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Solving Phosphorus Fertilization-Related Drip Irrigation Emitter Clogging by Adding Mn^{2+}

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Abstract: Drip irrigation with a fertilizer application could effectively alleviate the soil pollution caused by excessive phosphorus fertilizer. Phosphate fertilizer was dissolved in water and produced a chemical reaction with the ions in irrigation water. The new precipitates were generated, which caused more severe and complex blockage of drip irrigation emitters. Songhua River water was selected as the irrigation water. The experiment investigated the effects of three types of phosphorus fertilizers (urea phosphate, UP; potassium dihydrogen phosphate, PDP; ammonium polyphosphate, APP) and the concentrations (0.2, 0.3, and 0.4 g/L) on the blockage of drip irrigation emitter. The results showed that three types of phosphorus fertilizers intensified the degree of blockage compared with no fertilization, the order from small to large being UP < PDP < APP. The degree of blockage was directly proportional to the concentration of phosphate fertilizer. The system discharge variation ratio (Dra) under UP, PDP, and APP treatments decreased by an average of 6.2~27.7%, 13.8~33.8%, and 21.5~44.6%, respectively. The Christiansen coefficient of uniformity (CU) decreased by an average of 5.9~23.5%, 10.3~27.9%, and 19.1~38.2%. The UP was superior to PDP and APP from the perspective of drip irrigation evaluation indicators. The main reason was that UP reduced the pH value of the water source and inhibited the generation of carbonates. The APP was unable to lower the pH value and had the most serious blockage. The APP was coupled with three concentrations of Mn^{2+} (1, 2, and 3 mg/L) for drip irrigation, which could optimize the blockage problem and explore the efficacy of Mn^{2+}. The 2 mg/L Mn^{2+} could maximize the drip irrigation efficiency of the APP. The average increase in Dra and CU was 24.57% and 18.54% macroscopically. Mn^{2+} could alter the lattice parameters of carbonates and had a certain impact on their size and morphological distribution on a microscopic level. The results showed that fertilization with UP at a concentration of 0.2 g/L did not significantly exacerbate clogging. The drip irrigation effect of Songhua River water combined with 0.2 g/L concentration UP was the best. Moreover, 2 mg/L of Mn^{2+} was proposed to alleviate the clogging characteristics of APP4. This study could provide reference for improving the efficiency of the Songhua River drip irrigation system.

Keywords: drip irrigation emitter; phosphate fertigation; Mn^{2+}; blocking substances

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1. Introduction

Phosphorus (P) is an important element in all living organisms. Phosphorus promotes photosynthesis in plants that ensures better development of plant roots and stems [1]. The total phosphorus concentration should be 0.1% to 0.5% of the dry weight of plants.

The evaluation of plant uptake of available phosphorus mainly focuses on physical and chemical processes. These processes include adsorption and precipitation dissolution; the cumbersome absorption method reduces the efficiency of phosphorus fertilizer utilization [2,3]. The excessive application of phosphorus fertilizer has caused serious land pollution and increased the risk of phosphorus loss to surface water [4]. The pollution of phosphate fertilizers on ecosystems and phosphorus utilization rate has become one of the most important issues for sustainable development.

Drip irrigation emitters utilize the unique flow channel structure to drip soluble phosphorus fertilizer into the root zone of plants, which has the advantages of water-saving, controllability, and high precision [5,6]. The flow channel structure (only about 1 mm) and drip irrigation fertilization measures (a mixture of soluble fertilizer and drip irrigation water source) causes chemical precipitation blockage inside the drip irrigation emitters [7,8]. The irrigation water contains a large amount of Ca^{2+}, Mg^{2+} and phosphate fertilizer contained other ions ($HPO_4{}^{2-}$, etc.) that react with Ca^{2+} and Mg^{2+} [9]. The chemical reactions are promoted and form blocking substances in fertilized water, which causes the blockage of drip irrigation emitters and triggers a series of chain reactions. This includes the reduced uniformity of drip irrigation, uneven distribution of phosphorus in the plant root zone, frequent replacement of drip irrigation emitters, and increased maintenance costs of drip irrigation systems. The main challenge for the drip irrigation with fertilizer application was to alleviate the problem of blockage.

Previous studies had shown that drip irrigation technology improved the utilization efficiency of phosphorus fertilizer compared to conventional fertilization. Although the efficiency varies, drip irrigation had been proven to be an effective technology for improving phosphorus availability [10,11]. Zhou et al. [12] conducted drip irrigation experiments by mixing high sedimentation water with potassium dihydrogen phosphate. This phosphate fertilizer exacerbated the degree of clogging under different drip irrigation modes. Muhammad et al. [13] studied the clogging situation of using urea phosphate and monopotassium phosphate in saline drip irrigation systems. The urea phosphate at low concentrations could effectively alleviate the degree of blockage. Barrow et al. [14] showed that plants grow best near pH 5.5 and grow worst near neutral pH. The monovalent form of phosphorus in acidic solutions is more easily obtained from phosphate fertilizers. The utilization rate of phosphate fertilizer could reach its maximum value. Gryta [15] indicated that ammonium polyphosphate (APP) could block the growth sites of active crystals and reduced the formation of calcium carbonate by chelating Ca^{2+}. These two types of phosphate fertilizers increase the precipitation of phosphate, silicate, and quartz. To investigate the issue of whether the APP reduced the total amount of sediment values, Xiao et al. [16] indicated the dominant role of Ca^{2+} concentration in drip irrigation water. The phosphorus fertilizer reduced the clogging of drip irrigation emitters at low Ca^{2+} concentrations. The opposite was true at high Ca^{2+} concentrations. The reason was the competitive effect between $PO_4{}^{3-}$ and $CO_3{}^{2-}$ in phosphate fertilizer. The ion concentration in irrigation water could not be reduced through simple methods such as filtration. The effective way to alleviate phosphorus fertilizer blockage was changed to the operating mode of the drip irrigation system at present. Mills et al. [17] indicated that in simple Ca^{2+} containing solutions, Mn^{2+} could significantly reduce the growth of calcium carbonate. The degree of inhibition did not depend on the absolute concentration of Mn^{2+}. The Mn^{2+} is a micronutrient that participated in activating enzyme-catalyzed reactions in plants, which could affect respiration, amino acid synthesis, and lignin biosynthesis [18]. The small amounts of Mn^{2+} were added to drip irrigation water and could promote plant growth.

The Songhua River is the largest river in terms of basin area and flow in northeast China. It plays an irreplaceable role in agricultural irrigation development and water resource management. At present, the blockage problem of adding phosphate fertilizer in the drip irrigation system of Songhua River is still unclear. Previous studies have not clearly described the changes in clogging substances during drip irrigation. On the basis of elucidating the coupling mechanism of water phosphate fertilizer, the characteristics of blocking substances were elucidated from both macroscopic and microscopic perspectives. This study selected three types of phosphate fertilizers (urea phosphate UP, potassium dihydrogen phosphate PDP, and ammonium polyphosphate APP) based on the above reasons. The effect of phosphorus fertilizer on the clogging of drip irrigation emitters and the clogging situation of drip irrigation emitters after adding Mn^{2+} were explored. The purpose of this study was to: (1) study the effects of three types of phosphorus fertilizers on the clogging characteristics of drip irrigation emitters; (2) analyze the degree of blockage after the addition of Mn^{2+} to drip irrigation with fertilizer and the situation of the change at both macro and micro levels; (3) determine the required concentration of Mn^{2+} to alleviate the degree of blockage. The new perspective for alleviating the blockage problem of drip irrigation with fertilizer is provided.

2. Experimental Materials and Methods

2.1. Experimental Design and Instrument Preparation

The methodology for this study was established. The detailed technical roadmap is shown in Figure 1.

