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Influence and selection of nitrogen and phosphorus compound fertilizers on emitter clogging using brackish water in drip irrigation systems

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ABSTRACT

Emitter clogging is a major obstacle to the application of brackish water in drip irrigation systems, which can be aggravated with inappropriate fertilizer application. Among the major element fertilizers, nitrogen and phosphorus (NP) trigger a higher risk of clogging. However, the effect and selection of different types of NP compound fertilizers on emitter clogging remain unknown. This study investigated the effects of no fertilizer (CK), two types of industrial grade monoammonium phosphate (I_MAP) and diammonium phosphate (I_DAP), two types of agricultural grade monoammonium phosphate (A_MAP) and diammonium phosphate (A_DAP), and two types of new urea phosphate (UP) and ammonium polyphosphate (APP) on the clogging of three types of emitters. The results showed that the application of agricultural grade A_MAP and A_DAP fertilizers exacerbated emitter clogging compared to industrial grade fertilizers, decreasing the Christiansen of Uniformity (CU) by an average of 18.5%–22.8% and 21.4%–25.6%, respectively, mainly due to an increase in the content of insoluble particulate matter in the clogging material. Application of new UP and APP fertilizers reduced emitter clogging, increasing CU by 29.9%–37.1% and 10.2%–16.4%, respectively, compared to industrial grade fertilizers, mainly by decreasing the chemical precipitate content in the fouling material. Overall, the safe operation time of agricultural grade fertilizer system is about 1.2 years within the safe operation life (CU≥80%) of drip irrigation system, while the safe operation life of industrial grade and new NP compound fertilizers is about 1.6–3.4 times of that of agricultural grade fertilizers on average. It is suggested that in drip irrigation systems using brackish water, A_MAP fertilizer can be applied to annual crops whereas in perennial crops industrial and UP and APP should be applied. This study is of great significance for the application and promotion of brackish water drip fertigation technology.

1. Introduction

Water scarcity in agriculture has become a major constraint to the sustainable development of agricultural production (He et al., 2021; Han and Jia, 2022). Brackish water reserves are abundant and their use for irrigation has become a major way to alleviate water scarcity (Yin et al., 2022). However, unreasonable use of brackish water tends to exacerbate the level of salt stress in the crop root zone and could cause soil salinization (Liu et al., 2021). Drip irrigation is considered to be the most reliable method of applying brackish water for irrigation due to its high frequency and controllability (Xiao et al., 2023), which allows salts to accumulate at the edges of the wetted body and reduces the level of salt stress in the root zone (Slama et al., 2019). However, the key reason why brackish water is not widely used in drip irrigation system is that it contains a large number of salt ions (Chen et al., 2019), which are highly susceptible to clog drip irrigation emitters.

Fertilizer is often required for drip irrigation systems, and it has been shown that the coupling of components in fertilizers with multiple ions

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in brackish water can lead to changes in emitter clogging behavior (Wang et al., 2022c; Wang et al., 2023), being the clogging mechanism more complex. At present, nitrogen, phosphorous and potassium are the three primary nutrients most commonly used in fertilizers. In the past, nitrogen and potash were mainly applied through drip irrigation systems, while phosphate was usually applied as a base fertilizer (Fan et al., 2020). In recent years, some scholars have explored that applying phosphate fertilizer through drip irrigation systems can effectively improve the transport distance and utilization efficiency of phosphate fertilizer in soil (Dong et al., 2023). In general, potassium fertilizers (such as potassium chloride) pose less risk of emitter clogging, nitrogen fertilizers have a higher clogging risk, and phosphate fertilizers have the highest clogging risk (Shi et al., 2022). At the same time, farmers tend to use compound fertilizers. Compared with a single fertilizer, the nutrient content of a compound fertilizer is more balanced and easier to apply (Chen et al., 2021). Therefore, it is necessary to study the effect of NP compound fertilizers on emitter clogging. The production methods and types of different NP compound fertilizers may also be the key factors affecting the clogging of the emitters. In general, due to the different impurity content, fertilizers can be divided into industrial grade and agricultural grade. In general, the purity of agricultural grade fertilizers is lower, while, in contrast, industrial grade fertilizers have fewer impurities, having an effective fertilizer content of 98% (Li et al., 2021). Thus, due to its higher impurity amounts, agricultural grade fertilizers have a higher risk of emitter clogging than industrial grade fertilizers. The advantage of agricultural grade fertilizers is that they are cheaper. Therefore, the effect of NP compound fertilizers on clogging should be weighed against the cost of fertilization. At present, the research on the effect of NP fertilizers on emitter clogging is mainly focused on industrial grade fertilizers. Ma et al. (2020) concluded that the application of NP compound fertilizer slowed down the emitter clogging in drip irrigation systems by reducing the calcium carbonate content in the clogging material. Wang et al. (2020) found that, under the condition of low ion concentration, applying weak acid NP compound fertilizer can effectively reduce the formation of phosphate fouling. On the contrary, some scholars have found that NP compound fertilizer exacerbates emitter clogging. Yang et al. (2019) observed that application of NP compound fertilizers can increase the content of amorphous substances in the clogging material and exacerbate the clogging of emitters. Muhammad et al. (2021) found that even if urea phosphate, which is able to reduce the pH of water, is applied, it will also increase the carbonate and silicate substances, which will result in higher clogging occurrence. Overall, the current research results on the emitter clogging of brackish water drip irrigation system (BWDS) by NP compound fertilizers are inconsistent and have not been addressed the use of different purity grade fertilizers. In fact, the service life of drip irrigation belt is not fixed. For example, in the Xinjiang region of China, the service life of drip irrigation belt is often only 1 year (Wen et al., 2022), while in other areas may be 10 years or even longer (Goyal, 2012). Therefore, it should be necessary to establish fertilizer selection methods with different dripline service life. However, the effects of different types of NP compound fertilizer on BWDS emitter clogging and the appropriate selection method of NP compound fertilizer are unknown.

Therefore, the effects of the two most commonly used industrial grade NP compound fertilizers, the corresponding two agricultural grade NP compound fertilizers and two new types of NP compound fertilizers on the emitter clogging of drip irrigation system using brackish water were studied. The purpose of this study is: (1) Clarify the effects of different types of NP compound fertilizers on BWDS emitter clogging; (2) Clarify the mechanism of influence of different types of NP compound fertilizer on emitter clogging; (3) Weighing the relationship between the amount of fertilizer applied to the emitter clogging and the cost, propose a fertilizer selection method for BWDS.

2. Materials and methods

2.1. Experimental setup

The experiment was carried out at the Irrigation Experiment Station of the First Division Water Resources Management Center of Xinjiang Production and Construction Corps (81°2′E, 40°6′N). The experimental drip irrigation system is shown in Fig. 1. System is divided into three layers, each 15 m in length, with a drip irrigation belt internal diameter of 16 mm, each layer representing a single type of drip irrigation belt. There were 50 emitters evenly spaced along the drip irrigation belt with an average spacing of 30 cm between emitters. The head of the irrigation system had screen filters (length, width and height size: 290 × 260 × 150 mm, filter precision: 120 μm), as well as a two-stage manifold pressure regulator to ensure the pressure head of the water supplied into the system. No fertilizer (CK), monoammonium phosphate (A_MAP) and diammonium phosphate (A_DAP) of agricultural grade NP compound fertilizers, monoammonium phosphate (I_MAP) and diammonium phosphate (I_DAP) of industrial grade NP compound fertilizers, as well as urea phosphate (UP) and ammonium polyphosphate (APP) of new NP compound fertilizer were used in the experiment, and, therefore, there were a total of 7 treatments. The basic information of fertilizers is shown in Table S1 of the supplementary materials, and the concentration of NP compound fertilizer applied was 0.5 g/L (Mtaki et al., 2021). The experimental water source was selected from locally mixed underground brackish water with a total dissolved salt (TDS) concentration of 3 g/L. The experiment was conducted from May 1, 2022, to July 10, 2022, using alternating brackish water-fertilizer water-brackish water. The system was operated for 10 h per day, with the test running for a total of 64 days. Three different types of emitters were selected for the test, being their structural parameters shown in Table 1. There were eight replicates of drip irrigation belts for each treatment condition, which were used for sampling at different periods of the system's operation. And a flushing device was set up at the end of the system to carry out lateral flushing every 8 days of operation, with a flushing velocity of 0.45 m/s.

2.2. Effects of fertilizers on water quality

The application of NP compound fertilizers mainly affects the clogging of the emitter by influencing the water quality. In this study, the water quality parameters pH, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, PO_4^{2-}, total hardness, and zeta potential of the brackish water were tested. The water quality testing method relied on China Hangzhou Research Interest Information Technology Company Limited, in which Ca^{2+} and Mg^{2+} were determined by HJ 776–2015 Inductively Coupled Plasma Emission Spectrometry (ICPES) standard, and the instrumentation used was ICP-OES spectrometer (Agilent Technologies, USA, model: Avio220MAX). The SO_4^{2-} and PO_4^{2-} were determined following Ion Chromatography (ICC) (Metrohm, Switzerland, model: 940) Chinese standard method HJ 84–2016.

