

Enhancing Phosphorus Efficiency in Calcareous Soils: Role of Polyphosphate Properties in Nutrient Solubility, Maize Nutrient Uptake, and Growth

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Cite This: *ACS Omega* 2025, 10, 4057–4067



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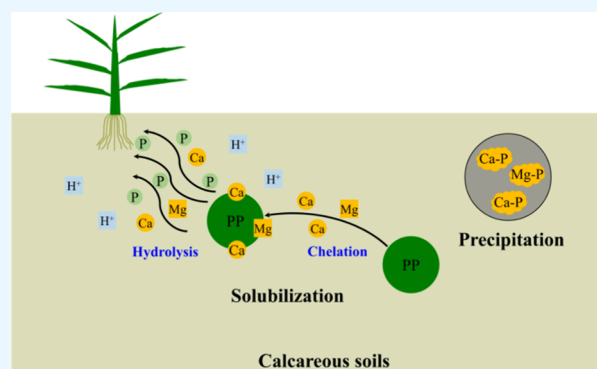
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ABSTRACT: Polyphosphate, which can improve crop yield and phosphorus use efficiency in calcareous soils, has gained increasing global attention. However, the effects of polyphosphate properties (pH and polymerization degree) on agronomic effects are still unclear. In this study, the nutrient solubility, nutrient release, nutrient uptake, and maize growth in calcareous soil of alkaline diammonium phosphate (DAP), acidic ammonium polyphosphate (APP) with a polymerization degree of 1.8, and alkaline potassium triphosphate (KTPP) with a higher polymerization degree of 2.8 were evaluated. The results showed that KTPP at pH 8.0 could significantly increase the solubility of Ca^{2+} by 24.3 times and 3.1 times than those by DAP and APP, respectively, and significantly increase the solubility of Mg^{2+} by 172.8 times and 1.6 times than those by DAP and APP, respectively. The nutrient release experiment indicated 100% P was released after 15 d for the three P fertilizers, and the cumulative released amounts of soluble Ca and Mg with KTPP were about 2.9 and 3.2 times higher than those of DAP, respectively. The result of the pot experiment demonstrated that KTPP significantly enhanced shoot biomass by 24.1% compared with that by DAP. The P, Ca, and Mg uptake of maize shoots with KTPP significantly improved by 49.7%, 20.9%, and 20.9%, respectively, compared to that of DAP. However, no significant differences in yield or nutrient uptake between the KTPP and APP treatments were observed. This study demonstrated that polyphosphate with a higher polymerization degree had a better effect on increasing the solubility of cations, crop yield, and nutrient uptake, and polyphosphate application provides a synergistic interaction between P and Ca in calcareous soil, which may promote the application of polyphosphate fertilizers to expand to large-scale agriculture.



1. INTRODUCTION

Phosphorus (P) is a critical macronutrient that influences plant growth and development. It participates in protein synthesis, enzyme activation, and sugar transport redox reactions, which are essential for achieving high crop yield and maintaining soil fertility status.^{1,2} High-analysis phosphate fertilizers, such as monoammonium phosphate (MAP) and diammonium phosphate (DAP), are predominant in the market. For example, in 2023, MAP and DAP production in China accounted for more than 86% of the total phosphate fertilizer production.³ However, the orthophosphate in DAP and MAP reacts quickly with calcium and magnesium ions in alkaline-calcareous soil to form insoluble compounds that are not absorbed by plants.^{4–7} Consequently, this results in the massive accumulation of P in the soil and a low P fertilizer-use efficiency (PUE).^{8,9}

Many efforts have been made to overcome these disadvantages, such as by using liquid fertilizers to increase the P diffusion distance in the soil, thus decreasing P precipitation.^{10–12} Coated phosphate fertilizers can slow the

initial dissolution of phosphate, minimize the opportunity to form stronger P bonds with Ca, and synchronize P availability with crop demand.^{13–15} Using polyphosphate instead of orthophosphate may be a novel way to improve PUE as it has many desirable properties, such as water solubility, better mobility, excellent chelating properties, and progressive hydrolysis into orthophosphate under suitable conditions.^{16–19} Therefore, polyphosphate can form chelates with Ca and Mg (pH-dependent), rather than precipitate into a mineral phase, gradually hydrolyze regardless of adsorption onto mineral surfaces, continuously provide available orthophosphate to

Received: November 15, 2024

Revised: January 5, 2025

Accepted: January 14, 2025

Published: January 21, 2025

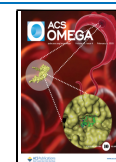


Table 1. Nutrient Contents and P Species Composition of DAP, APP, and KTPP

	nutrient content (%)			P species composition and contents (P ₂ O ₅) (%)			polymerization degree	pH ^a
	N	P ₂ O ₅	K ₂ O	P ₁	P ₂	P ₃		
DAP	21.2	53.7		100.0			1.0	7.8
APP	18.0	70.1		24.9	72.4	2.7	1.8	4.6
KTPP		48.4	43.6	3.5	10.7	85.8	2.8	9.1

^aMeasured at a solid:liquid ratio of 1:100.

plants, and consequently enhance P uptake and crop productivity in calcareous soil.^{20,21}