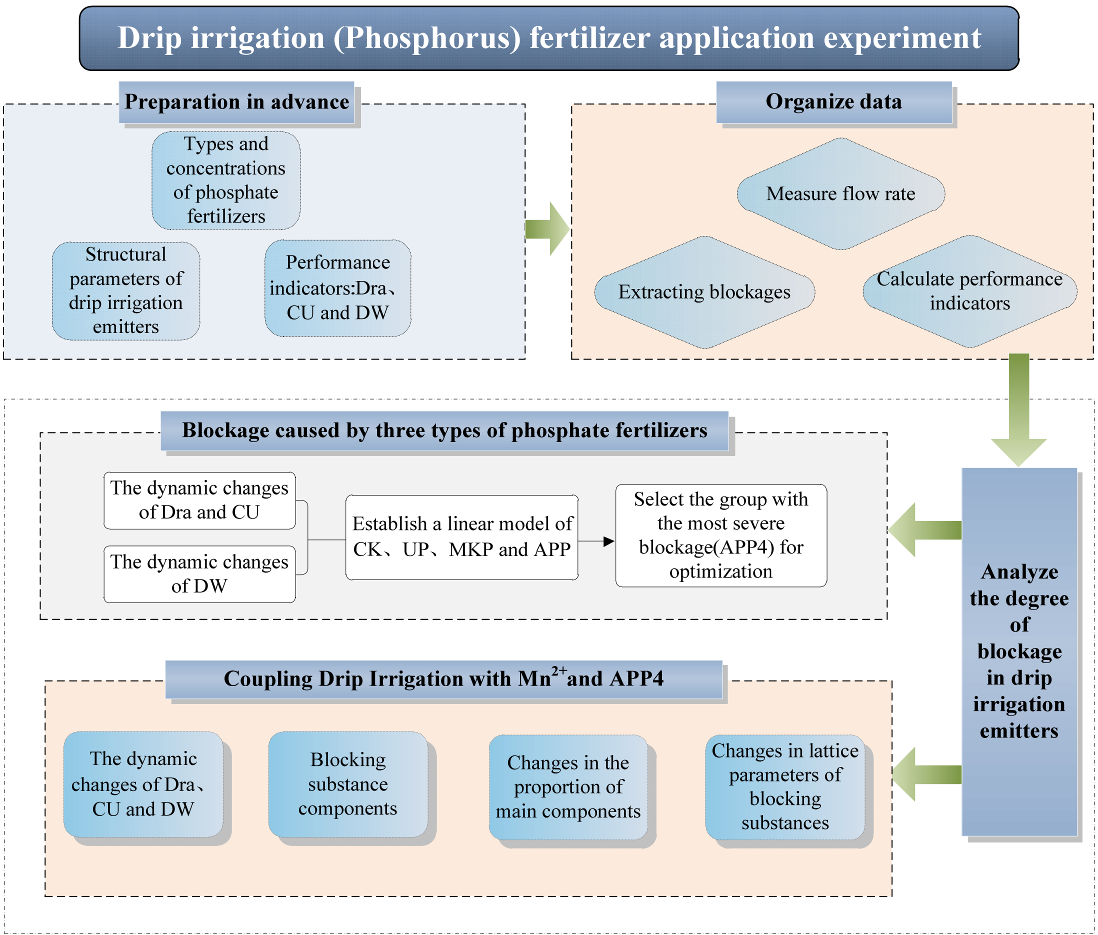


Figure 1. Experimental flow chart of drip irrigation with fertilizer application.

The experiment was conducted at an irrigation station in Harbin, Heilongjiang Province. The irrigation water used was from the Songhua River with multiple samples of water sources used in the drip irrigation experiments. The drip irrigation experiments were conducted for 12 h every day. The temperature and pH values were measured using a thermometer and pH detector at 2:00 pm every day. The water quality was sampled every two days during the experiment. The average ± standard deviation of the water quality is shown in Table 1 and the changes in water pH during experiments are shown in Table 2.

Table 1. Water quality parameters.

pH	Total Suspended Solids (mg/L)	Electrical Conductivity (ms/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Work Pressure (MPa)	Water Temperature (°C)
7.6 ± 0.5	43.6 ± 7.2	754 ± 14	41.7 ± 6.3	34.8 ± 4.7	0.1	16 ± 3

Table 2. The average and standard deviation of water pH under different treatments.

CK	UP2	UP3	UP4	PDP2	PDP3	PDP4	APP2	APP3	APP4
7.6 ± 0.3	6.3 ± 0.3	5.1 ± 0.3	3.7 ± 0.3	7.2 ± 0.3	6.9 ± 0.3	6.7 ± 0.3	7.6 ± 0.3	7.6 ± 0.3	7.6 ± 0.3

Three types of water-soluble fertilizers (urea phosphate, UP; potassium dihydrogen phosphate, PDP; ammonium polyphosphate, APP) and three levels of fertilization (0.2, 0.3, and 0.4 g/L) were applied. The non-fertilized treatment was used a control treatment (CK). The processing methods are summarized in Table 3.

Table 3. Experimental arrangement for drip irrigation.

Experiment Number	Fertilizer	Chemical Composition	Fertilizer Concentration/(g/L)
Ck	-	-	-
UP2	Urea phosphate	$CO(NH_2)_2{\cdot}H_3PO_4$	0.2
UP3	Urea phosphate	$CO(NH_2)_2{\cdot}H_3PO_4$	0.3
UP4	Urea phosphate	$CO(NH_2)_2{\cdot}H_3PO_4$	0.4
PDP2	Potassium dihydrogen phosphate	KH_2PO_4	0.2
PDP3	Potassium dihydrogen phosphate	KH_2PO_4	0.3
PDP4	Potassium dihydrogen phosphate	KH_2PO_4	0.4
APP2	Ammonium polyphosphate	$(NH_4)_{n+2}P_nO_{3n+1}$	0.2
APP3	Ammonium polyphosphate	$(NH_4)_{n+2}P_nO_{3n+1}$	0.3
APP4	Ammonium polyphosphate	$(NH_4)_{n+2}P_nO_{3n+1}$	0.4

The experimental platform for drip irrigation emitters is shown in Figure 2. The filtration equipment of this system consists of two sand filters (T-shaped laminated filter and T-shaped mesh filter). This study aimed to exclude the influence of drip irrigation emitter structure type on experimental factors; the experimental platform had six subunits. The subunits both had an independent layer and used a type of labyrinth drip irrigation emitter (marked as FE1-FE6). The structural parameters of drip irrigation emitters are shown in Table 4. The subunit consisted of 5 drip irrigation branches and 25 drip irrigation emitters. The drip irrigation branch had a length of 1.5 m, inner diameter of 16 mm, wall thickness of 0.2 mm, and hole spacing of 25 cm. The return pipe was installed at the end. The operating pressure of the drip irrigation system was constant at 0.1 MPa and the water tank was equipped with a stirring device to maintain a constant concentration during the operation of the drip irrigation system.

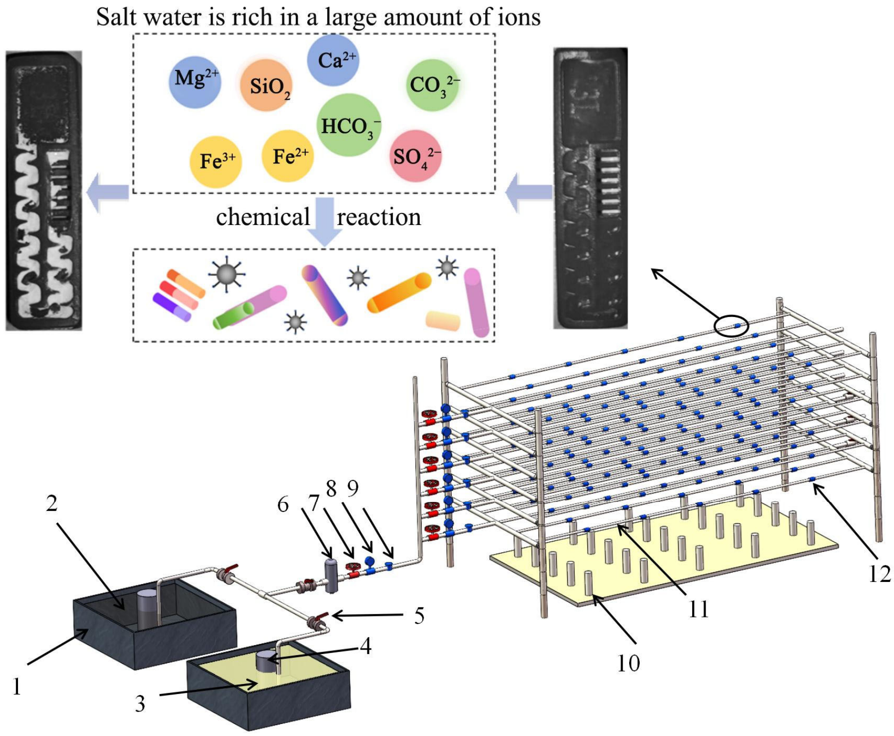


Figure 2. Schematic layout of the drip irrigation testing unit: 1. Water tank; 2. Songhua river water tank; 3. Fertilizer tank; 4. Water pump; 5. Valves; 6. Filter; 7. Pressure reducing valve; 8. Pressure gauge; 9. Water meter; 10. Measuring cylinder; 11. Water pipes; 12. Drip irrigation emitter.

Table 4. Structural parameters of drip irrigation emitters.

Label	Initial Flow (L/h)	Flow Path Length (mm)	Flow Path Width (mm)	Flow Path Depth (mm)	Flow Index	Structural Style
FE1	2.55	26	1	0.7	0.52	
FE2	2.47	22	0.6	0.7	0.56	
FE3	2.70	13	0.8	0.6	0.55	
FE4	2.63	23	0.8	0.7	0.54	
FE5	2.59	24	0.7	0.8	0.55	
FE6	2.71	26	0.8	0.8	0.56	

Note: The flow measuring channel size was measured using an electron microscope. The initial flow and flow index were tested according to the Chinese standard [19].