2.3. Evaluation of emitter hydraulic performance

During operation of the system, all 50 emitters on each drip irrigation belt were tested for flow and dry weight every 8 days. The weighing method was used to test the emitter discharge, which was collected during 3 min. Before each flow test, the pressure was adjusted at the head of the drip irrigation system to ensure that the system pressure was stabilized at 0.1 MPa when testing the flow rate, and finally, the discharge of each emitter was calculated using a high-precision electronic balance (with an accuracy of 10^{-3} g).

After calibrating the measured flow rate using the method proposed by Pei et al. (2013), the average discharge variation rate (Dra) was used to determine the degree of emitter clogging, and the Christiansen of Uniformity (CU) to evaluate the irrigation uniformity of the emitter

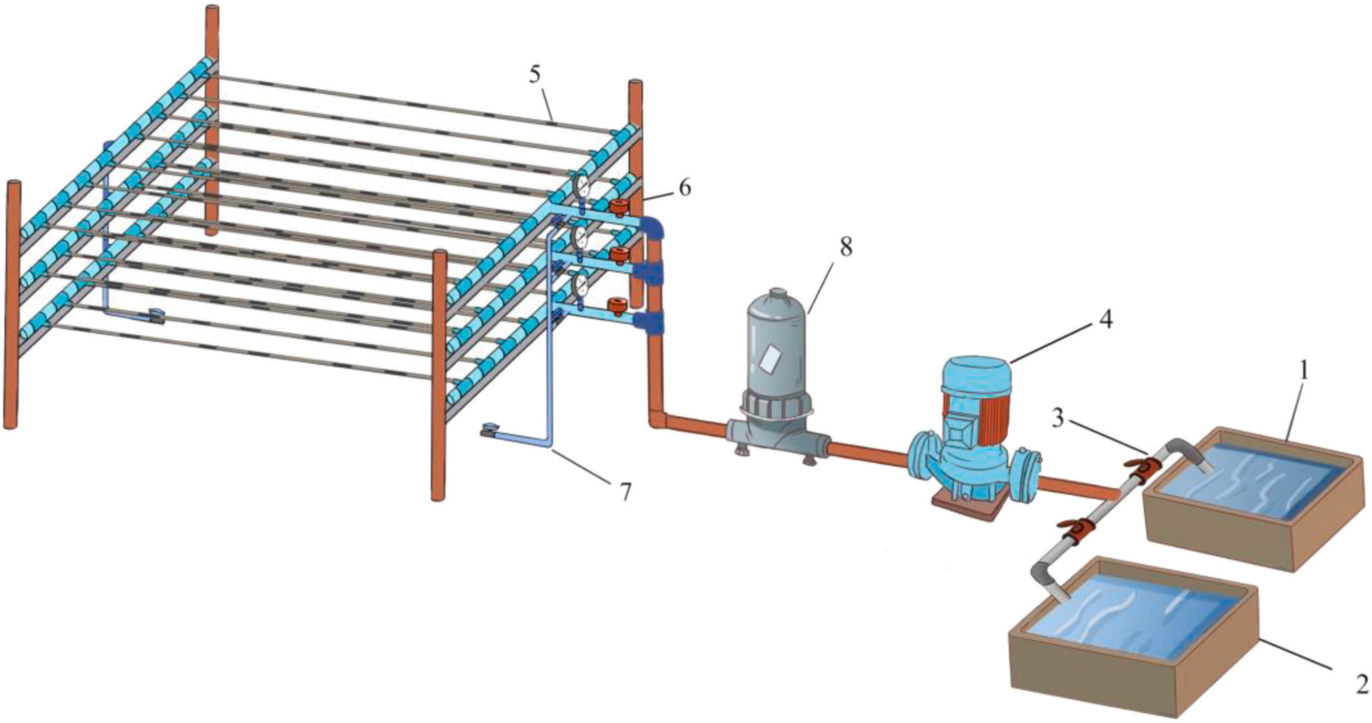
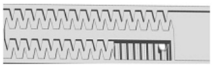
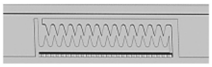
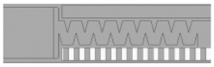


Fig. 1. Experimental drip irrigation system. 1-fertilizer tank, 2- brackish water tank, 3-water inlet, 4-water pump, 5-emitters, 6- precise adjusting valve, 7-exhaust device, 8-screen filter.

Table 1

Main parameters of the drip irrigation emitter.

Emitter	Rated discharge (L/h)	Flow length (mm)	Flow width (mm)	Flow depth (mm)	Discharge coefficient	Flow index	Emitter flow channel structure sketch
E1	1.00	34.41	0.85	0.72	3.61	0.53	
E2	1.60	27.48	1.07	1.14	5.40	0.52	
E3	2.00	25.29	0.87	1.04	6.50	0.61	

Note: the flow channels' dimensions were obtained by an electron microscope after peeling the emitters, and the rated discharge, discharge coefficient, flow index was tested according to China standard (GB/T17188-1997).

(Christiansen, 1942).

$$Dra = \frac{\sum_{i=1}^{n} \frac{q_{it}}{q_{i0}}}{n} \times 100\% \tag{1}$$

where q_{i0} is the initial discharge for emitter i, L h^{-1}; q_{it} is the discharge at t hour for emitter i, L h^{-1}; and n is total number of emitters installed along the lateral.

The corrected emitters' discharge (q_i^t) was used to calculate the Christiansen of Uniformity (CU) of the lateral, as shown in (3).

$$\overline{q}^t = \frac{\sum_{i=1}^{n} q_i^t}{n} \tag{2}$$

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

Where $\overline{q}^t$is the average flow rate of each emitter on the dripline after measuring it at time t, L/h; and q_i^t is the discharge at t hour; The meaning of other parameters is the same as that of (1).

2.4. Safety operating life assessment of emitter

Under the condition of CU=80%, below which the drip irrigation system is considered clogged, the corresponding running time (RT) was calculated (Table S3), Once RT was determined, the area corresponding to S_1 and S_2 for Dra was computed (Fig. 2). According to Eqs. (4) and (5), the irrigation water amount (IWA) in m^3/ha was calculated (Table S4).

$$k = \frac{S_1}{S_1 + S_2} \tag{4}$$

$$IWA = k \times Q \times RT \times \frac{L}{d} \tag{5}$$

Where S_1 is the effective cross-section area between Dra and runtime for CU=80%, and S_1 +S_2 is the rated overwater area between Dra and runtime for CU=80% conditions. Q is the flow rate of the emitter, m^3/h; RT is the corresponding running time, h; L is the length of drip irrigation belt for one hectare of land (considering a distance between emitters of 0.3 m, and a distance between drip irrigation belt of 1.1 m), where 9000

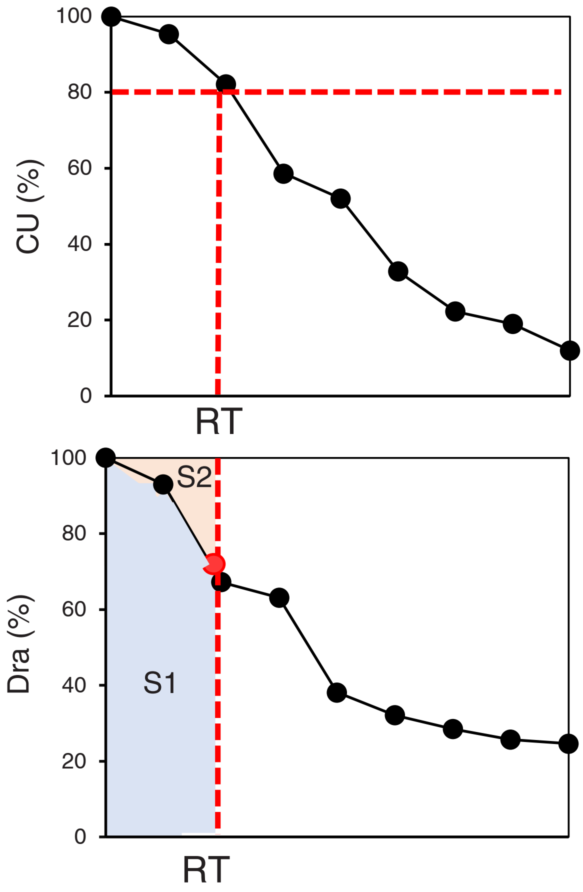


Fig. 2. Schematic diagram for calculating the safe operating life of the drip irrigation systems.

is taken in the formula and the unit is m; d is the spacing of the emitter runners, where 0.3 m is taken in the formula. $\frac{L}{d}$ is the total number of emitters per hectare.

Then the useful years of the drip irrigation system operation Y were calculated as:

$$Y = \frac{IWA}{AIW} \tag{6}$$

Where AIW is the annual irrigation water of a crop, with reference to the annual irrigation amount of cotton (Wang et al., 2022b), tomato (Wei et al., 2021), rice (Ma et al., 2019) and winter wheat (Zhang et al., 2016) in Xinjiang, China, In this study, the annual irrigation water per hectare was 3000–9000 m^3.