However, the polymerization degree of agricultural polyphosphate is generally less than 10, and the distribution of P species may cover PO₄³⁻–P₉O₂₈¹¹⁻ with different rates.^{22,23} The agronomic effects of polyphosphate are governed by the mutual interaction of multifarious factors in practice rather than by a single pH or cation factor,^{24–29} such as the intrinsic properties of polyphosphate (pH, linear, polymerization degree, and polymerization rate), soil properties (pH, temperature, soil minerals), and crop types, resulting in inconsistent or controversial results in published studies. For example, no significant agronomic difference has been found between orthophosphate and polyphosphate in acidic soils,³⁰ mainly because the polymerization degree of polyphosphate products is low, which allows them to be hydrolyzed quickly in the soil. Polyphosphate hydrolysis increases as the pH decreases in aqueous solution, although its hydrolysis rate is greater in calcareous soil than that in acidic soil, which may be due to the different properties of acidic and calcareous soils.³¹ The promotion of soil P availability in calcareous soil by ammonium polyphosphate (APP) application can be explained by more than 53.8% of the total variance in the soil pH changes within 0.2.³² However, when selecting polyphosphate fertilizers for crops, greater attention is often paid to the higher polymerization degree, rather than to the differing pH values of polyphosphate products.³³ This focus may limit the mechanistic study of polyphosphate across a wide range of agricultural scenarios as acidic fertilizers may perform better on calcareous soils.^{34–37}

Potassium tripolyphosphate (KTPP) is an alkaline substance with the molecular formula K₃P₃O₁₀, contains more than 85% tripolyphosphate, and is often used as a corrosion inhibitor, food stabilizer, and textile processing agent.^{16,38} From the perspective of fertilizer product development, KTPP has the potential to be a highly efficient P fertilizer. However, there has been little research conducted to explore alkaline polyphosphates under specific agricultural scenarios. Investigating KTPP with high alkalinity and higher polymerization degree could facilitate the expansion of polyphosphate fertilizers to large-scale agriculture.^{38,39} Furthermore, the North China Plain, a vital agricultural region, is characterized by its alkaline calcareous soil, which supports a predominant crop rotation system that switches between winter wheat and summer maize.⁴⁰ Maize, known as a phosphorus-sensitive crop, benefits significantly from the application of P fertilizers in nutrient utilization, crop yield and quality.³⁷ Consequently, gaining comprehensive insight into the behavior of polyphosphate fertilizers is crucial for guiding the strategic use of phosphate fertilizers, which is essential for optimizing crop cultivation in calcareous soils.

We hypothesized that the application of polyphosphates would be more effective than that of DAP (orthophosphate, pH 7.8), and KTPP with a higher polymerization degree

(polymerization degree 2.8, pH 9.1) would behave better than APP (polymerization degree 1.8, pH 4.6) in dissolving more cations in solution, releasing more nutrients (P, Ca, and Mg) from calcareous soil, and enhancing maize biomass and nutrient uptake. Consequently, this study compared the nutrient solubility, release, uptake, and maize growth between KTPP and both DAP and APP in calcareous soil.

2. MATERIALS AND METHODS

2.1. Experiment Design. Our research consisted of three experiments, which were conducted in a laboratory at the National Innovation Center for Agri-tech, Nanjing (32.0°N, 118.8°E), and the indoor temperature was maintained at 18–24 °C during the experiment.

The P fertilizers used in this study includes DAP, APP, and KTPP. DAP (analytic reagent), was obtained from Sinopharm Chemical Reagent Co., Ltd. APP and KTPP (industrial grade) were provided by Research & Development Center, Yunnan Yuntianhua Co. Ltd. The distributions of different P species were determined using the ion chromatographic method⁴¹ by a Thermo Scientific ICS-600 chromatography system.²⁷ The details are presented in Table 1 and Figure S1.

The Ca²⁺ and Mg²⁺ solutions used in the solubility experiment were provided by CaCl₂ and MgCl₂·6H₂O, respectively, and these reagents were analytically pure and provided by Sinopharm Chemical Reagent Co., Ltd.

The calcareous soil used both in the column and pot experiment, was obtained from Qyzhou County, Hebei Province, China. The soil was collected from the top 10 cm of the site, air-dried, and then sieved to <2 mm. Selected soil properties are listed in Table 2.

To further investigate the contribution of KTPP in the calcareous soil to P uptake and maize growth, a pot experiment

Table 2. Selected Properties of the Calcareous Soil

property	value
pH ^a	7.8
organic C (%) ^b	1.6
total N (g kg ⁻¹) ^c	0.5
Olsen-P (mg kg ⁻¹) ^d	13.8
exchangeable K (mg kg ⁻¹) ^e	283.2
exchangeable Ca (cmol kg ⁻¹) ^f	114.7
exchangeable Mg (cmol kg ⁻¹) ^f	5.5

^aSoil pH was measured at a soil:deionized water ratio of 1:2.5 (weight: volume) using a pH meter. ^bTotal soil organic C content was measured using the potassium dichromate volumetric method.⁴²

^cTotal N was measured by the semimicro-Kjeldahl method.⁴² ^dOlsen P in the calcareous soil was measured by the Olsen method.⁴³

^eExchangeable K was measured by the flame photometry method.⁴²

^fExchangeable Ca and Mg were measured using the ammonium acetate (pH 7.0) method.⁴⁴

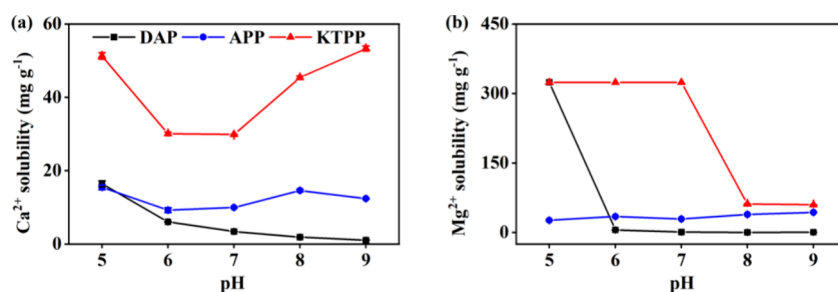


Figure 1. Solubility of (a) Ca^{2+} and (b) Mg^{2+} in DAP, APP, and KTPP solutions with different pH values. All results in the figures were presented as the mean of three replicates.

was conducted in the greenhouse using maize (*Zea mays* L. cv. Zhengdan 958).