2.2. The Performance Evaluation Parameters of Drip Irrigation Emitters

The blockage evaluation in drip irrigation experiments was conducted via flow detection. Flow detection was performed by measuring the flow rate of drip irrigation emitters at a given time. In the experiment, the weighing method was used to test the flow rate, the time for measuring the flow rate was set to 5 min. The high-precision electronic balance was used to measure the flow rate in the measuring cylinder. The influence of water temperature on water was eliminated by using Formula (1) to calculate the flow rate of water [20].

$$qT_i = \left(1 + \frac{57.35x - 28.24}{100} \times \frac{T_i - 20}{20}\right) \times q_{20} \quad (1)$$

In the Formula (1): qT_i is the corrected discharge of emitters, L/h; T_i is the water temperature during the test, °C; q_{20} is the design discharge of emitters under 20 °C, L/h; x is flow index.

The system discharge variation ratio (Dra) is the percentage of the average flow rate of drip irrigation emitters to the rated flow rate, which indicates the degree of flow reduction [21]. It is defined as no blockage when the Dra is greater than 75%. It is defined as general blockage when Dra is between 50% and 75%. It is defined as a serious congestion case when Dra is between 25% and 50%. It is defined as completely blocked when Dra is less than 25%. The calculation formula is as follows:

$$Dra = \frac{\sum_i^n \frac{q_i^t}{q_i^0}}{\mathrm{n}} \times 100\% \quad (2)$$

The Christiansen coefficient of uniformity (CU) was calculated based on the Christiansen formula, which comprehensively reflects the working performance of drip irrigation emitters [22]. The performance of drip irrigation emitters is optimal when the CU is greater than 89%. It is moderate when CU is between 71% and 89%. It is poor when CU is less than 71%. The calculation formula is as follows:

$$CU = 100\left(1 - \frac{\sum_{i=1}^n |q_i^t - \overline{q}^t|}{n\overline{q}^t}\right) \quad (3)$$

$$\overline{q}^t = \frac{\sum_{i=1}^n q_i^t}{n} \quad (4)$$

In the Formulas (2) and (3): ${q^0}_i$ is the initial flow rate of the No. i drip irrigation emitter; ${q^t}_i$ is the No. i drip irrigation emitter flow rate tested at sampling time t; $\overline{q}^t$ is the average flow rate of each drip irrigation device along the horizontal direction at sampling time t; n is the total number of emitters along the lateral.

2.3. Extraction and Testing of Blockages

The DW was tested every 4 days. The samples were collected in each subsystem during the experiment. The drip irrigation emitters from the front, middle and end of the pipeline were randomly selected. In order to obtain dry blockage material, the blockage material sample was subjected to constant temperature (60 °C) treatment in a blast dryer for 60 min. The ultrasonic cleaning machine was used to remove blockages (manufacturer: Chaowei, Suzhou, China; Type: GVS-10L; Frequency: 100 Hz). The samples were placed in a zipper bag and added to 20 mL of deionized water. The blocked substance sample was weighed via high-precision electronic scale (with an accuracy of 10^{-4} g). The average value of DW was calculated finally.

The clogging substances were analyzed via the X-ray diffractometer (manufacture: Bruker, Karlsruhe, Germany; type: D8-Advance) to achieve polycrystalline diffraction patterns. The working voltage of the diffractometer was 40 kV and the current was 40 mA. The scanning angle was typically 5~90°. The scanning method was diffraction. Each scan should not exceed 10 min. Copper targets were applied and the wave length was 1.5406 Å. The XRD analysis chart was analyzed via JADE9 software to obtain the mineral content and crystal characteristics of the blockage material. The size and morphology of the blockage material were detected using scanning electron microscopy (SEM) (manufactured: Hitachi Regules8100, type: Tescan Mira4, Guoyi Quantum, AnHui, China.). The sample was sprayed with gold and the working voltage was 20 kV, with a magnification of 2000–5000 times.

2.4. Statistical Analysis

Data were subjected to statistical analysis using SPSS (ver. 19.0 IBM, Chicago, IL, USA). The significance of the independent variable was determined to be $p < 0.05$. Independent *t*-tests were applied to determine significant differences between treatments. Multiple factor analysis of variance (ANOVA) was used to determine the differences in fertilizer type, concentration, drip irrigation system performance parameters (Dra and CU), and DW (the dry weight of clogging substances). The linear regression models were used to analyze the correlation between CK and three types of phosphorus fertilizer drip irrigation treatments.

3. Results

3.1. Effect of Phosphate Fertilizer on Drip Irrigation Emitter Performance

The Dra and CU of drip irrigation emitters under different fertilization treatments are shown in Figure 3. The curve trend was generally characterized by a slow decline in the early stage (0–12 d) and later stage (32–40 d), and a rapid decline in the middle stage (12–32 d). The Dra of UP, PDP, and APP decreased by an average of 6.2%, 18.5%, 27.7%, 13.8%, 24.6%, 33.8%, 21.5%, 30.8%, and 44.6% compared to CK. The average decline in CU was 5.9%, 11.8%, 23.5%, 10.3%, 21.6%, 27.9%, 19.1%, 32.4%, and 38.2%. Overall, the emitter clogging was worse after fertigation. The independent *t*-test between drip irrigation with phosphate fertilizers and CK are shown in Table 5. The results show that most treatments had statistical significance with CK, the fertilizer type and concentration had a significant impact on Dra and CU in drip irrigation systems ($p < 0.05$). The correlation between CK and phosphate fertilizer treatments indicated that phosphorus fertilizer exacerbated clogging of drip irrigation emitters (Figure 4). Its characteristic was that the slope of the fitting curve was greater than 1. The three types of phosphate fertilizers showed the most severe blockage under the treatment of 0.4 g/L, followed by 0.3 g/L, 0.2 g/L. The blockage caused by the same phosphate fertilizer was positively correlated with concentration. The fitting curve quality of Dra and CU was well ($R^2 > 0.94$). The performance of the Songhua River drip irrigation system could be referred to this linear regression equation to quickly predict the degree of blockage and take preventive measures. The UP could significantly alleviate the degree of blockage compared to traditional phosphate fertilizer PDP. The Dra and CU under drip irrigation of UP increased by 8.9%, 8.2%, 9.3%, and 4.9%, 11.1%, and 6.1%, respectively. The APP exacerbated the blockage of drip irrigation emitters. The Dra and CU under drip irrigation of APP reduced by 10.7%, 10.2%, and 16.3% and 9.8%, 14.8%, and 14.3%, respectively. The UP should be used as the preferred phosphate fertilizer when the concentration is the same.

Table 5. Independent *t*-test analysis of Dra and CU under phosphorus fertilizer treatment.

Clogging Parameters	Statistical Parameters	UP2	UP3	UP4	PDP2	PDP3	PDP4	APP2	APP3	APP4
Dra	t-value	0.66	1.97 *	2.37 *	1.77 *	2.01 *	2.47 *	2.34 *	2.49 *	2.81 *
	standard deviation	12.68	15.78	18.11	14.76	17.15	19.21	15.84	17.49	20.24
	Mean value difference	2.93	10.14	13.20	8.60	10.80	14.33	11.92	13.53	16.97
CU	t-value	0.59	1.17	1.98 *	0.76	1.32 *	1.99 *	1.42 *	2.28 *	2.52 *
	standard deviation	11.82	12.92	15.83	12.53	13.95	16.05	14.59	17.42	19.16
	Mean value difference	2.45	5.13	9.87	3.26	6.07	9.72	6.73	12.13	14.48

Note: * indicates significant ($p < 0.05$).