2.5. Analysis of fertilizer and emitter clogging substance fractions

Fertilizer was tested for insoluble matter using high-performance liquid chromatography (HPLC) (Agilent Technologies, USA, model ICPMS7500, plasma RF power: 1200 W; plasma gas flow rate: 15.0 L/min; auxiliary gas flow rate: 1.0 L/min; carrier gas flow rate: 1.0 L/min, acquisition mode: mass spectrometry, repeated 3 times). The insoluble sample in the clogging substance was stuck on the conductive adhesive for XPS (X-ray Photoelectron Spectroscopy) test (Thermo Scientific, USA, model Escalab250X), using AI Ka target (hv=1486.6 eV), power 150 W, sensitivity 350 keps, vacuum of the analyzing chamber 10^{-8} mbar. The angle between the detector and the sample surface was 90°, and the analyzing area was 700 * 300 μm. The fluence energy was set to 160 eV for the broad spectrum and 40 eV for the narrow spectrum, and the scanning step was 1 eV for the broad spectrum and 0.1 eV for the narrow spectrum.

The samples were taken at 8, 16, 24, 32, 40, 48, 56, and 64 days of system operation, respectively, and analyzed following the sampling procedure and methods of Wang et al. (2022c). Firstly, the emitter mixed samples were put into self-sealing bags, added deionized water, placed in ultrasonic cleaning for dismemberment treatment for 20 min, and made into suspension. Then, 50 mL of suspension was poured into centrifuge tubes for centrifugation, and then the centrifuge tube samples were dried, and weighed using a high-precision balance, and finally got the dry weight (DW) of clogged material. The dried clogged material was fully ground, and the polycrystalline diffraction image was determined using an X-ray diffractometer (Bruker Corp, Germany; model: D8-Advance). It was analyzed by Topas software (Bruker Corp) to obtain polycrystalline diffraction patterns and phase compositions. At the same time, the apparent morphology of the clogged material at the end of the experiment (i.e., after 64 days) was obtained with a scanning electron microscopy (SEM) Tescan, Czech Republic, model: Vega Compact) at an operating voltage of 25 kV and a magnification scale between 400 and 15,000.

2.6. Statistical analysis

The significant differences ($p < 0.05$) in water quality parameters between treatments were determined by analysis of variance (ANOVA). Data on water quality parameters, mineral fractions, and clogging performance were standardized using SPSS (ver. 24.0, IBM Analytics, USA), Spearman's correlation analysis was performed, and structural equation modeling analysis (SEMA) was used with amosv22.0 (IBM, USA). The hypothesis testing was performed to evaluate the correlation between clogging substances and clogging performance.

3. Results

3.1. Different NP compound fertilizers on water quality parameters of brackish water

As shown in Fig. 3a-h, application of different NP compound fertilizers significantly affected the brackish water quality. Compared with CK treatment, the application of chemical fertilizer significantly reduced the pH of brackish water except for I_DAP treatment. Applying agricultural grade A_MAP and A_DAP fertilizers increased the total hardness by 40.9–73.2 mg/L and 99.9–132.2 mg/L, respectively, regarding industrial grade I_MAP and I_DAP fertilizers. Compared with industrial grade I_MAP and I_DAP fertilizers, the application of new UP and APP fertilizers reduced the total hardness by 31.7–64.0 mg/L and 22.7–55.0 mg/L, respectively. However, A_MAP was not different from control and A_DAP had significantly greater total hardness. The results of zeta potential change showed that, compared with industrial grade I_MAP and I_DAP fertilizers, applying agricultural grade A_MAP and A_DAP fertilizers reduced zeta potential by 6.5–6.9 mV and 7.1–7.4 mV, respectively. Conversely, the zeta potential was increased by 3.5–3.8 mV and 1.9–2.2 mV by applying new UP and APP fertilizers, respectively, regarding I_MAP and I_DAP. Meanwhile, compared with industrial grade I_MAP and I_DAP fertilizers, the application of agricultural grade A_MAP and A_DAP fertilizers significantly ($p < 0.05$) increased the content of Ca^{2+} and Mg^{2+} by 35.6–98.8 mg/L and 9.9–26.9 mg/L, respectively. Compared with industrial grade I_MAP and I_DAP fertilizers, the application of new UP and APP fertilizers significantly ($p < 0.05$) decreased the Ca^{2+} and Mg^{2+} content by 29.0–59.9 mg/L and 2.1–8.0 mg/L, respectively. At the same time, the Ca content of A_DAP was significantly higher than CK. The application of agricultural grade A_MAP and A_DAP fertilizers significantly ($p < 0.05$) increased SO_4^{2-} and PO_4^{3-} by 49.9–202.9 mg/L and 16.2–37.8 mg/L compared to industrial grade I_MAP and I_DAP fertilizers. Compared to the industrial grade I_DAP fertilizers, the application of new UP and APP fertilizers resulted in a PO_4^{3-} significantly ($p < 0.05$) decreased by

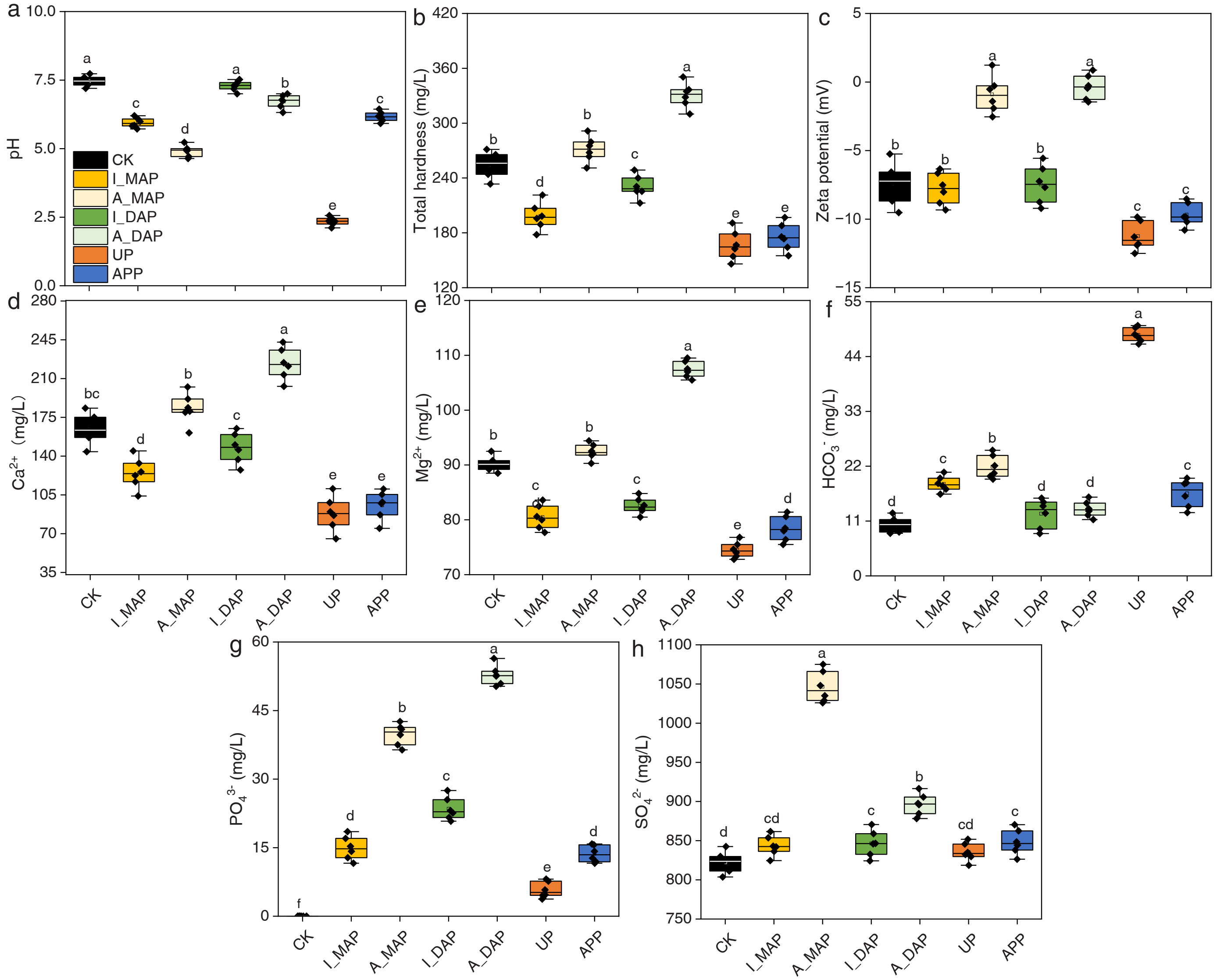


Fig. 3. Variation of water quality parameters for different treatments. The small boxes in the graphs represent the values of different water quality parameters in the interval of 25%–75%, and the different letters above the boxes show if there were significant differences ($p < 0.05$) between treatments for each water quality parameter.

9.8–17.7 mg/L, while HCO_3^- significantly ($p < 0.05$) increased by 4.1–35.9 mg/L, respectively.