2.2. Solubility of Cations in Different P Solutions. This experiment was designed to assess the solubility of cations (Ca^{2+} and Mg^{2+}) in different P fertilizer solutions, including DAP, APP, and KTPP. The objective was to verify the ability of KTPP to dissolve more nutrients and minimize the formation of insoluble compounds. The solubilities of Ca^{2+} and Mg^{2+} in these P solutions were determined using a dynamic method.^{45–47}

A series of 30 g L^{-1} P solutions were prepared, and their pH values were adjusted by 1:1 HCl and $\text{NH}_3\cdot\text{H}_2\text{O}$ to 5.0, 6.0, 7.0, 8.0, and 9.0. Different P solutions were added to a 250 mL beaker under atmospheric pressure. Cation solution with a concentration of 0.2 mol L^{-1} was added dropwise to the P solution, and the mixed solution was left to equalize. If nothing precipitated from the mixed solution, then an additional amount of cationic solution was added. When the last amount of the cation solution caused precipitation, solid–liquid-phase equilibria were established during the equilibrium time. The total amount of cation solution consumed before the last addition was considered to be the cation solubility in the KTPP solution.

The solubilities (x , mg g^{-1}) of Ca^{2+} and Mg^{2+} in different P solutions were calculated using the following equation:

$$x = \frac{c \times V \times M}{m} \quad (2.1)$$

where c is the molar concentration of the Ca^{2+} or Mg^{2+} solution (mol L^{-1}), V is the total addition volume of the Ca^{2+} or Mg^{2+} solution (L), M is the molar mass of Ca^{2+} or Mg^{2+} (g mol^{-1}), and m is the mass of the different P fertilizers in the solution (g).

2.3. Nutrient Release Behavior from the Soil Ccolumn. A column perfusion test was performed to evaluate the dynamic P release behavior of KTPP in a calcareous soil using a method similar to that of Baird et al.^{48,49} and the results were compared with those for DAP and APP.

The two ends of a polypropylene column (150 mm height \times 30 mm diameter) were covered with glass wool to minimize surface disturbances during the experiment. Approximately 42 g of calcareous soil was packed into the column to a suitable compactness, and 1 g of each of the three fertilizers was placed in the middle of the soil column. Deionized water was continuously pumped from the bottom of the column through the soil–fertilizer–soil configuration to the top of the column at a flow rate of 10 mL h^{-1} by using a peristaltic pump. The eluates were collected at regular intervals of 5 h every 24 h using a fraction collector within 15 d, analyzed individually during the first day, and bulked together from 2 to 15 d. The

eluate was analyzed after appropriate dilution using inductively coupled plasma optical emission spectrometry (ICP–OES; iCAP PRO, Thermo Scientific, USA), and the pH values were determined.

The mechanism of Ca and Mg release from the soil was described and interpreted using different kinetic models, known as the zero-order (2.2), first-order (2.3), and korsmeyer-peppas (2.4) models:^{50,51}

$$q_t = At + B \quad (2.2)$$

$$q_t = A \ln(t) + B \quad (2.3)$$

$$q_t = At^B \quad (2.4)$$

where q_t represents the amount of Ca and Mg released at time t and equilibrium, respectively, and A and B are solubility rate constants.

2.4. Maize Response to KTPP in the Calcareous Soil. A pot experiment was conducted to investigate the effects of KTPP on the maize yield and P uptake in calcareous soil. Four treatments were included: CK (no phosphate fertilizer), DAP, APP, and KTPP, which were supplied in solution and equivalent to 100 mg P kg^{-1} soil.

Plastic pots (100 mm height \times 160 mm diameter) were filled with 500 g of calcareous soil. Before the maize seeds were planted, all the essential nutrients were uniformly added to the soil in solution as follows (mg kg^{-1} soil): 200 N ($\text{CO}(\text{NH}_2)_2$), 200 K (K_2SO_4), 20 Mg (MgSO_4), 0.9 Fe (EDTA-FeNa), 0.7 B (H_3BO_3), 0.3 Mn ($\text{MnSO}_4\cdot\text{H}_2\text{O}$), 0.7 Zn ($\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$), 0.04 Cu ($\text{CuSO}_4\cdot 5\text{H}_2\text{O}$), and 0.04 Mo ($\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$). Seeds were surface-sterilized in 10% H_2O_2 for 30 min, rinsed with deionized water, soaked in saturated CaSO_4 solution for 12 h, and then germinated in Petri dishes covered with wet filter papers at 22 °C for 1–2 d. Three seeds were planted per pot, lightly covered with topsoil, and thinned to two after 2 d. The soil was watered daily to maintain 70% of the field water capacity by weight. Pots were assigned in a randomized complete block design with three replicates of each treatment.