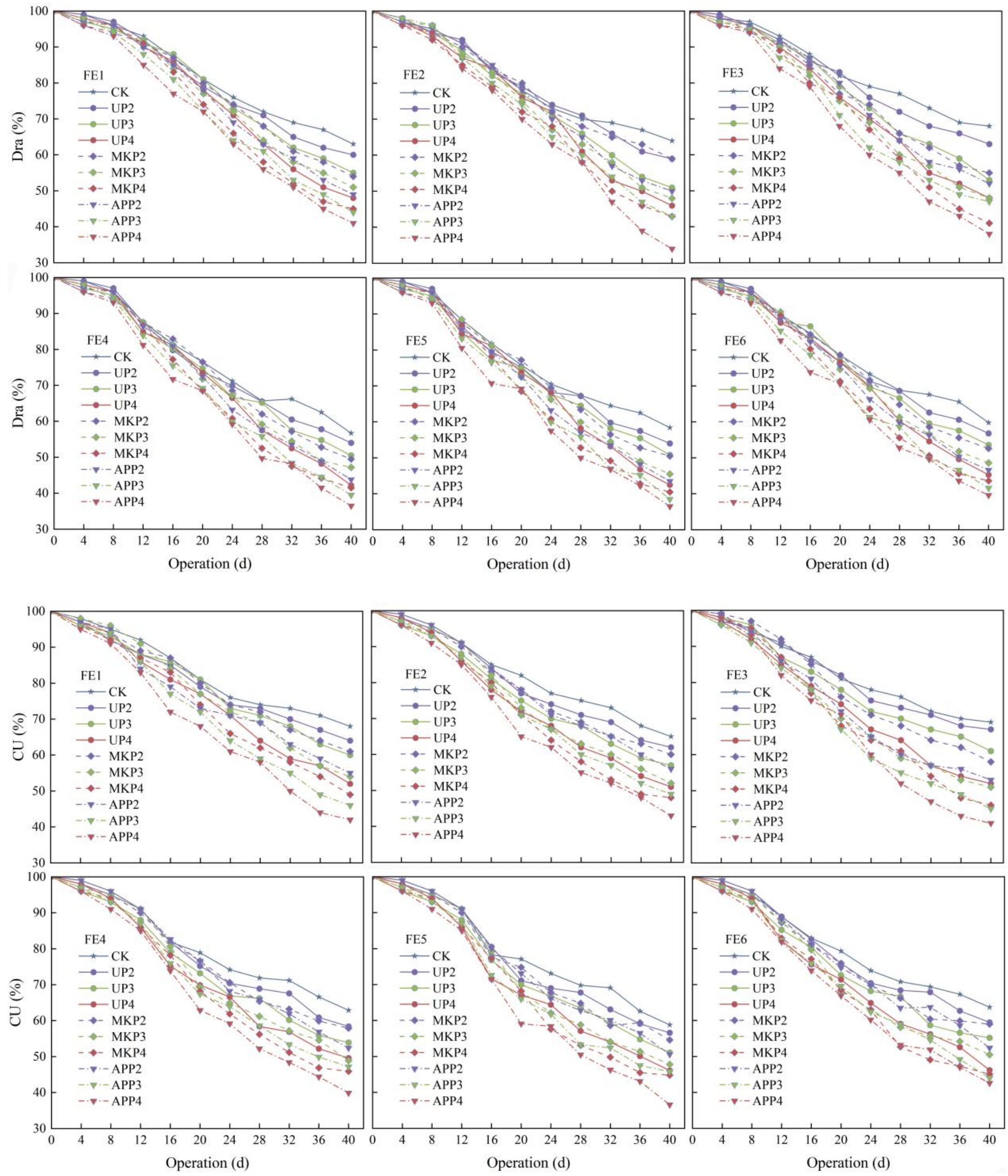
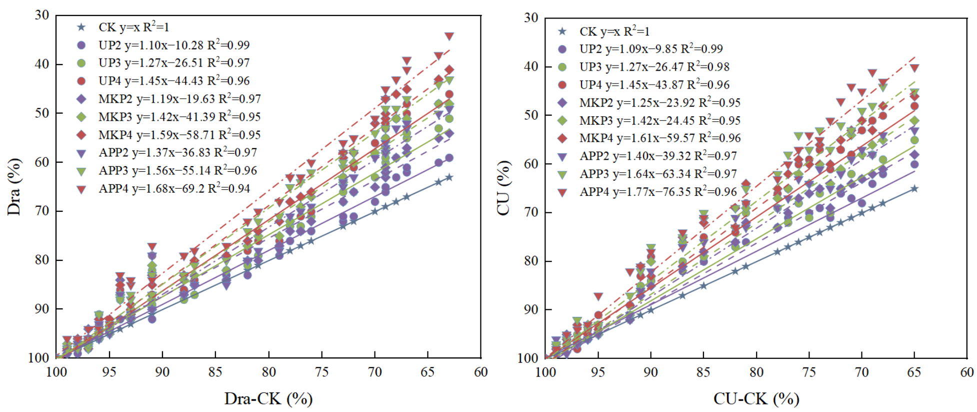


Figure 3. The dynamic changes in the phosphate fertilizer drip irrigation system discharge variation ratio (Dra) and the Christiansen coefficient of uniformity (CU).



(**a**) (**b**)

Figure 4. The correlation between Dra (**a**) and CU (**b**) between CK and phosphorus fertilizer treatment.

3.2. Effect of Phosphate Fertilizer on the Dry Weight of Clogging Substances

The dry weight (DW) of clogging substances inside different drip irrigation emitters showed a similar trend under different treatments (Figure 5). It showed that the DW grew slowly in the early stages of the experiment (0–12 days) and rapidly in the middle and late stages (12–40 days). The DW treated with drip irrigation increased by an average of 10.3%, 24.2%, 38.9%, 19.7%, 34.2%, 45.6%, 30.3%, 52.1%, and 58.2% compared to CK. The independent *t*-tests between phosphorus fertilizers and CK are shown in Table 6. The results showed that most treatments had statistical significance with CK. Fertilizer type and concentration had a significant impact on DW ($p < 0.05$). The correlation between CK and phosphorus fertilizer treatments (Figure 6) indicated that phosphorus fertilization led to an increase in DW, which is characterized by a slope of the fitting curve greater than 1. The larger the slope of the fitting curve, the greater the clogging of substances. The fitting curve quality of DW was well ($R^2 > 0.93$). Compared with traditional phosphorus fertilizer PDP, the average reduction in DW under UP treatments was 10.1%, 8.2%, and 6.9%. The average increase in DW under APP treatments was 8.6%, 10.7%, and 7.4%. The changing trend of the DW curve and the slope of the fitted curve were consistent with Dra and CU, which indicated that an increase in clogging material led to a decrease in the performance of drip irrigation emitters. The 0.2 g/L UP had no significant effect on Dra, CU, or DW. The UP could reduce the content of clogging substances and improve drip irrigation efficiency.

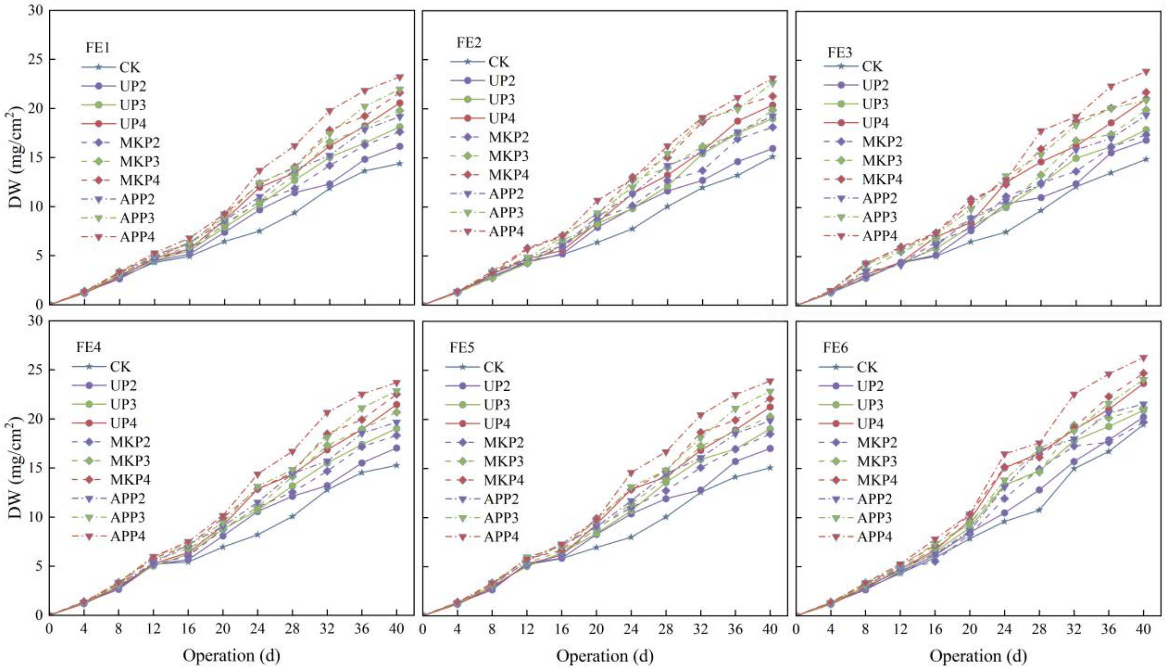


Figure 5. The dynamic changes of dry weight (DW) of blockages in phosphate fertilizer drip irrigation system.

Table 6. Independent *t*-test analysis of DW under phosphorus fertilizer treatment.

Clogging Parameters	Statistical Parameters	UP2	UP3	UP4	PDP2	PDP3	PDP4	APP2	APP3	APP4
DW	t-value	−0.75	−1.21 *	−1.71 *	−1.16 *	−1.52 *	−1.94 *	−1.60 *	−1.92 *	−2.18 *
	standard deviation	5.45	6.33	7.41	5.98	6.75	7.43	6.84	7.71	8.35
	Mean value difference	−1.37	−2.41	−3.81	−2.23	−3.18	−4.34	−3.37	−4.42	−5.34

Note: * indicates significant ($p < 0.05$).