3.2. *Effect of different NP compound fertilizers on emitter clogging*

The application of different types of NP compound fertilizers significantly affected the CU and Dra of the BWDS (Fig. 4a-h). Both CU and Dra of the drip irrigation system showed a trend of rapid decrease from 0 to 40 days, followed by a slow decrease from 40 to 64 days. With the system in operation, the application of A_MAP and A_DAP fertilizers significantly exacerbated clogging of the drip irrigation system compared to the CK treatment, resulting in a decrease in Dra and CU by 2.1%–22.6% and 8.9%–36.9%, respectively, whereas application of I_MAP, I_DAP, UP, and APP fertilizers significantly slowed down clogging of the drip irrigation system, resulting in an increase in Dra and CU by 3.4%–56.3% and 3.2%–65.0%, respectively. The application of agricultural grade A_MAP and A_DAP fertilizers reduced the Dra of emitters E1, E2, and E3 by an average of 12.2%–20.5%, 24.5%–28.4%, and 20.8%–27.5%, respectively, compared to the industrial grade I_MAP and I_DAP fertilizers. Meanwhile, the application of agricultural grade A_MAP and A_DAP fertilizers resulted in an average reduction of 29.4%–40.8%, 19.2%–47.9% and 14.8%–34.9% in CU of emitters E1, E2 and E3, respectively, as compared to industrial grade I_MAP and I_DAP fertilizers. In contrast, compared to industrial grade I_MAP and I_DAP fertilizers, the application of the new UP fertilizer resulted in an average increase of 48.2%–51.0%, 21.5%–26.9% and 20.8%–29.8% in Dra and an average increase of 54.6%–59.9%, 29.1%–39.7%, and 14.7%–26.1% in CU for the drip irrigation system for E1, E2, and E3, respectively. Also, with the APP fertilizer, Dra and CU for E1, E2, and E3 emitters increased between 1.8%–24.1% and 1.8%–59.9%, respectively, at the end of the system operation, compared to the industrial grade I_MAP and I_DAP fertilizers.

Moreover, the application of different NP compound fertilizers also significantly affected the DW of the drip irrigation system compared to the CK treatment (Fig. 4i-l). The application of agricultural grade A_MAP and A_DAP fertilizers increased in DW of emitters E1, E2 and E3 by 23.1%–132.8%, 11.5%–40.6% and 17.9%–31.3%, respectively, compared to industrial grade I_MAP and I_DAP fertilizers, whereas the application of the UP and APP fertilizers decreased DW by 13.9%–59.7%, 7.4%–26.7%, and 6.2%–9.7%, respectively. The SEM images

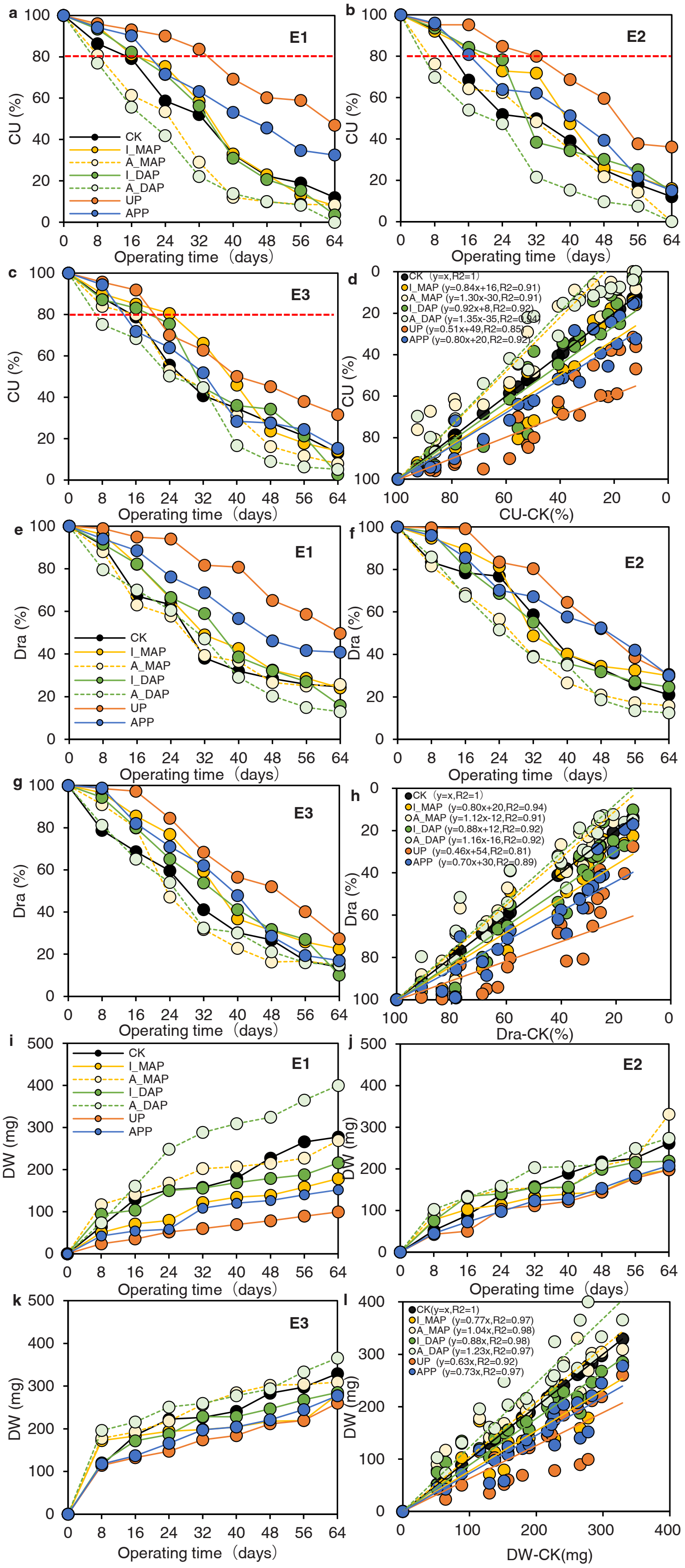


Fig. 4. Effect of NP compound fertilizers on the clogging performance in BWDS. Fig. 4a, b and c show the dynamic changes of CU in BWDS with different types of emitters, Fig. 4d depicts the correlation of CU with different NP compound fertilizer treatments. Fig. 4e, f and g show the dynamics of Dra with different types of fertilizer in BWDS, and Fig. 4h shows the correlation between Dra and different NP compound fertilizer treatments. Fig. 4i, j, and k shows the dynamic changes of DW in BWDS with the different emitter types, and Fig. 4l is the correlation of DW with different NP compound fertilizer treatments.

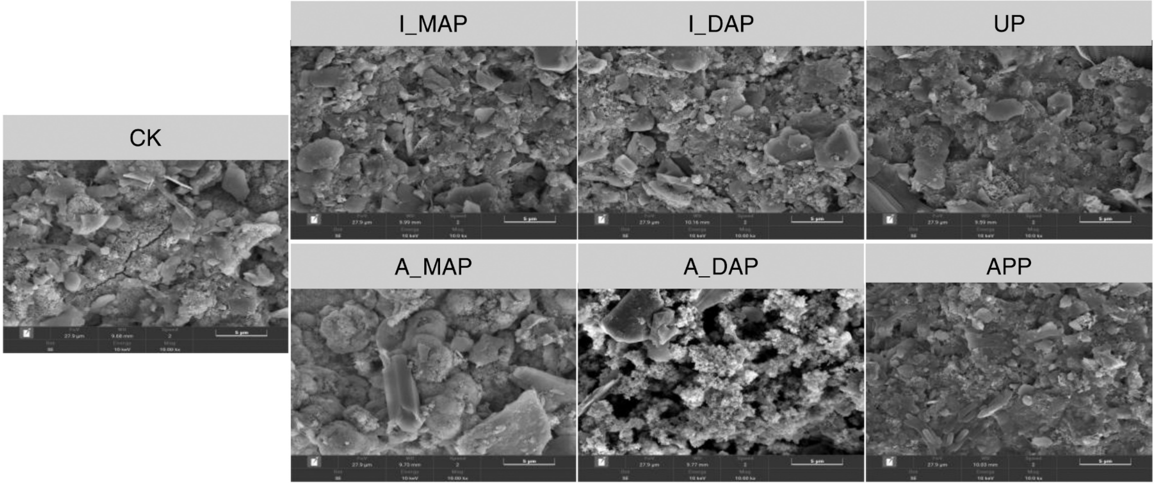


Fig. 5. Scanning electron microcopy (SEM) variations of different NP compound fertilizers.

(Fig. 5) showed some differences in the clogging material between the different NP compound fertilizers. Compared with I_MAP and I_DAP, A_MAP and A_DAP showed large and thick fouling particles and tightly bonded together, and the surface of fouling was not only rough, but also covered the whole surface of the flow emitter channel. In contrast, the fouling particle structure of UP and APP is smaller and relatively loose, the roughness between fouling is reduced, and the fragmentation distribution in the flow channel is easier to flow.