Before harvest, the plant height and diameter were measured. The leaf length and leaf width were measured by a ruler, and then the leaf area was calculated by leaf length \times leaf width $\times k$, where the value of k is 0.5 for partially expanded leaves and 0.75 for completely expanded leaves.³⁶ At harvest (35 days after sowing), shoots were cut at the soil surface and oven-dried at 105 °C for 30 min and then at 70 °C for 3 days until constant weight. Afterward, shoots were ground into powder and digested with 5 mL concentrated H_2SO_4 and 2 mL 30% v/v H_2O_2 . The P, Ca, and Mg concentrations in maize shoots were analyzed by using ICP–OES.

PUE was calculated using the following equation:⁵²

$$\text{PUE}(\%) = \frac{U_p - U_c}{P_{\text{added}}} \times 100\% \quad (2.5)$$

where U_p is shoot P uptake in the P addition treatment (mg), U_c is shoot P uptake in the control treatment (mg), and P_{added} is the amount of P applied in the P addition treatment (mg).

2.5. Statistical Analysis. The effects of the different P fertilizer treatments on nutrient solubility, nutrient release, shoot biomass, and nutrient uptake were analyzed by one-way analysis of variance (ANOVA) using SPSS 26 (IBM SPSS Statistics, NY, USA). Significant differences were determined using Tukey's test at $p < 0.05$. Pearson's correlation analysis and principal component analysis was used to evaluate the relationships between cation solubility, P release, and nutrient uptake with different P fertilizers.

3. RESULTS

3.1. Solubility of Ca^{2+} and Mg^{2+} in KTPP Solution. The solubilities of Ca^{2+} and Mg^{2+} in the KTPP solution are higher than those in the DAP and APP solutions (Figure 1). When the pH of the P solution exceeded 7, the solubility of Ca^{2+} in the KTPP solution exceeded 29.9 mg g^{-1} , contrasting with the DAP solution where it remained below 3.4 mg g^{-1} . When the pH of the P solution was maintained at 8.0 (close to the calcareous soil used), the solubility of Ca^{2+} in KTPP was significantly increased by 24.3 and 3.1 times over DAP and APP, respectively, and the solubility of Mg^{2+} in KTPP was significantly increased by 172.8 and 1.6 times over DAP and APP, respectively. When the solution pH was increased, the solubilities of Ca^{2+} and Mg^{2+} in the DAP solution decreased. At KTPP solution pH values of 5.0, 6.0, and 7.0 and a DAP solution pH of 5.0, a peculiar phenomenon occurred where precipitation did not occur, even when the solubility of Mg^{2+} exceeded 324 mg g^{-1} .

The relationship between the polymerization degree of different P fertilizers and the cation solubilities at a solution pH of 8.0 is shown in Figure 2. As the polymerization degree of the

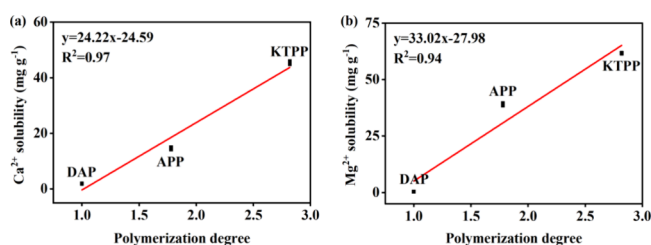


Figure 2. Correlations between the polymerization degree of different P fertilizers with cation solubilities at pH 8: (a) Ca^{2+} and (b) Mg^{2+} .

P fertilizers increased, the soluble amounts of Ca^{2+} and Mg^{2+} increased linearly when the pH value of the reactive solution was close to that of the calcareous soil.

3.2. P Released from the Calcareous Soil Column. All three P fertilizers manifested a burst release of P in the first 5 h (Figure 3a,b), and the KTPP treatment showed the fastest release behavior as P was almost completely released after 5 h. The cumulative release of P from the DAP, APP, and KTPP treatments showed a significant difference within the first 5 h, although no significant difference was observed after 15 days, and 100% of P was released from the release solutions with the three P fertilizers.

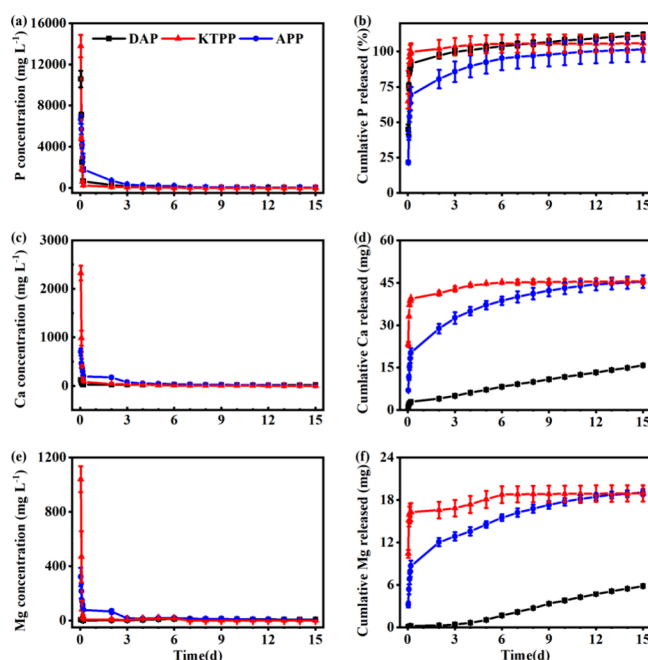


Figure 3. Dissolution kinetics of nutrients released from the calcareous soil with different P fertilizers: concentrations of (a) P, (c) Ca, and (e) Mg released at each time interval and cumulative amounts of (b) P (as % of P added), (d) Ca, and (f) Mg released.