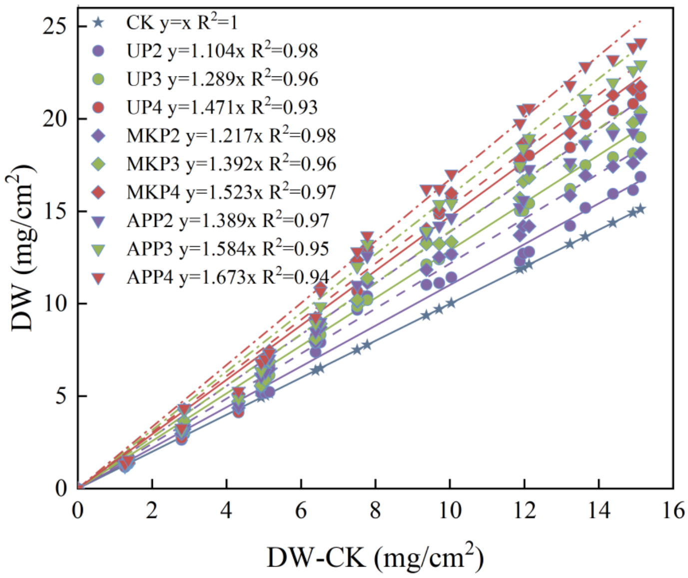


Figure 6. The correlation between DW between CK and phosphorus fertilizer treatment.

3.3. Effect of Mn^{2+} on Drip Irrigation with Fertilizer Application

The drip irrigation with fertilizer application of APP4 caused the most severe blockage. The drip irrigation experiment was conducted by coupling 0.4 g/L APP with different concentrations of Mn^{2+}, which demonstrated that Mn^{2+} could alleviate the blockage degree of drip irrigation with fertilizer. The four experimental methods are summarized in Table 7.

Table 7. Experimental arrangement for coupled drip irrigation of APP4 and Mn^{2+}.

Experiment Number	Sediment Concentration (g/L)	The Group with the Most Severe Blockage	Mn^{2+} Concentration /(mg/L)
APP4	2	APP4	0
Mn1	2	APP4	1
Mn2	2	APP4	2
Mn3	2	APP4	3

The dynamic changes in Dra, CU, and DW under four drip irrigation modes are shown in Figures 7 and 8. The Mn^{2+} could affect the degree of blockages in APP4. The blockage degree of drip irrigation emitters was alleviated under the treatment of Mn1 and Mn2 in the middle and later stages (12–40 days), while Mn3 exacerbated the blockage degree of drip irrigation emitters in the later stages (32–40 days). The Dra and CU of Mn1 increased by an average of 13.16% and 7.33%, while the DW decreased by an average of 5.13%. The Dra and CU of Mn2 increased by an average of 24.57% and 18.54%, while the DW decreased by an average of 13.27%. The average Dra and CU of Mn3 decreased by 8.79% and 12.7%, while the average DW increased by 8.43%. The results indicate that the 2 mg/L of Mn^{2+} could alleviate the blockage of APP4 to the greatest extent possible. The multiple comparison analysis of Dra, CU, and DW are shown in Table 8. There were significant differences in most multiple comparison analyses, which indicated that the concentration of Mn^{2+} had a significant impact on the Dra, CU, and DW of APP4 ($p < 0.05$). The 0.2 mg/L Mn^{2+} could be added when coupled with drip irrigation between Songhua River water and APP.

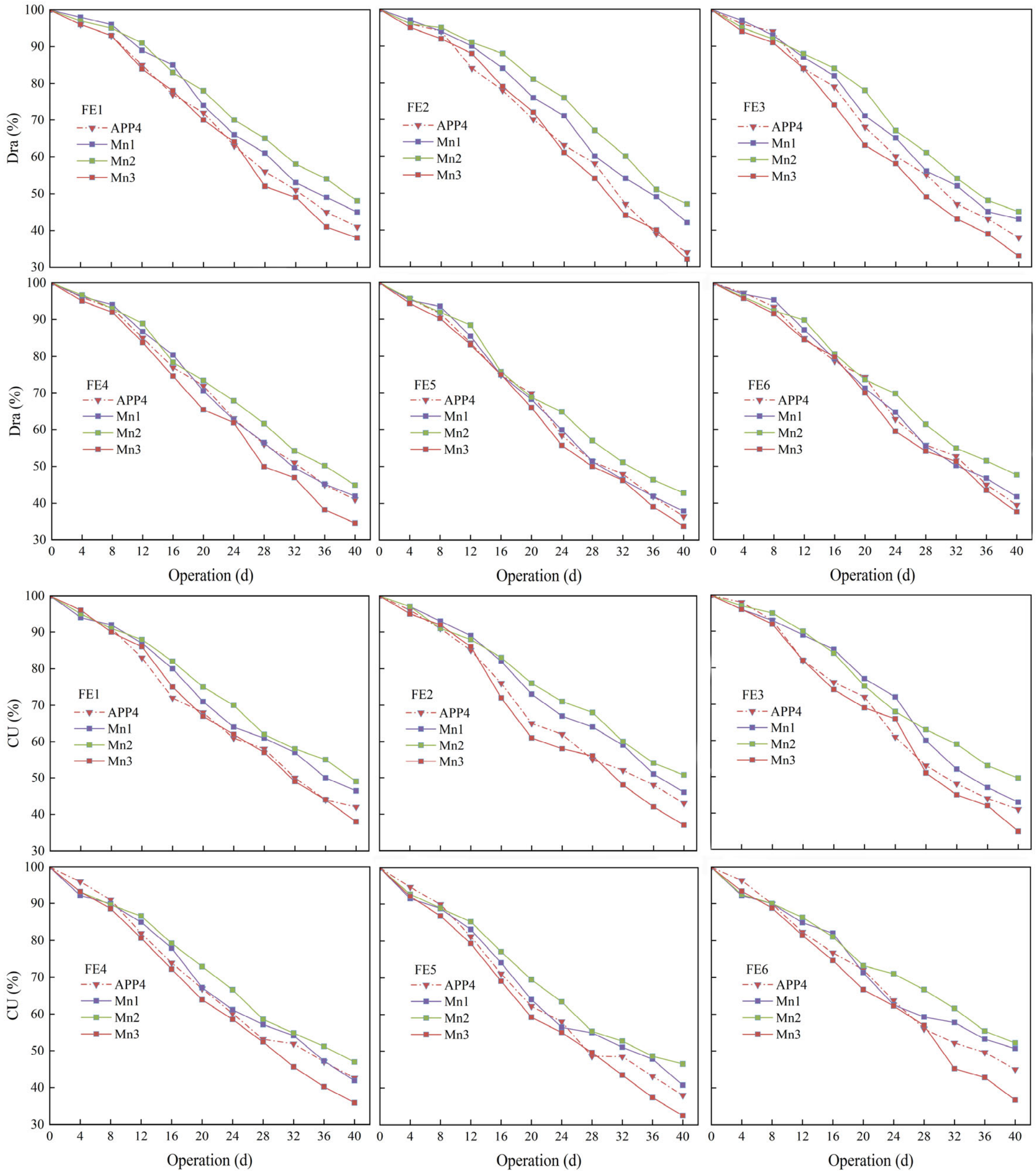


Figure 7. The dynamic changes in the system discharge variation ratio (Dra) and the Christiansen coefficient of uniformity (CU).

Table 8. Multiple comparative analysis of Dra, CU and DW under coupled drip irrigation of APP4 and Mn^{2+}.

Phosphate Fertilizer Type	Phosphate Fertilizer Type	Dra Mean Value Difference	CU Mean Value Difference	DW Mean Value Difference
APP4	Mn1	−5.68 *	−3.15 *	1.19
	Mn2	−9.13 *	−7.56 *	3.11 *
	Mn3	3.27	5.23 *	−1.98 *
Mn1	APP4	5.68 *	3.15 *	−1.19
	Mn2	−3.27	−4.62 *	1.92 *
	Mn3	9.13 *	8.48 *	−3.18 *
Mn2	APP4	9.13 *	7.56 *	−3.11 *
	Mn1	3.27	4.62 *	−1.91 *
	Mn3	12.28 *	13.11 *	−5.09 *
Mn3	APP4	−3.27	−5.23 *	1.98 *
	Mn1	−9.13 *	−8.48 *	3.18 *
	Mn2	−12.28 *	−13.11 *	5.09 *

Note: * indicates significant ($p < 0.05$).