3.3. Mineral fraction changes of different NP compound fertilizers on emitter fouling

Fig. 6a shows the X-ray diffraction pattern of the mineral components of emitter fouling by the different NP compound fertilizers, and Fig. 6b shows the percentage of mineral component fouling with the different fertilizers tested. The results show that the mineral component fouling mainly includes quartz [SiO_2], calcite [$CaCO_3$], chlorite [$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$], muscovite [$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$], augelite [$Al_2(PO_4)(OH)_3$], brushite [$CaPO_3(OH)_2H_2O$], cyanite [$Al_2SiO_5$] and hydroxyapatite [$Ca_5(PO_4)_3OH$]. According to their chemical composition, they were classified as carbonate fouling (calcite), silicate fouling (quartz, chlorite, muscovite, and cyanite), and phosphate fouling (augelite, brushite, and hydroxyapatite), with percentages ranging from 1.4%−38.3%, 24.2–86.2% and 0.0%−63.6%, respectively.

With the increase in the operating time of the BWDS, the total amount of fouling material showed a gradual increase. For carbonate fouling (Fig. 7a), the application of different NP compound fertilizers significantly ($p < 0.05$) reduced the carbonate fouling content regarding the control, with the application of agricultural grade A_MAP and A_DAP fertilizers decreasing the calcite content by 1.3 mg/cm^2 and increasing it by 6.1 mg/cm^2, respectively. The application of APP significantly ($p < 0.05$) increased it by 16.2 mg/cm^2, when compared with the industrial grade I_MAP fertilizer. The calcite content decreased by 12.3 mg/cm^2 and 4.9 mg/cm^2 for agricultural grade A_MAP and A_DAP fertilizers, respectively, and decreased by 15.3 mg/cm^2 and increased by 5.2 mg/cm^2 with UP and APP fertilizers, respectively, compared to industrial grade I_DAP fertilizer.

As for silicate fouling (Fig. 7b, c, d, e, and Fig. S1), compared with industrial grade I_MAP fertilizer, the silicate content of agricultural grade A_MAP and A_DAP fertilizer increased by 36.2 mg/cm^2 and 44.4 mg/cm^2, respectively, and the silicate content of new UP and APP fertilizer increased by 71.2 mg/cm^2 and 62.6 mg/cm^2, respectively. The silicate content increased by 11.9 mg/cm^2 and 20.1 mg/cm^2 for application of agricultural grade A_MAP and A_DAP fertilizers, respectively, and by 38.4 mg/cm^2 and 46.9 mg/cm^2 for application of new UP and APP fertilizers, respectively, as compared to industrial grade I_DAP fertilizer. Regarding the phosphate fouling (Fig. 7f, g, h, and Fig. S1), the

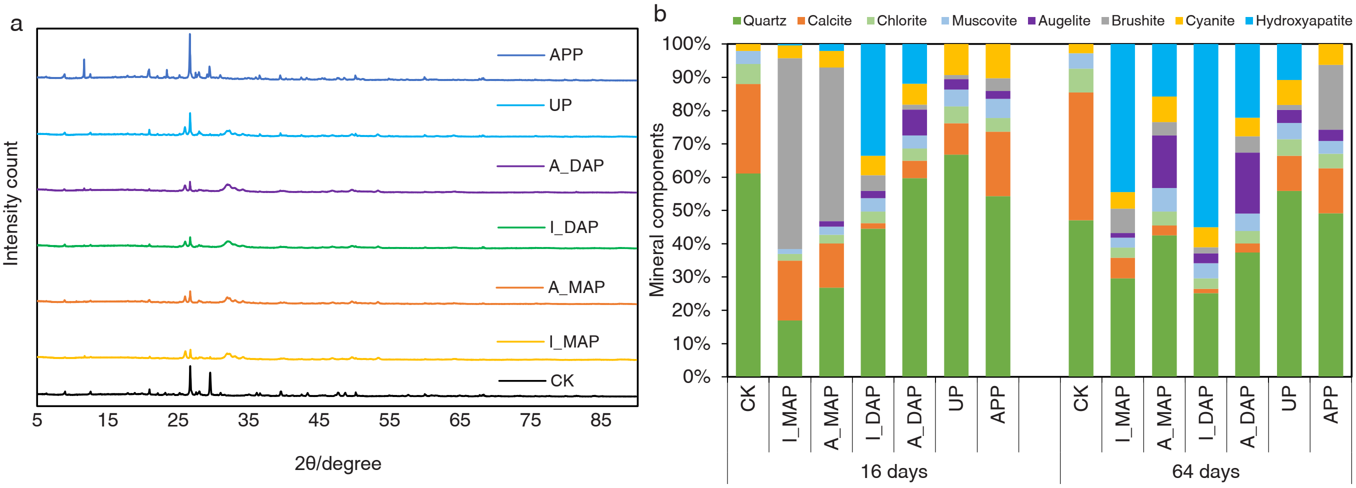


Fig. 6. Mineral fractions of different NP compound fertilizers. Fig. 6a shows the XRD spectrum, while Fig. 6b shows the percentage plot of the mineral components.

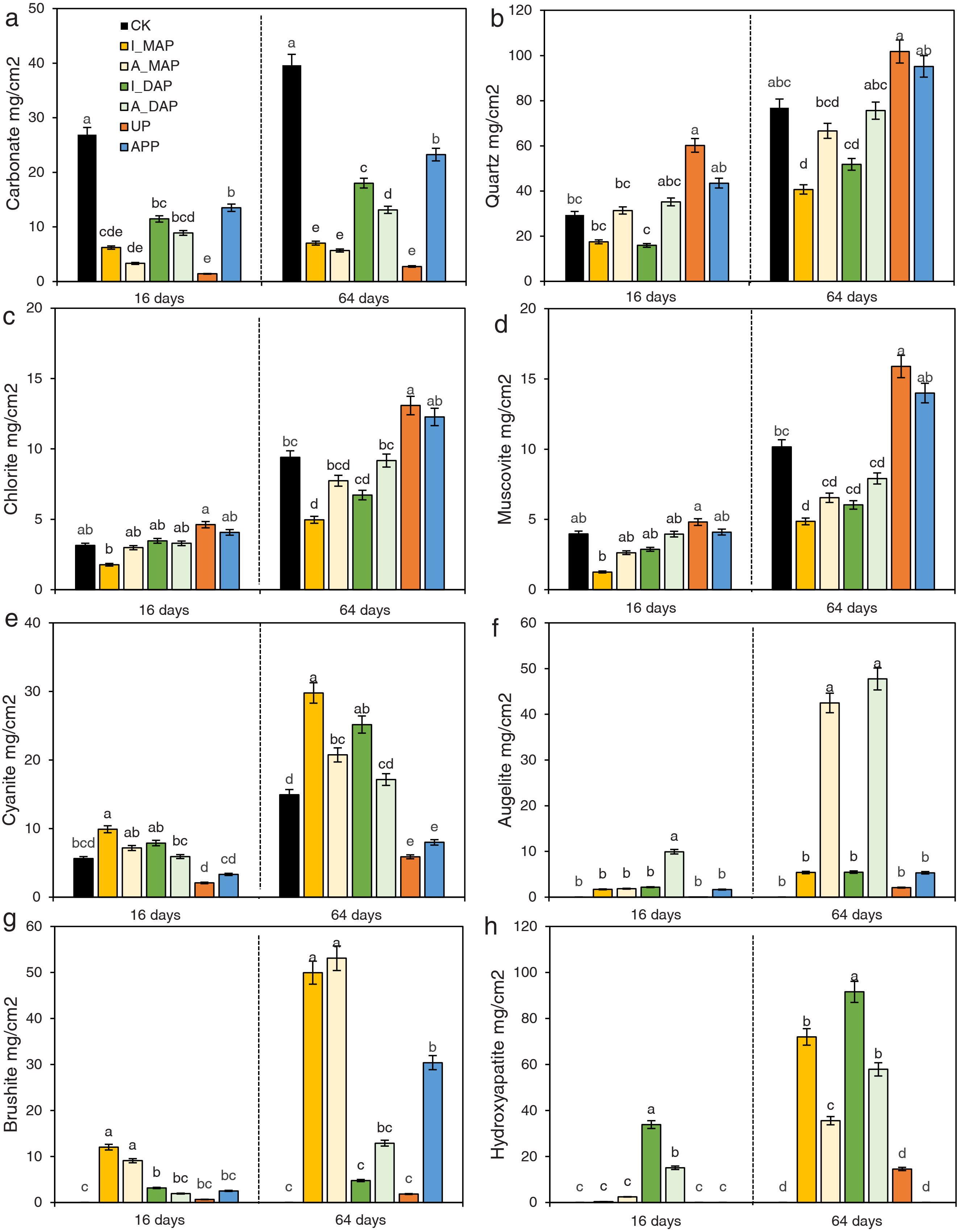


Fig. 7. Variation in mineral fraction content of different NP compound fertilizers. Fig. 7a shows calcite fouling; Fig. 7b, c, d, and e show quartz, chlorite, muscovite, and cyanite, respectively; and Figs. f, g, and h depict augelite, brushite, and hydroxyapatite, respectively.

phosphate content increased by 14.0 mg/cm^2 and 32.4 mg/cm^2 for the application of agricultural grade A_MAP and A_DAP fertilizers, respectively, and decreased by 64.3 mg/cm^2 and 50.4 mg/cm^2 for the application of the new UP and APP fertilizers, respectively, compared to the industrial grade I_MAP fertilizers. Compared with the industrial grade I_DAP fertilizers, the phosphate content increased by 12.9 mg/cm^2 and 31.3 mg/cm^2 with agricultural grade A_MAP and A_DAP fertilizers, respectively, and decreased by 65.3 mg/cm^2 and 51.4 mg/cm^2 with the new UP and APP fertilizers, respectively.