The release of Ca and Mg with KTPP was significantly higher in the first 5 h than that with DAP and APP, although it was similar to that with APP after 15 days (Figure 3). The amounts of soluble Ca and Mg with KTPP released cumulatively were approximately 2.9-fold and 3.2-fold higher than those with DAP, respectively. Simultaneously, the pH of the eluate solution with APP was significantly lower than that with DAP and KTPP over 15 days (Figure S2).

The kinetics of dissolution of Ca and Mg from calcareous soil have been documented as their cumulative elutions over time from a column. The kinetic constants for the release behavior of Ca and Mg from DAP, APP, and KTPP at equilibrium time were determined using the linear forms of zero-order, first-order, and Korsmeyer–Peppas models (Table 3 and 4).

The zero-order model best described the cumulative release of Ca from DAP-treated soil, indicating that the release rate of Ca remains constant over time, with a more significant increase observed during extended periods. In contrast, the release of Ca from APP and KTPP treatments is more accurately described by the first-order model, indicating a distinct release pattern, while the kinetic constant B for KTPP is significantly larger.

3.3. Plant Growth and Nutrient Uptake. In the pot experiment, the application of P fertilizer significantly improved the fundamental morphological indicators and nutrient uptake of the plants compared with those of CK. KTPP significantly increased the stem diameter, leaf area, and shoot biomass of maize by 3.7%, 10.7%, 19.5%, and 24.1% over DAP, respectively (Figure 4). Also, KTPP marginally increased the stem diameter, leaf area, and shoot biomass of maize by 2.2%, 4.5%, 6.5%, and 11.4% over APP, with no significant difference observed between APP and KTPP.

APP significantly increased the P concentration in maize shoots, although no significant difference existed in P uptake

Table 3. Kinetic Parameters of Zero-Order, First-Order, and Korsmeyer–Peppas Models for Mg Release from DAP, APP, and KTPP^a

treatment	zero-order			first-order			Korsmeyer–Peppas		
	A	B	R ²	A	B	R ²	A	B	R ²
DAP	0.92	2.29	0.99	2.15	6.21	0.79	4.90	0.33	0.94
APP	2.18	19.67	0.80	6.30	27.81	0.99	22.28	0.29	0.97
KTPP	0.78	37.08	0.49	2.61	39.65	0.82	40.81	0.06	0.78

^aWhile the release of Mg from DAP, APP, and KTPP treatments is accurately described by the Korsmeyer–Peppas model, the exponents A and B have significant difference providing insights into the mechanisms that governs the release kinetics.

Table 4. Kinetic Parameters of Zero-Order, First-Order, and Korsmeyer–Peppas Models for Mg Release from DAP, APP, and KTPP

treatment	zero-order			first-order			Korsmeyer–Peppas		
	A	B	R ²	A	B	R ²	A	B	R ²
DAP	0.39	−0.29	0.97	0.82	1.49	0.60	0.10	1.56	0.99
APP	0.89	8.14	0.84	2.50	11.57	0.97	9.90	0.25	0.98
KTPP	0.31	15.52	0.56	0.95	16.61	0.79	15.85	0.08	0.80

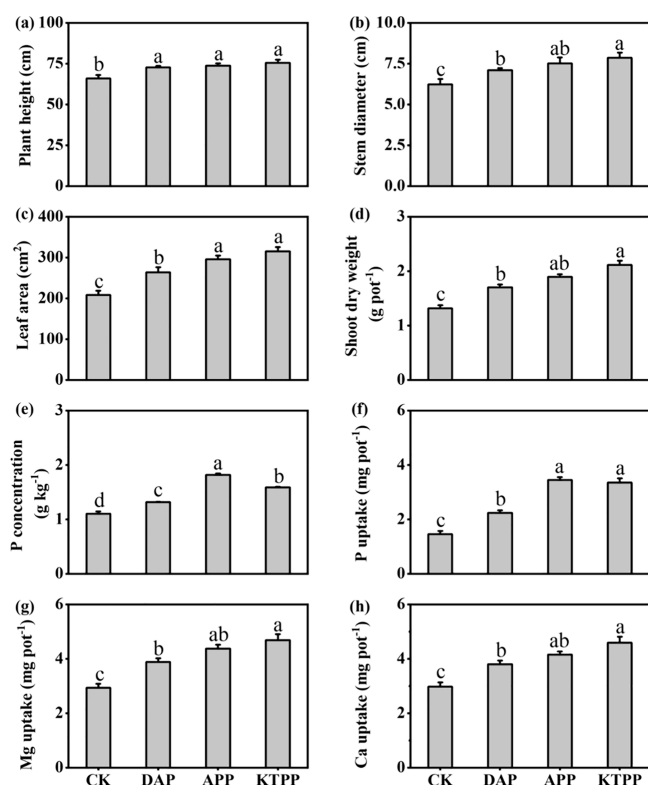


Figure 4. Effects of different P fertilizers on the maize growth in the calcareous soil: (a) plant height, (b) stem diameter, (c) leaf area, and (d) shoot dry weight. Nutrient status with different P fertilizers in maize shoots of (e) P concentration, (f) P uptake, (g) Ca uptake, and (h) Mg uptake. Error bars denote the standard errors of three replicated pots. Different letters above the bars indicate significant differences ($P < 0.05$).

between APP and KTPP (Figure 4). The P uptake of maize shoots with APP and KTPP significantly improved by 53.9% and 49.7%, respectively, compared to that with DAP. KTPP exhibited the best performance in Ca and Mg uptake. The amounts of Ca and Mg taken up by maize shoots in the KTPP treatment were 20.9% and 20.9% higher than those in the DAP treatment and 9.2% and 12.8% higher than those in the APP treatment, respectively.