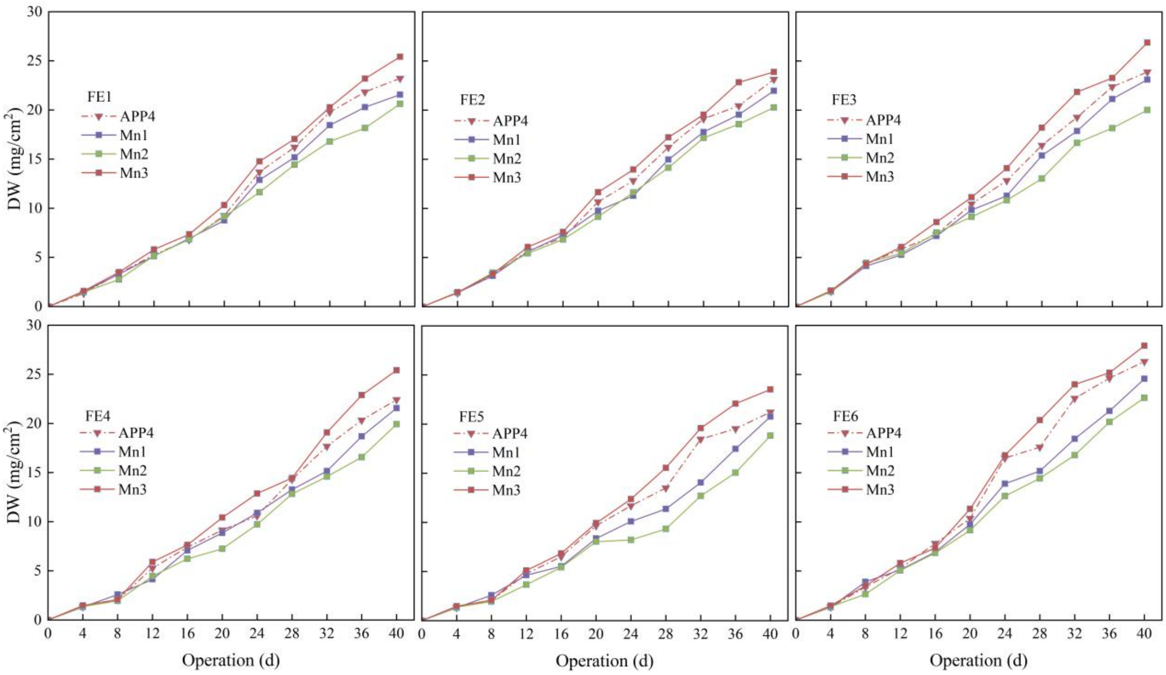


Figure 8. The dynamic changes in dry weight (DW) of blockages.

3.4. The Mineral Composition, Lattice Parameters, and Morphology of Blocking Substances

The performance of drip irrigation emitters was closely related to clogging substances combined with Sections 3.1 and 3.2. Further research is needed to investigate the changes in the content, composition, and lattice parameters of blocking substances. The blocking substances of drip irrigation with fertilizer application (UP4, PDP4, APP4, and Mn2) were selected. The composition of the blocking material was analyzed by using XRD (Figure 9). The main components of blockages were classified into carbonates ($CaCO_3$, $CaMg(CO_3)_2$), quartz (SiO_2) and other substances (such as muscovite, alkaline feldspar, chlorite, calcium feldspar, etc.) on chemical elements. The content of each substance is shown in Figure 10. The content of carbonate and quartz changed as the types of phosphate fertilizers changed. The content of carbonate and quartz in UP4 accounted for 42.7% and 26.9%. PDP4 was 59.1% and 16.8%. APP4 was 67.9% and 14.9%. Mn2 was 44.8% and 19.5%. The UP4 had the lowest carbonate content and 2 mg/L Mn^{2+} reduced the carbonate content. The content of silicates under these two treatments was higher than APP4. The carbonate had a major impact on the clogging problem of phosphate fertilizer drip irrigation.

The lattice parameters reflected the growth of calcium carbonate. The lattice parameters indirectly express whether phosphorus fertilizer promotes or inhibits the growth of calcium carbonate. The larger lattice parameter indicated that the growth of calcium carbonate was promoted. The lattice size a, b, c, and crystal lattice volume (Cv) of calcium carbonate are shown in Figure 11. The XRD results indicate that calcium carbonate crystal was the hexagonal crystal system. The lattice parameters showed a trend of UP4 < PDP4 < APP4, while the lattice parameters of Mn2 were all smaller than APP4. The crystal lattice volume of calcium carbonate in APP4 was the largest. When APP4 was compared with UP4, PDP4, and Mn2, the a-axis increased by 0.0028~0.004 Å, the b-axis increased by 0.0028~0.004 Å, the c-axis increased by 0.032~0.072 Å, and the Cv increased by 0.37~0.49.

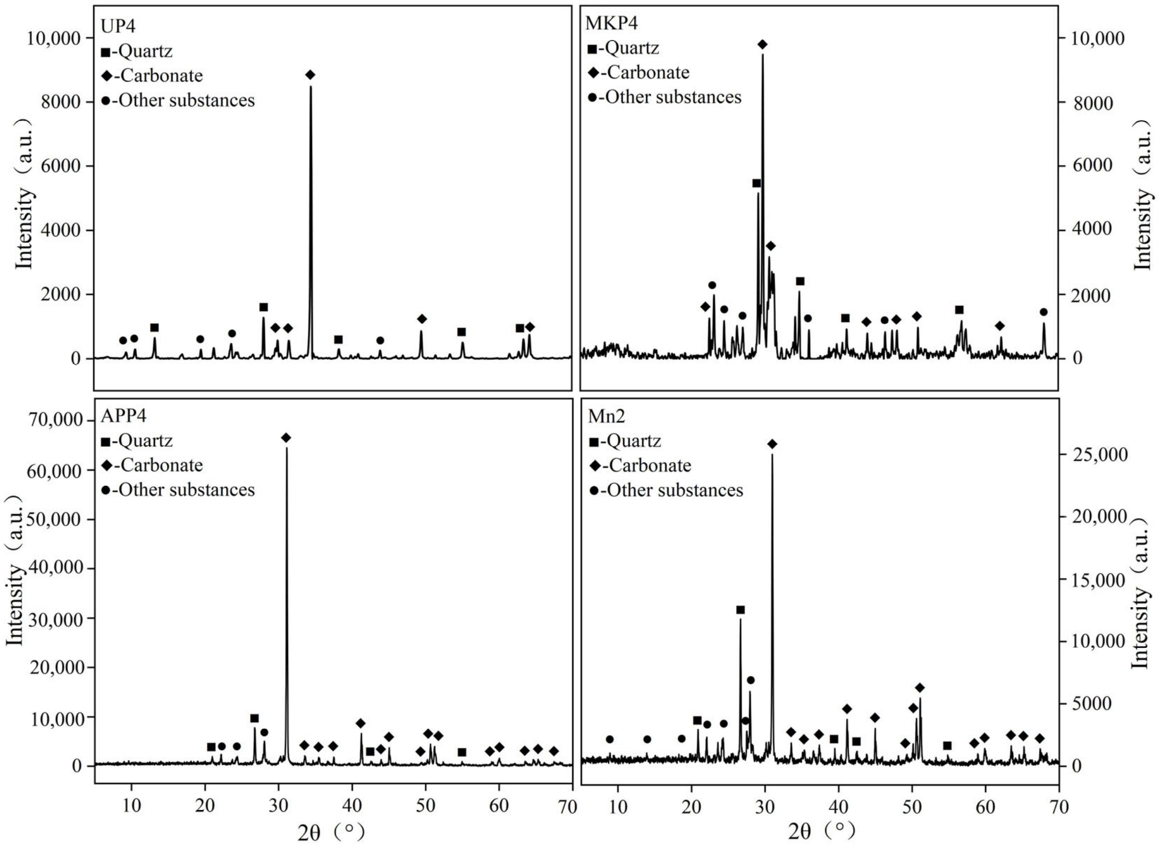


Figure 9. The XRD qualitative analysis chart.

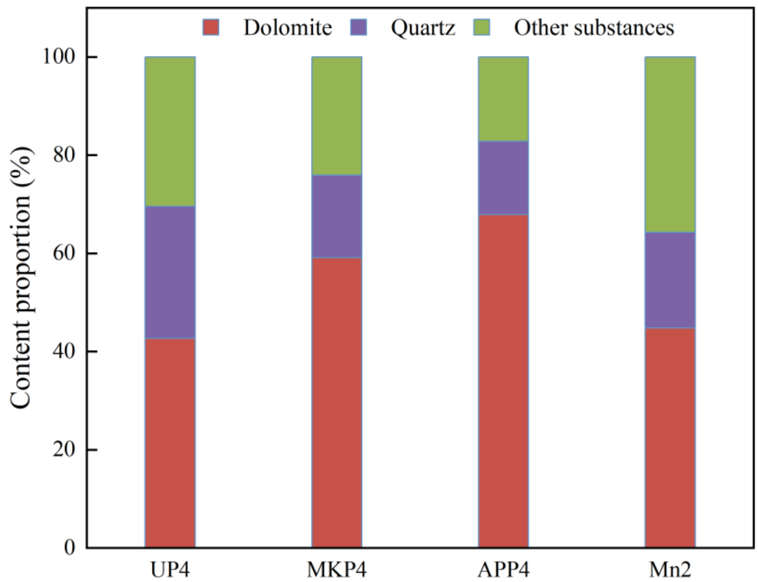


Figure 10. The mineral composition of blocking substances.