3.4. Analysis of impact pathways

As shown in Fig. 8a, the application of different NP compound fertilizers, as well as pH, Ca^{2+}, HCO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$, zeta potential and insoluble substance amount significantly affected calcite fouling ($p < 0.01$); pH, Ca^{2+}, HCO$_3^-$, PO$_4^{3-}$ and total hardness showed a

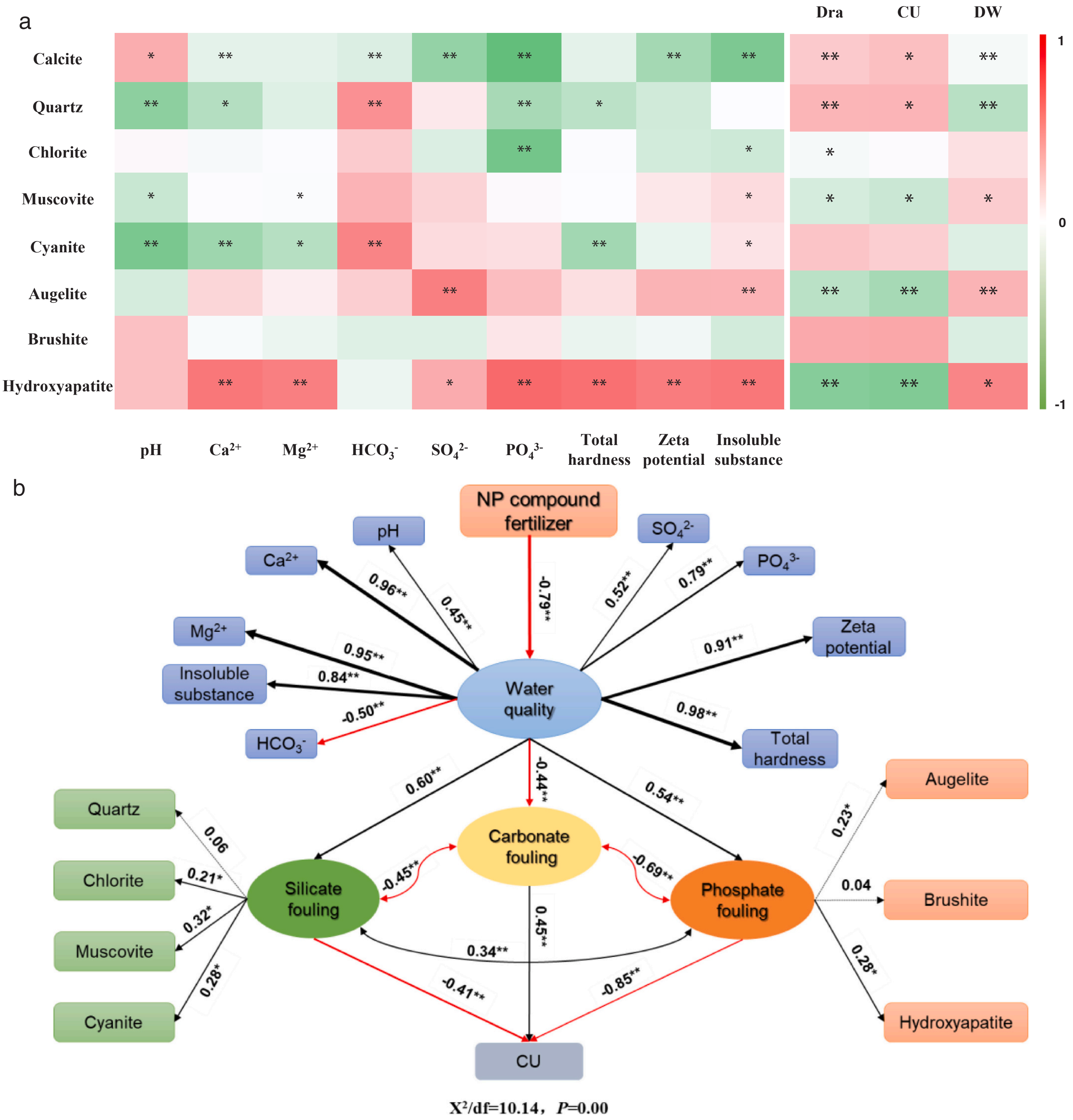


Fig. 8. Impact path analysis of different NP compound fertilizers on BWDS，a is the Pearson correlation of water quality parameters, clogging characteristics, and fouling components, and b is the structural equation model analysis (SEMA). Numbers near the path arrows indicate standardized path coefficients (β), and the width of the arrow is proportional to the degree of the path coefficient. Black and red arrows indicate positive and negative relationships, respectively; significance is indicated with * for $p < 0.05$ and ** for $p < 0.01$.

significant effect ($p < 0.01$) on quartz; PO_4^{3-} and insoluble substance had a significant effect ($p < 0.01$) on chlorite; Mg^{2+} and insoluble substance on muscovite ($p < 0.05$); pH, Ca^{2+}, Mg^{2+}, HCO_3^-, total hardness and insoluble substance on cyanite ($p < 0.01$), SO_4^{2-} and insoluble substance on augelite fouling ($p < 0.01$); Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-}, total hardness, zeta potential and insoluble substance on hydroxyapatite ($p < 0.01$). Meanwhile, calcite in carbonate fouling significantly ($p < 0.01$) affected Dra, CU and DW. Quartz and muscovite in silicate fouling had significant ($p < 0.01$) effects on Dra, CU and DW. On the other hand, augelite and hydroxyapatite in phosphate fouling had significant ($p < 0.01$) effects on Dra, CU and DW.

Moreover, the structural equation modeling analysis (Fig. 8b) showed that the application of different NP compound fertilizers firstly affected brackish water quality, where the path coefficients of the effects on Ca^{2+}, Mg^{2+}, total hardness, zeta potential, and insoluble substance were all greater than 0.84, whereas the path coefficients of the effects on pH, HCO_3^-, SO_4^{2-}, and PO_4^{3-} ranged from 0.45 to 0.79. In addition to affecting the water quality, the carbonate fouling, silicate fouling and phosphate fouling content were also affected, with path coefficients of −0.44 for carbonate fouling, 0.60 for silicate fouling, and 0.54 for phosphate fouling, respectively. Dra had influence path coefficients of 0.45, −0.41 and −0.85 for carbonate fouling, silicate fouling and phosphate fouling, respectively.

