; investigation, Z.Z., Q.Y. and H.R.; resources, Z.Z., Q.Y., H.R. and T.J.; data curation, Z.Z. and Q.Y.; writing—original draft, Z.Z., D.X. and H.R.; writing—review and editing, Z.Z., Q.Y. and T.J.; supervision, D.X.; funding acquisition, Z.Z. and T.J. All authors have read and agreed to the published version of the manuscript.

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