The scanning electron microscopy (SEM) images of calcium carbonate precipitation under four different drip irrigation with fertilizer application are shown in Figure 12. The apparent morphology of calcium carbonate showed certain differences under the four treatments. The shape of calcium carbonate particles in UP4 was irregular, many particles had not formed a hexahedral shape, and the surface was rough. A small number of particles in PDP4 had formed a hexahedral shape and the surface was smooth. The shape of calcium carbonate particles in APP4 was mostly hexahedral. The surface had layered ripples with a more regular and dense structure. The shape of calcium carbonate treated with Mn2 was irregular. There were many small and irregular particles attached to the surface. The reason was that Mn^{2+} adsorbed on the surface of calcium carbonate crystals. The Mn^{2+} and Ca^{2+} simultaneously participated in a chemical reaction and produced additional manganese carbonate in subsequent chemical reactions. The lattice of calcium carbonate underwent certain distortions and its surface structure became looser. There were more hexahedral particles (calcium carbonate) in the four sets of images, which indicated that calcium carbonate was the main component in the blocking substances. The SEM images match well with the XRD results.

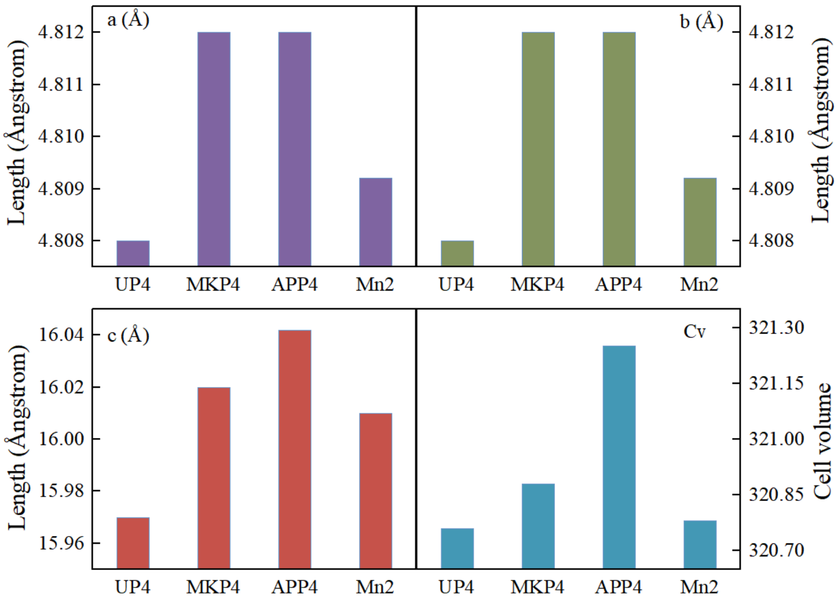


Figure 11. The lattice parameters ((**a**–**c**)-axis) and crystal lattice volume (Cv) under different treatments.

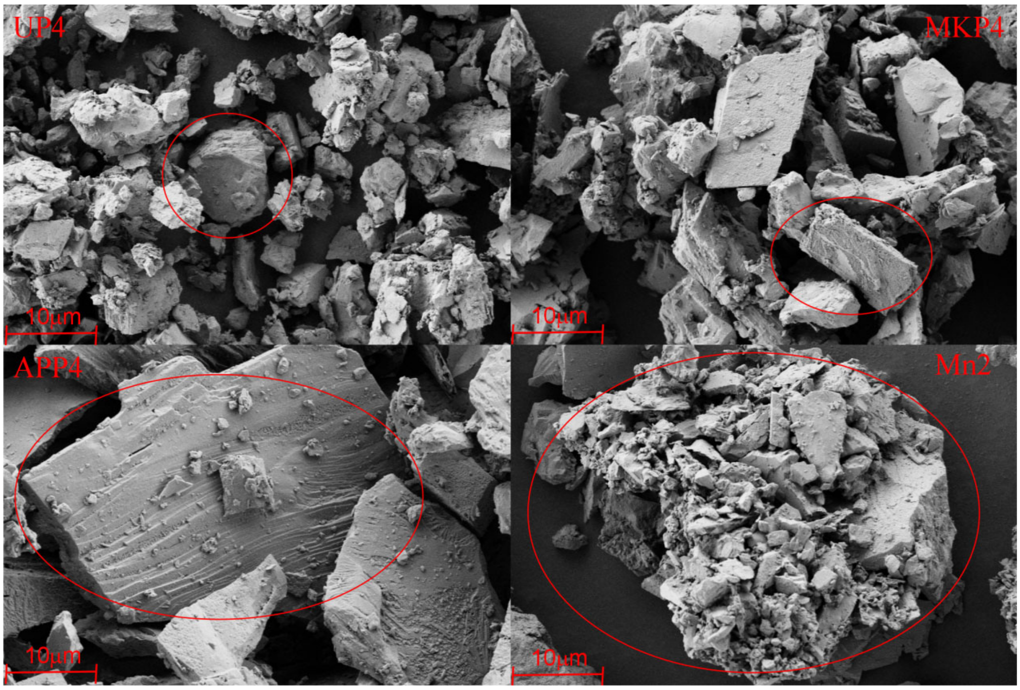


Figure 12. The $CaCO_3$ precipitation morphology under different treatments (red circles indicate the presence of calcium carbonate).

4. Discussion

The high accumulation of soil phosphorus concentration was excessive in the application of phosphorus fertilizer. The effective management of agricultural phosphorus fertilizer remains a global concern [23]. The blockage mechanism of drip irrigation with fertilizer application could improve drip irrigation efficiency, reduce phosphorus fertilizer waste in agricultural cultivation, and protect soil resources [24]. The results indicated that the content of carbonate precipitation formed under UP, PDP, and APP drip irrigation with fertilizer application would be higher. This result is similar to other studies [12,13,16]. This was mainly due to the low solubility of carbonates; the calcium and magnesium ions in saltwater would preferentially react with bicarbonate to form carbonate precipitates [25].

The degree of blockage of drip irrigation emitters was significantly influenced by the type and concentration of phosphorus fertilizer. The drip irrigation efficiency under UP treatment was better than PDP and APP. Ma et al. [26] indicated that the application of UP reduced the pH of water and the carbonate content in drip irrigation with fertilizer application. The chemical reaction was suppressed and the solubility of carbonates in water was improved. The solubility of Ca^{2+} and carbonate were increased. Thus, the production of blocking substances was reduced [27]. The anions bis (urea) bis (dihydrogen phosphate) and bicarbonate produced by the UP fertilizer dissolved in water reacted with calcium and magnesium ions [28], and the two formed a competitive relationship. Moreover, bis (urea) bis (dihydrogen phosphate) calcium magnesium compounds were soluble and easily passed through the entire flow channel, further reducing the risk of carbonate precipitation. The UP fertilization reduced the content of carbonate while the degree of blockage increased compared to CK. In this study, it was found that UP4 had the highest silicate content, which indicated an increase in physical blockage. The pH value at room temperature (around 25 °C) significantly affected its dissolution rate [29]. In acidic solutions, H ions only reacted with surface silicate groups. The bond energy of silicon oxygen bonds was relatively high and only a small amount of silicon oxygen bonds were broken. This meant that the silicate groups would be treated as a whole and difficult to remove independently [30,31]. In fact, a large amount of clogging substances existed at the end of drip irrigation emitter. After the water inside the channel evaporated under sunlight, the silicate transformed into a saturated state and formed particles. The drip irrigation emitter had different levels of sensitivity to particle size. The larger sand particles directly occupied the channel and caused physical blockages. The mixing sand particles of different sizes formed a stable skeleton structure, which promoted flocculation and chemical reactions. The blockage problem of UP fertilizer in this study should be attributed to physical chemical blockage.