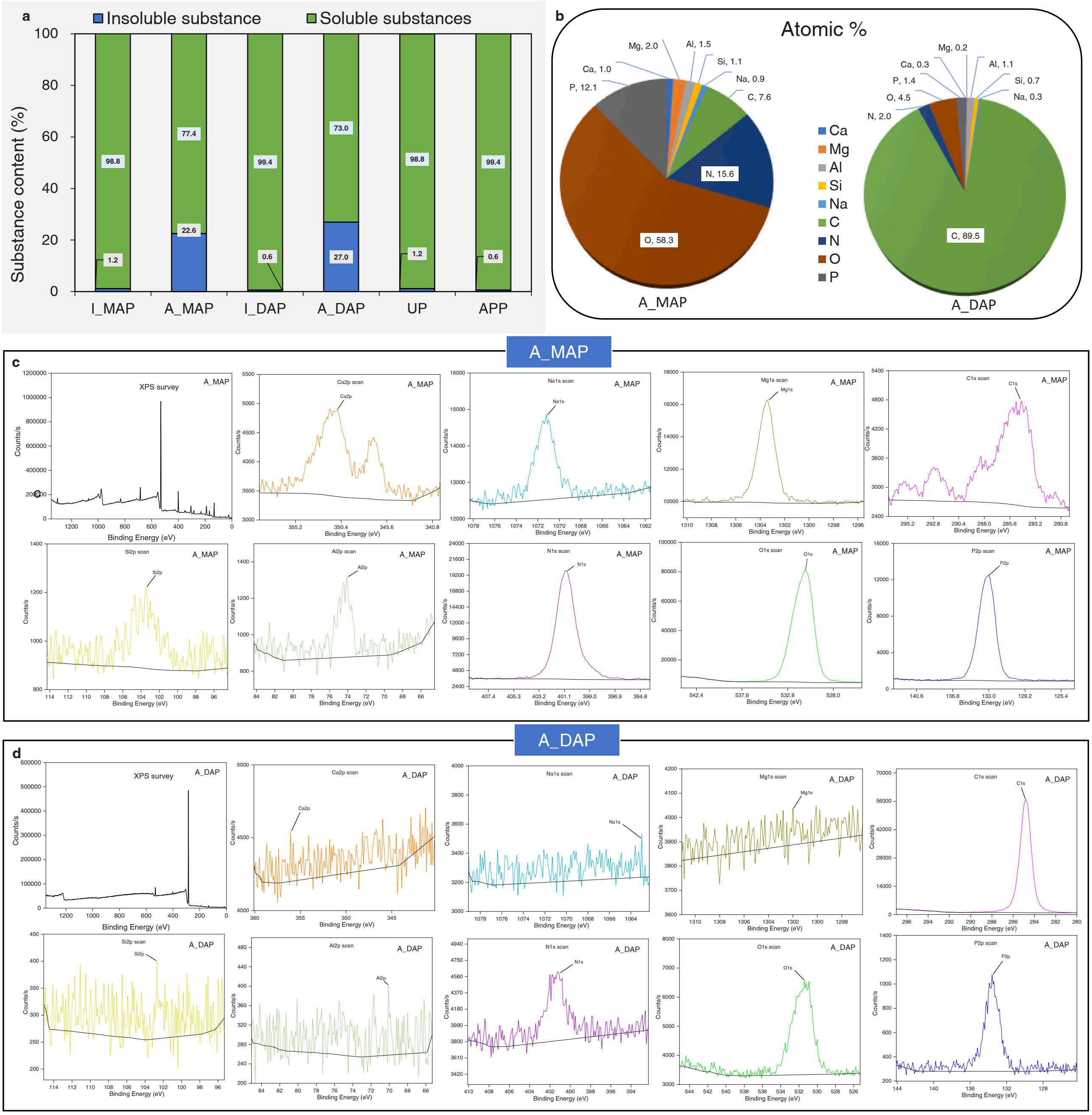


Fig. 9. Variation of insoluble substances in fertilizers. Fig. 9a shows the content of soluble and insoluble substance of different nitrogen and phosphorus fertilizers. Fig. 9b shows the impurity composition and content of insoluble substance. c and d are XPS spectra of insoluble substance.

4. Discussion

4.1. *Effect mechanism of agricultural grade NP compound fertilizers on emitter clogging*

This study found that application of A_MAP fertilizer, compared to industrial grade NP compound fertilizers, considerably exacerbated the emitter clogging when using brackish water, and significantly increased silicate fouling compared to I_MAP fertilizer, as well as increased phosphate fouling. We found that A_MAP fertilizer had 2.6% insoluble matter and 97.4% soluble matter (Fig. 9a). The specific impurity composition contained inside the 2.6% insoluble matter was determined by X-ray photoelectron spectroscopy (XPS) analysis (Fig. 9b, c), which showed that the impurities contained elements such as Ca, Mg, Al, S, Na, C, N, O and P, mainly Ca, Mg, Al, Si, C, N, O and P. These water-insoluble impurities exist in the brackish water mainly in the form of silicates, phosphates, and oxides of nitrogen and phosphorus, which may be adsorbed on the fouling surface, displacing and adsorbing out cations such as Ca^{2+} and Mg^{2+}. This fact, coupled with the negative charged in the surface of the insoluble fouling, allows the electrostatic adsorption of the positively charged ions contained in the brackish water, generating a potential difference and ultimately coagulation in the form of fouling, which leads to an increase in silicate fouling. Meanwhile, since A_MAP fertilizer contains 49% P_2O_5 and 11% NH_4^+-N, and I_MAP fertilizer contains 61% P_2O_5 and 12% NH_4^+-N, the pH of the acidic solution can be maintained in the drip irrigation system. Compared to the industrial grade MAP fertilizers, the agricultural grade MAP fertilizers contain lower levels of P_2O_5 and NH_4^+-N. At the same time, A_MAP fertilizers ionize NH_4^+ and $H_2PO_4^-$, which together with Ca^{2+} and Mg^{2+} produce $Ca(H_2PO_4)_2$ or $Mg(H_2PO_4)_2$, forming Ca-P and Mg-P precipitates. On the one hand, due to the negative charge contained on the surface of Ca-Mg fouling, a certain amount of Al^{3+} is adsorbed and eventually forms a coagulation effect of Ca-Mg fouling and phosphate fouling (Iler, 1975). This leads to the formation of a large amount of augelite fouling. At the same time, due to the porous medium of phosphate, the augelite fouling has an extremely strong adsorption function, which leads to the adsorption of a large amount of the Ca-P and Mg-P precipitated and the formation of a large amount of Al-P fouling, which in turn increases the content of augelite.

The application of A_DAP fertilizer likewise noticeably exacerbated the clogging of the drip irrigation system, mainly by significantly increasing the content of augelite compared to I_DAP fertilizer. A_DAP fertilizer contained 46% P_2O_5 and 18% NH_4^+-N, while I_DAP fertilizer contained 53% P_2O_5 and 21% NH_4^+-N. At the same time, we found that the insoluble matter of A_DAP fertilizer was 27.0% and the soluble matter was 73.0% (Fig. 9a). The specific impurity components contained inside the 26.9% insoluble matter were mainly Al, C, N, O and P (Fig. 9b, c). These insoluble impurities are mainly present in the drip irrigation system in the form of phosphates and carbon and nitrogen oxides. On the one hand, since A_DAP fertilizer is weakly alkaline, it may result in exacerbating emitter clogging. On the other hand, A_DAP fertilizer is able to ionize abundant NH_4^+ and HPO_4^{2-}, which can easily form $CaHPO_4$ or $MgHPO_4$ precipitation dirt with Ca^{2+} and Mg^{2+} present in brackish water, increasing therefore emitter clogging. At the same time, brackish water and A_DAP contain a large amount of Ca^{2+} and Mg^{2+}, a part of which forms carbonate fouling by transforming with HCO_3^-. A portion of Ca^{2+}, Mg^{2+}, and PO_4^{3-} produced by electrolysis of A_DAP react to form phosphates.PO_4^{3-} and Ca^{2+} react in water to form $CaHPO_4$, dicalcium phosphate. Dicalcium phosphate then hydrolyzes to $CaHPO_4$ and is rapidly converted to $Ca_4H(PO_4)_3$, which is further converted to $Ca_5(PO_4)_3OH$ (Tung and Skrtic, 2001), which in turn increases the amount of phosphate fouling in the drip irrigation system. This is consistent with the result that the weak alkalinity of DAP may exacerbate emitters clogging (Wang et al., 2020), which may correspond to the A_DAP fertilizer in this study. It is also consistent with a study that shows that A_DAP fertilizer significantly accelerates the combination of phosphate with Ca^{2+} and others in the irrigation water to form phosphate compounds (Yang et al., 2020), which in turn leads to more emitter clogging.

In addition to this, industrial grade MAP and DAP fertilizers are formulated differently from agricultural grade MAP and DAP fertilizers in that industrial grade fertilizers are usually formulated according to specific process needs, whereas agricultural grade fertilizers are formulated mainly depending on the soil and the nutrients required by the crop (Patil et al., 2021). Meanwhile, industrial grade fertilizers usually facilitate large-scale chemical reactions and production to create productivity and economic benefits, whereas agricultural grade fertilizers are mainly used for crop production and yield enhancement (Jbari et al., 2020).

4.2. *Effect mechanism of new NP compound fertilizers on emitters clogging*

The application of UP fertilizer significantly reduced emitter clogging. This is mainly due to the fact that UP fertilizer contains 44% P_2O_5 and 17% NH_4^+-N, and urea phosphate is a chemical adduct between urea and phosphoric acid molecules. Each kilogram of UP produces 6.3 mol H^+ when dissolved, which significantly reduces the pH of brackish water, promoting the transformation of H^+ and CO_3^{2-} to HCO_3^-, and reducing the ability of the brackish water to form $CaCO_3$ by the reaction of Ca^{2+} and CO_3^{2-}, thus inhibiting the formation of calcite fouling. At the same time, UP is able to react with $CaCO_3$, which in turn allows reducing the formation of calcium carbonate fouling. This finding is consistent with Ma et al. (2020) conclusion that UP fertilizers are less likely to react with calcium and magnesium ions in water and are often used as fouling inhibitors. It also increased the amount of chlorite and muscovite in silicate fouling and decreased the amount of cyanite. This may be due to the fact that the decrease in pH promotes the condensation of silicate fouling, thereby increasing chlorite and muscovite deposition. Coupled with the fact that the fouling particles in the water source are negatively charged and the addition of fertilizers brings in a large amount of positive charge, the bilayer is compressed under electrostatic attraction, which in turn increases the intensity of flocculation and sedimentation of chlorite and muscovite fouling (Liu et al., 2017). Meanwhile, the adsorption capacity of Ca^{2+} and Mg^{2+} with chlorite and muscovite fouling was reduced due to the reduction of the pH of brackish water caused by UP, which reduced the permeability and surface porosity of chlorite and muscovite fouling (Shafiq et al., 2018), and exacerbated their aggregation. At the same time, the adsorption capacity between Ca^{2+} and Mg^{2+} and Al^{3+} was increased, leading to a decrease in the adsorption between Al^{3+} and chlorite and muscovite fouling, which in turn reduced the content of cyanite fouling.