The application of KTPP significantly enhanced shoot biomass, P concentration, P uptake, Ca uptake, and Mg uptake in maize shoots compared to DAP, improving PUE by 141.7% (Figure 5). APP was also superior to DAP in terms of

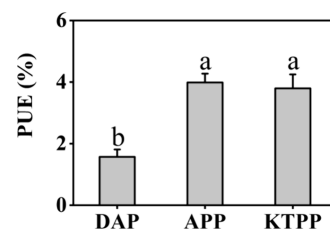


Figure 5. Effects of different P fertilizers on PUE of maize in the pot experiment at harvest (35 days after sowing). Error bars denote the standard errors of three replicated pots. Different letters above the bars indicate significant differences ($P < 0.05$).

agricultural effects, increasing PUE by 153.8%. However, no significant difference existed in PUE between the APP and KTPP treatments in the calcareous soil during the maize seedling stage.

3.4. Relationship of the P Fertilizer Properties and Their Effects. The properties of P fertilizers can affect experimental results to some degree. The polymerization degree of P fertilizers showed strong positive correlations with the solubility of Ca^{2+} and Mg^{2+} in the P fertilizer solution, the amounts of Ca and Mg released from the calcareous soil, the amounts of Ca and Mg taken up by maize shoots, the shoot biomass, and PUE in the calcareous soil (Figure 6). However, the pH of the P fertilizers exhibited no significant relationship with these indicators, although it affected the experimental results.

Simultaneously, the results of the three experiments had mutual effects. For example, the amount of P uptake was significantly correlated with PUE, and Ca solubility had a positive effect on both the amount of Ca released and Ca uptake. A positive and significant correlation was also present between P uptake and Ca and Mg uptake, indicating a synergistic effect of Ca and Mg with P. Additionally, Ca and Mg exhibited significant interactions. For instance, the solubility of Ca has a notable impact on the nutrient release

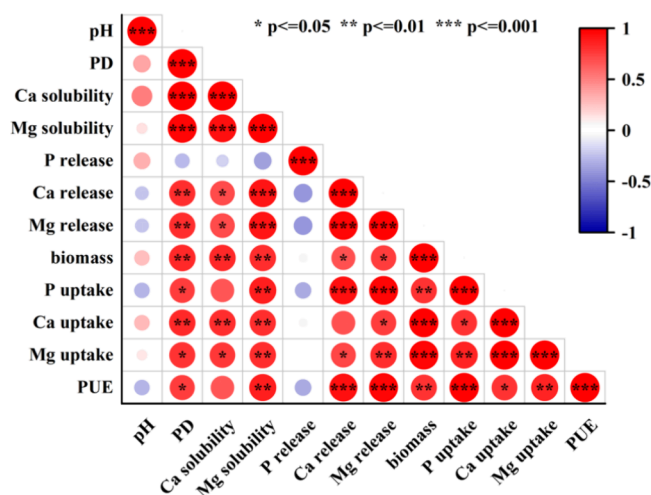


Figure 6. Pearson's correlation heatmap of cation solubility, nutrient release, nutrient uptake, and PUE with different P fertilizers. Red and blue circles donate positive and negative correlations, respectively. The size of each circle indicates the degree of correlation, and an asterisk within a circle signifies statistical significance between the variables. For clarification, the abbreviation PD is used in the figure to represent "polymerization degree".

and uptake of Mg, while the solubility of Mg similarly affected the nutrient release and uptake of Ca.

Principal Component 1 (PC1) and Principal Component 2 (PC2) accounted for 71.4% and 17.3% of the variance, respectively (Figure 7). The direction of the arrows for pH and polymerization degree indicates that the polymerization degree is a representative indicator of PC1, while pH is a core indicator of PC2 (Figure 7a). The PCA score plot (Figure 7b) reveals a distinct separation among different P fertilizers, with three of them distributed across three quadrants, suggesting that the effects of these fertilizers are significantly different.

By calculating the comprehensive scores for the principal components, we found that pH scored 0.09 and the polymerization degree scored 0.23 (Table S1). This further demonstrates that polymerization degree has a greater impact on the effectiveness of phosphate fertilizers, which is consistent with the results obtained from Pearson's correlation analysis.

4. DISCUSSION

4.1. Effects of KTPP on Mobilizing Ca and Mg. Plants can easily uptake orthophosphate, typically in the form of monovalent and dihydrogen phosphate ions. The application

of orthophosphate fertilizer increases soil P, which is crucial for sustaining crop production, provided that it is accessible to plants. However, orthophosphate can strongly adsorb to oxides and precipitate with Al, Fe, and Ca, forming unavailable forms (nonlabile P), thus limiting its availability to plants. In alkaline-weathered soils, common in semiarid and arid climates, high levels of Ca^{2+} and Mg^{2+} in the soil solution limit P solubility through the formation of soluble Ca–P compounds, consequently reducing the PUE of orthophosphate fertilizers.^{53,54} These results are consistent with our findings that the solubilities of Ca^{2+} and Mg^{2+} in DAP solutions decrease with increasing pH (Figure 1).