The application of PDP and APP in drip irrigation fertilization led to more severe blockage. The main reason was that PDP and APP fertilizers did not lower the pH of the irrigation water and promoted the precipitation of carbonates. Another reason was that PDP and APP can accelerate particle precipitation. PDP fertilizer contains KH_2, which has a certain adsorption capacity when dissolved in water. The particle flocculation, aggregation, and sedimentation were promoted [32]. This adsorption promoted the attachment of carbonate ions and calcium magnesium ions to the surface of particles, which led to more stable chemical reactions and increased carbonate content [33]. The precipitates generated via the chemical reactions adhered to the wall of the flow channel and the roughness of the flow channel wall increased. The motion state of particles in the flow channel were changed and accelerated the accumulation of particles. Therefore, PDP fertilizer increased the probability of both physical and chemical blockages occurring simultaneously. Gryta [15] showed that APP as a scale inhibitor could block the growth sites of active crystals and reduced the formation of calcium carbonate. The reason was the calcium ion concentration in irrigation water was very low. The calcium ion content in the irrigation water used in this study (Songhua River water) was relatively high. The compounds in APP fertilizers formed a chain structure and chain type hydrogen phosphate salts had weak chelation ability towards calcium ions. The APP was difficult to bind with Ca^{2+} after dissolving in water, which resulted in an increase in free Ca^{2+} in the solution. Carbonate ions could easily capture surrounding calcium ions [34]. Shen et al. [35] found that the content of nitrogen and phosphorus (nutrients for microorganisms) in APP was relatively high, which caused an increase in microbial content and diversity. Microorganisms grew and reproduced in large quantities and secreted sticky extracellular polymers. Secretions adsorb suspended particles and promote the deposition of blockages.

The study found that the addition of 1 or 2 mg/L Mn^{2+} to APP4 alleviated the degree of blockage. The main reason was that the Mn^{2+} in the solution limited the formation of calcium carbonate. The diffusion coefficient of Mn^{2+} was lower than Ca^{2+} and its binding ability with carbonate ions was slightly higher. The presence of Mn^{2+} competed with Ca^{2+}. Metal carbonates are all composed of ions. The substance that interacted between Mn^{2+} and carbonate was not a free ion in solution, but rather an ion pair, hydrated substance, or possibly a larger multi-core cluster. Habermann et al. [36] indicated that the hydration degree of Mn^{2+} was stronger than that of Ca^{2+}. The Mn^{2+} attached to other ion sites at a faster rate. The atomic bond distance of calcium magnesium carbonate crystals decreased during their formation compared with other metal carbonates. This reduction led to an increase in the repulsive force of carbonate ions [37]. The addition of Mn^{2+} shortened the bond distance of $CaCO_3$ and prevented the formation of calcium carbonate. The XRD results indicated that the lattice parameters of calcium carbonate obtained from Mn2 were relatively small. The reason was that Mn^{2+} had an inhibitory effect on the growth kinetics of calcium carbonate in solution, which was related to its adsorption capacity. Han et al. [38] indicated that Mn^{2+} adsorbed into calcium carbonate crystals and formed cluster like structures. The part of Ca^{2+} in calcium carbonate was replaced by Mn^{2+} and the presence of Mn^{2+} also caused lattice distortion. The 3 mg/L of Mn^{2+} exacerbated the degree of blockage. The reason was that the concentration of Mn^{2+} was too high. Dromgole and Walter [39] demonstrated that calcium carbonate was highly inhibited in Mn^{2+} solutions with very low concentrations. This inhibitory effect began to form calcium rhodochrosite at higher concentrations. The nucleation surface of $CaCO_3$ still adsorbed Mn^{2+} even if the surface sites of $CaCO_3$ were saturated. The $MnCO_3$ separated from the surface of $CaCO_3$ and slowly precipitated subsequently [40]. More precipitates were generated in the flow channel of drip irrigation emitters due to the lower solubility of manganese carbonate.

The study analyzed the dynamic changes in the degree of blockage and the blockage substances under drip irrigation with fertilizer application. The influence of Mn^{2+} on blockage from both macro and micro perspectives were explained. The results showed that the blockage caused by the three types of phosphorus fertilizers was in the order of UP < PDP < APP. The 2 mg/L of Mn^{2+} alleviated the blockage degree of APP4 to the greatest extent.

5. The Preventive Strategies for Drip Irrigation of Phosphate Fertilizer

This study analyzed the dynamic changes in blockage degree and blockage substances under drip irrigation with phosphate fertilizer. Regarding the clogging phenomenon of phosphate fertilizer drip irrigation, future research areas can be carried out from the following four points:

(1) Types of phosphate fertilizers. We suggest the use of UP for drip irrigation. The blockage under UP treatment after fertilization was relatively light and the performance of drip irrigation emitter would not significantly decrease under low concentration conditions. The crops only absorbed phosphorus in the form of H_2PO_4 [41]. UP

fertilization could lower the pH value of water and soil. The conversion of phosphate to H_2PO_4 form was promoted and the effectiveness and utilization efficiency of phosphorus were improved [42]. In addition, drip irrigation technology is mainly used in saline alkali areas [43]. UP could be used as a soil amendment to reduce soil salinity and alkalinity. It is not advisable to use UP in acidic soil. Future research should explore the availability of phosphate fertilizers in different soils.

(2) The concentration of Phosphate fertilizer. The results of this study found a positive correlation between the degree of blockage and concentration at concentrations of 0.2~0.4 g/L. The optimal concentration of phosphorus fertilizer required for crops varies [44]. Low concentration phosphorus fertilizer would prolong the total drip irrigation time, which is not conducive to crop growth in the optimal season. The selection of phosphate fertilizer concentration should take into account both clogging issues and crop growth conditions.

(3) Types of drip irrigation emitters. The channel structure was a direct factor that affected the anticlogging performance of drip irrigation emitters and did not change with external factors [45]. This study used a labyrinth drip irrigation emitter. Many scholars had optimized flow channel structure, such as inverted labyrinth flow channel [46] and stellate water-retaining labyrinth channels [47]. Xu et al. created a pit drip irrigation emitter and leaf vein drip irrigation emitter based on plant bionics [48,49]. These scholars demonstrated through CFD and sediment experiments that these drip irrigation emitters could reduce sand sedimentation. It is still unclear whether they could alleviate chemical blockages. The phosphorus fertilizer drip irrigation experiments could be combined with these new drip irrigation emitters.

(4) Carbonate control. The commonly used method for removing carbonates is to add acid regularly. This method is prone to damaging soils, crops, and increased precipitation of silicates [50]. Regarding environmental issues, previous studies have shown that Merus rings [51], nano bubble generators [52], and electrochemical reactors [53] could be used. Finally, we propose the use of Mn^{2+} to reduce carbonate precipitation. This method is easy to operate and promotes crop growth. Other ions that may be crucial for alleviating carbonate stress but have not been widely studied include Fe^{2+}, Fe^{3+}, and Cu^{2+}.

6. Conclusions

This study selected three different types of phosphate fertilizers (UP, PDP, and APP) for drip irrigation experiments. The performance of the drip irrigation emitter and the dry weight of clogging substances were calculated. In order to alleviate the problem of blockage, Mn^{2+} was selected to optimize the drip irrigation mode with the most severe blockage (APP4). Finally, with the help of modern techniques such as XRD and SEM, the characteristics of the blocking material were analyzed.

The Songhua River water source was selected as the irrigation water source in the drip irrigation fertilizer application. The research found that the performance indicators of the drip irrigation emitters changed within the normal range, which indicated that the combination of Songhua River water source and phosphate fertilizer had good feasibility. The phosphorus fertilizer treatments caused blockage situations and the degree of blockage was proportional to the concentration. The Dra of UP, PDP, and APP treatments decreased by 6.2~27.7%, 13.8~33.8%, and 21.5~44.6%, respectively, compared with CK. The CU decreased by 5.9~23.5%, 10.3~27.9%, and 19.1~38.2%. The DW increased by 10.3~38.9%, 9.7~45.6%, and 30.3~58.2%. The drip irrigation fertilization should choose UP fertilizer with a concentration of 0.2 g/L.

The addition of Mn^{2+} in the APP treatment could change the degree of blockage. The degree of blockage was first alleviated and then became severe within the concentration range of 1~3 mg/L. The 2 mg/L of Mn^{2+} increased Dra by 24.57%, CU by 18.54%, and reduced DW by 13.27% in the APP4 drip irrigation. When using APP fertilizer drip irrigation, 2 mg/L Mn^{2+} should be added to improve drip irrigation efficiency.

There are still some issues that need to be investigated in the future. The Mn^{2+} needs to be applied in different types and concentrations of phosphate fertilizers. The suitability of coupling Mn^{2+} with phosphate fertilizers needs to be explored. It is necessary to combine the changes in blocking substances with time. The mechanism of Mn^{2+} on blocking substances at different stages should be researched.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Abbreviations

UP	Urea phosphate
PDP	Potassium dihydrogen phosphate
APP	Ammonium polyphosphate
Dra	The system discharge variation ratio
CU	The Christiansen coefficient of uniformity
DW	The dry weight of clogging substances
XRD	X-ray diffractometer
SEM	Scanning electron microscopy
APP4	Irrigation water with ammonium polyphosphate concentration of 0.4 g/L
Mn1	Irrigation water mixed with 0.4 g/L ammonium polyphosphate and 1 mg/L Mn^{2+}
Mn2	Irrigation water mixed with 0.4 g/L ammonium polyphosphate and 2 mg/L Mn^{2+}
Mn3	Irrigation water mixed with 0.4 g/L ammonium polyphosphate and 3 mg/L Mn^{2+}
Cv	Crystal lattice volume

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