APP fertilizer also caused less emitter clogging. The APP fertilizer contains 60% P_2O_5 and 18% NH_4^+-N. Under acidic conditions, the polyphosphate is able to release H^+ during the absorption of NH_4^+-N, and the production of H^+ promotes the decomposition of the polyphosphate, converting it into $H_2PO_4^-$ that can be absorbed and utilized by the crop. The $H_2PO_4^-$ reacts with Ca^{2+} and Mg^{2+} to produce water soluble $Ca(H_2PO_4)_2$ or $Mg(H_2PO_4)_2$, which reduces the chance of Ca^{2+} reacting with CO_3^{2-} to form $CaCO_3$, which in turn diminishes the amount of calcite in the drip irrigation system. Moreover, APP fertilizer is a long-chain mixture that has the effect of chelating and shielding some specific metal cations such as Ca^{2+} and Mg^{2+} in the solution (Haohan et al., 2019). The shielding effect of APP fertilizer reduces the probability of Ca^{2+} and Mg^{2+}, among other cations, to react to form carbonate fouling in the emitter. The reduction of carbonate fouling was accompanied by a reduction in the content of cyanite in silicate fouling, which on the one hand may be from the precipitation and flocculation of solid particles in brackish water (Zhou et al., 2018). On the other hand, it may be that numerous cations in APP attracts solid particles such as negatively charged sediments common in brackish water (Zhou et al., 2019), and under the polymerization of APP, Ca^{2+} and Mg^{2+} occupy the binding sites of Al^{3+}, which promotes the formation of calcium and magnesium precipitates, resulting in the change of the crystalline structure and morphology of cyanite fouling (Chew and Mat, 2015), thus reducing the amount of cyanite fouling.

4.3. NP compound fertilizers selection

This study found that the application of UP and APP fertilizers significantly mitigated emitter clogging when using brackish water compared to industrial grade I_MAP and I_DAP fertilizers, whereas the application of agricultural grade A_MAP and A_DAP fertilizers exacerbated emitter clogging. However, in practical field applications, the combined effects of cost, soil texture, and environmental factors should need to be considered in addition to clogging (Goyal and Mansour, 2015; Ma et al., 2020). In terms of price (Table S2), the average price of industrial grade MAP and DAP fertilizers were 735$/t and 644$/t, respectively, while the average price of agricultural grade MAP and DAP were 438$/t and 441$/t, respectively. Although the cost of agricultural grade MAP fertilizers was reduced by 40.5% as compared to that of industrial grade MAP fertilizers, this led to a significant increase in emitter clogging. In terms of soil environment, although some researchers have suggested that the application of phosphate fertilizers at higher concentrations increases the risk of soil metal toxicity (Cheraghi et al., 2013), Salah et al. (2021) concluded that MAP fertilizers have a positive effect on increasing crop yields and decreasing the levels of toxic heavy metals in the soil environment. On the other hand, DAP fertilizers have the potential to reduce the solubility of heavy metals in the soil environment (Abou Zied, 2007), which can effectively reduce the adverse effects of heavy metals on the soil. In addition to effects of cost, soil texture, and environmental factors, effects on crops such as demand, tolerance, toxicity must also be considered. Since the effective phosphorus content of different NP fertilizers is different, the requirement for different crops is also different, in general, the effective content of industrial grade NP fertilizers is significantly higher than that of agricultural grade NP fertilizers (Table S1), making the requirement of agricultural grade NP fertilizers relatively higher than that of industrial grade NP fertilizers for the same crop. And different seeds or crops respond significantly differently to fertilizer toxicity, which is determined by crop genetics (Makaza and Khiari, 2023). MAP and DAP fertilizers have lower salt toxicity indices compared to other fertilizers (Dockerill et al., 2019), but high exposure to seeds reduces the rate of germination and increases seedling mortality(Nedljimi et al., 2020). And salt tolerance varies among crop varieties and its tolerance is related to the ease of potassium uptake by the crop (Hussain et al., 2014) in order to avoid the accumulation of high sodium content.

Meanwhile, the market price of applying UP and APP fertilizers is 1351$/t and 1153$/t respectively, which is 62.1%–67.6% and 61.8%–67.4% higher than that of I_MAP and I_DAP fertilizers respectively. In this regard, UP and APP fertilizers, which have slightly higher fertilizer prices and obvious anti-clogging effects, can be used for low-concentration fertilization. However, from the point of view of environmental impact, UP fertilizer is more suitable for alkaline soil (Cherrat et al., 2020), and APP fertilizer, with good water solubility and chelating effect, is also more suitable for alkaline soil compared with acidic soil (Wang et al., 2022a). As a kind of highly efficient and environmentally friendly composite fertilizer, MAP is widely used in agriculture (Pizzeghello et al., 2019). However, DAP fertilizer is prone to the risk of eutrophication of water bodies, which affects environmental safety (Gonzalez-Cencerrado et al., 2020). Meanwhile, under the condition of safe operation of drip irrigation system ($CU>80\%$), the service years of drip irrigation belt was calculated for different types of fertilizers (Table 2). The results showed that the agricultural grade fertilizers are suitable for drip irrigation of 1 year-cycle crops since the safe operation of the system is about 1.2 years (Table 2, $Y\geq1$ year in agricultural grade fertilizers). The industrial grade and new NP compound fertilizers can be applied to perennial crop drip irrigation since the average safe operating life of the system is about 1.6–3.4 times that of agricultural grade fertilizers. It should be pointed out that, in the system layout shown in the manuscript (0.3 m between emitters, 1.1 m between laterals), only the cost of drip irrigation belt and fertilizer amount for 1 ha is considered, and, therefore, the costs of filters, fertilizer tanks, pumps and other installation costs were not included (Table S5). The price of E1, E2 and E3 drip irrigation belt alone without fertilizer is 5.4 $/year, 5.4 $/year and 2.5 $/year, respectively, under the safe operation of the system for one year. Since the cost of dripline and agricultural grade fertilizer is similar, it is recommended to choose agricultural grade A_MAP fertilizer under the same conditions. If the drip irrigation belt must last 2 years, then is better to apply I_DAP, and if the lifespan should be extended to 3 years, the best option is to apply I_MAP and APP. Using UP fertilizer, the safe service life of drip irrigation belt can reach 4 years. In this regard, A_MAP fertilizer can be applied to fertigate annual crops using brackish water, while for perennial crops, industrial grade NP compound fertilizer and new NP compound fertilizer should be reasonably selected according to the service life of the drip irrigation belt.

5. Conclusions

From this study, the following main points were concluded:

(1) Compared with industrial grade I_MAP and I_DAP fertilizers, the application of agricultural grade A_MAP and A_DAP fertilizers aggravated emitter clogging when using brackish water, reducing and the end of system operation the average relative flow by 18.5%–22.8% and 21.4%–25.6%, respectively. The application of UP and APP fertilizer alleviated emitter clogging and increased the average relative flow by 29.9%–37.1% and 10.2%–16.4%, respectively.

(2) The higher emitter clogging observed with A_MAP and A_DAP fertilizers were mainly caused by the increase in the content of augelite in silicates and phosphates, which increased by 13.3%–67.8% and 14.9%–37.6% in silicates and phosphates,

Table 2

Safe years of operation based on different annual irrigation water (AIW) ranges ($CU \geq 80\%$).

AIW (m^3/ha)	Emitter	CK (years)	A_MAP (years)	A_DAP (years)	I_MAP (years)	I_DAP (years)	UP (years)	APP (years)
3000-4500	E1	1.1	0.7	0.5	1.4	1.3	2.7	1.6
	E2	1.4	0.8	0.7	2.4	2.1	4.0	2.6
	E3	2.1	2.1	1.0	2.9	2.4	3.6	3.3
4500-6000	E1	0.8	0.5	0.4	0.9	0.9	1.9	1.1
	E2	1.0	0.6	0.5	1.6	1.4	2.8	1.8
	E3	1.5	1.4	0.7	2.0	1.7	2.6	2.3
6000-7500	E1	0.6	0.4	0.3	0.7	0.7	1.4	0.8
	E2	0.8	0.4	0.4	1.3	1.1	2.1	1.4
	E3	1.1	1.1	0.5	1.6	1.3	2.0	1.8
7500-9000	E1	0.5	0.3	0.2	0.6	0.6	1.2	0.7
	E2	0.6	0.4	0.3	1.0	0.9	1.7	1.1
	E3	1.0	1.0	0.4	1.3	1.1	1.6	1.5

respectively, compared with I_MAP and I_DAP fertilizers. Conversely, UP and APP fertilizers decreased phosphate content by 58.5%–74.6% and 59.0%–74.9%, respectively. Therefore, the application of different NP compound fertilizers affected the quality of brackish water, and then affected the contents of carbonate fouling, silicate fouling and phosphate fouling.

(3) Under the condition of safe operating life of drip irrigation system (i.e., maintaining CU≥80%), the different NP compound fertilizers present diverse results for different types of emitters. Considering the effect of clogging, cost, soil environment and other factors, A_MAP fertilizers can be applied to annual crops, while drip irrigation belt for perennial crop drip irrigation should be rationally selected from industrial grade and new NP compound fertilizers according to their service life.

CRediT authorship contribution statement

Xiao Yang: Conceptualization, Methodology, Resources, Writing – review & editing. **Li Yunkai:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Maitusong Memetmin:** Funding acquisition, Project administration. **Puig-Bargués Jaume:** Investigation, Validation, Writing – review & editing. **Ma Changjian:** Investigation, Validation. **Wang Yayu:** Data curation, Formal analysis, Investigation, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agwat.2023.108644.

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