PP can bind to cations, which can chelate recalcitrant elements from the soil solid phase into soluble ionic forms through complexation reactions.¹¹ As polyphosphates, both KTPP and APP can chelate Ca^{2+} and Mg^{2+} . However, KTPP, with a higher polymerization degree, was a stronger complexing agent and more effective than APP in increasing cation solubility, which is consistent with the reported results.^{55–58}

Additionally, there was competition between H^+ and the metal cations for polyphosphate because both were positive ions.^{27,59} Acidic conditions would inhibit the chelation of polyphosphate with metal cations and weaken the precipitation of cations from P.⁶⁰ This was especially evident in the peculiar phenomenon shown in Figure 1b and was likely related to the low pH of the P solution. Simultaneously, the solubility of Mg^{2+} in APP solution at pH 5.0 was lower, which may have been due to the formation of $(\text{NH}_4)_2\text{MgP}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$.^{45,61} However, alkaline conditions led to a decrease in the H^+ concentration in the solution and promoted the chelation of metal cations by polyphosphate.^{20,45} More research can be conducted on the solubility changes with polyphosphate in a more detailed pH range, and the sediment or chelate can be characterized to verify these speculations.

Therefore, the changes in the dissolution law of metal cations by KTPP conformed to the principles of the acid dissolution reaction and ligand chelation, which could prevent the precipitation reaction between orthophosphate and metal cations.

4.2. Effects of KTPP on Nutrient Release. The ability of polyphosphate in preventing or hindering precipitation or dissolving the precipitates of alkaline earth metals was recognized,^{56,62} leading to immobilization reactions of PP that differed somewhat from those of orthophosphate. Polyphosphate can bond to soil cations through desorption/dissolution to form stable soluble complexes^{27,32} and then

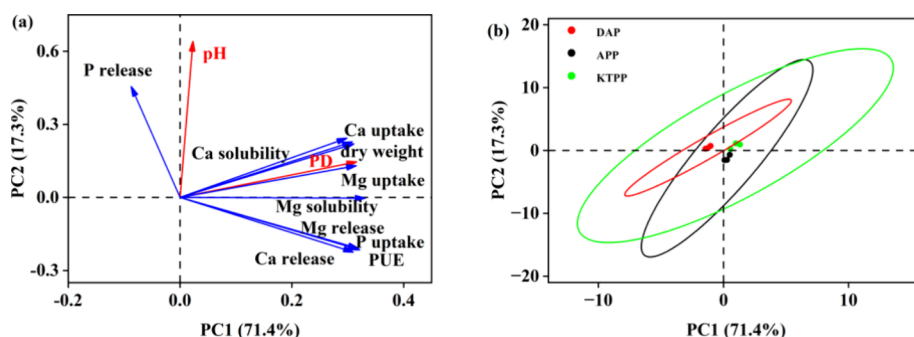


Figure 7. Principal Component Analysis of the loading plot (a) and score plot (b) for the relationships between cation solubility, nutrient release, and nutrient uptake with different P fertilizers. For clarity, the abbreviation PD is used in the figure to represent "polymerization degree".

gradually hydrolyze into orthophosphate^{31,63} to maintain the available P content in the soil for a certain period.^{64,65}

The nutrient release experiment indicated that more than 100% of P was recovered from the released solutions after 15 days with the three P fertilizers, indicating high solubility and very low retention of P in the calcareous soil. Therefore, when evaluating the release characteristics of water-soluble fertilizers in soil, experiments should be conducted after granulation to avoid the premature dissolution of fertilizers.⁶⁶ The differences in the cumulative P dissolution and release rates between the KTPP and APP treatments could be related to the solution pH caused by the dissolution of the fertilizer powders (Figure S2).⁶⁷

APP and KTPP can both mobilize the release of Ca and Mg from calcareous soil,⁶⁸ in comparison with DAP, but KTPP with a higher polymerization degree could not solubilize with more cations, which was not consistent with our initial hypothesis, and this was likely related to the high pH of KTPP. The eluate pH of APP was significantly lower than those of DAP and KTPP for 15 d (Figure S2), which simulated the acidification effect to facilitate the dissolution and release of Ca and Mg (Figure 3).⁶⁹

From the perspective of elemental release kinetics, the zero-order model provides a better fit for the release of Ca and Mg from DAP-treated soil, indicating a slow and consistent release with a high correlation coefficient ($R^2 = 0.97$) for Mg.⁷⁰ Additionally, the Korsmeyer–Peppas model with a B value of 1.56 (>0.89) suggests a Super Case II transport mechanism⁷¹ for Mg release. In contrast, Ca release from APP and KTPP treatments follows a first-order model, with KTPP showing a greater release due to larger kinetic constant B .⁷² Mg release in APP and KTPP treatments, with B values ≤ 0.45 , indicates a Fickian diffusional release mechanism, influenced more by initial release amounts than time.⁵⁰ In summary, the kinetic analysis reveals distinct release patterns for Ca and Mg from different treatments, with DAP showing a slow and consistent release, while APP and KTPP display complex dynamics influenced by both initial conditions and release mechanisms.

The combined effects of multiple factors led to similar mobilization of Ca and Mg by APP and KTPP, so KTPP could be more conducive to improving the nutrient (P, Ca, and Mg) uptake of crops by mobilizing elements^{73,74} in calcareous soil during a long period of cultivation, although KTPP is an alkaline P fertilizer that may increase the pH of the soil solution and promote the precipitation reaction between P and Ca.^{30,37}

4.3. Effects of KTPP on Improving Crop Yield and Nutrient Uptake. Commonly, plants can primarily absorb orthophosphate (H_2PO_4^- and HPO_4^{2-}), although only a small portion of polyphosphate can be directly absorbed.⁷⁵ Thus, a certain amount of polyphosphate remained in the condensed form at the initial stage until it was completely hydrolyzed to orthophosphate,⁷⁶ so polyphosphate application could increase the mobility and availability of P fertilizer in the soil^{56,62} and reduce long-term P immobilization.⁶⁹ However, in practice, the effects of polyphosphate on chelation and hydrolysis are governed by the mutual interaction of multifarious factors rather than by a single pH or cation factor, such as the intrinsic properties of polyphosphate (pH, polymerization degree, and polymerization rate), soil properties (pH, temperature, moisture, and soil minerals), and the interaction between chemical and biological factors.^{77–79}

Compared with APP, KTPP with higher polymerization degree and pH requires more time to completely hydrolyze on calcareous soil to maintain available P in the soil for longer, which may better synchronize P availability with crop demand,^{27,28} thus promoting PUE. However, in the pot experiment, KTPP and APP consistently influenced maize growth and nutritional status, but were better than DAP (Figure 4). This result can be attributed to plants favoring the uptake of the polyphosphate fertilizer with lower polymerization degree during the short growth period (5 weeks).⁶⁹ After long-term cultivation, KTPP may exhibit better agronomic effects; however, this hypothesis requires further experimental verification.

KTPP with higher polymerization degree could dissolve more cations and improve the content of available nutrients in the soil,²¹ and the complexation of Ca with polyphosphate may cause an increase in PUE.⁶⁹ However, no significant differences were observed in the uptake of Ca and Mg by APP and KTPP. This could be attributed to several factors. First, the addition of APP at a lower pH level may decrease the soil pH (Figure S2 and Table S1). Second, the hydrolysis of polyphosphates is accompanied by acidification of the medium.⁷⁵ Additionally, plants can release protons after absorbing ammonium nitrogen from APP, which further acidifies the rhizosphere.⁸⁰ These cumulative effects lead to localized soil acidification, which increases the availability of P in the soil.⁸¹ This, in turn, causes the dissolution of insoluble substances in soil minerals and significantly presents them in a more available form.^{21,24} However, polyphosphate hydrolysis can release H^+ and decrease soil pH,⁵⁴ whereas KTPP undergoes a longer hydrolysis process than APP and is acidified during long-term cultivation. Such factors led to a similar uptake of Ca and Mg by crops in APP and KTPP. Longer culture tests or analytical measurements of soil available nutrients and pH may be more conducive to the study of such multifactorial conditions.

At the same time, the different relative atomic masses lead to variations in the reactivities of Ca and Mg. Generally, polyphosphates are significantly more effective at solubilizing Mg^{2+} than Ca^{2+} (Table 1), which aligns with previous research.⁶² However, a significant correlation exists between Ca and Mg (Figure 5). This is likely because both Ca and Mg are divalent cations and alkali earth metals,⁸² and the suspected mechanisms by which polyphosphates sequester them are thought to be similar.⁸³ This results in the formation of similar products with phosphates and polyphosphates.⁴⁵ Therefore, studies aimed at improving PUE in calcareous soils could focus on the main factors, such as high pH values and high levels of available Ca^{2+} , that contribute to P precipitation.

Thus, polyphosphate application provides distinct benefits in reducing the fixation and precipitation of P, shifting the precipitation reaction of P and Ca into a synergistic interaction,⁸⁴ beyond merely providing P as a nutrient for plants. KTPP not only increases the dry weight of crops in short-term pot culture but also promotes the absorption of medium and trace elements in calcareous soils, which is beneficial for crop yield and PUE.

5. CONCLUSIONS

KTPP significantly increased the solubility of Ca^{2+} and Mg^{2+} in solutions with a pH range of 5.0–9.0, outperforming both DAP and APP. Also, it consistently mobilized more Ca and Mg from calcareous soil, maintaining their availability, and

significantly improved Ca and Mg absorption by maize shoots compared to DAP. However, no significant differences in yield or nutrient uptake were observed between KTPP and APP in the short term cultivation. This study found that polyphosphate with higher polymerization degree was more effective in enhancing cation solubility, crop yield, and nutrient uptake in soil and promoted a synergistic interaction between P and Ca in calcareous soil. Thus, polyphosphate can intelligently match crop P requirements and enhance PUE, thereby alleviating environmental stress and demonstrating broad application prospects in future agriculture. Future research should assess the variable effects of polyphosphate with different polymerization degrees and rates on various crops and their impact on soil microbial communities across different soil conditions, aiming to identify the most effective polyphosphate formulations, enabling the precise regulation and efficient use of polyphosphate fertilizers, which is crucial for green agricultural development.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c10415>.

Chromatograms for the P species of APP and KTPP, pH in the collected fractions, pH and cumulative release of P (as % of P added) in the fractions collected, and eigenvalue of the principal components and their contribution rates and cumulative contribution rates (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (2022YFD1901500/2022YFD1901503).

■ ABBREVIATIONS USED

APP, Ammonium polyphosphate
DAP, Diammonium phosphate
MAP, Monoammonium phosphate
PUE, Phosphorus fertilizer-use efficiency
KTPP, Potassium tripolyphosphate

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