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The Effects of Struvite on Biomass and Soil Phosphorus Availability and Uptake in Chinese Cabbage, Cowpea, and Maize

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Abstract: Struvite ($MgNH_4PO_4 \cdot 6H_2O$), a mineral with low water solubility that can be recovered from industrial wastewater, has the potential to be used as a slow-release phosphorus (P) fertilizer. However, the effect of struvite on the yield and P uptake efficiency of different crops remains unclear. In this study, the effects of struvite, diammonium phosphate (DAP), and a mixed fertilizer consisting of struvite + DAP (MIX) on biomass, P uptake, and soil P fractions of Chinese cabbage, cowpea, and maize were investigated in pot experiments. The results showed that compared to DAP, the mixed fertilizer reduced the biomass of Chinese cabbage by 47%, while there was no difference in the biomass of cowpea and maize under P fertilizer application. There was no difference in total P concentration in Chinese cabbage and cowpea plants between DAP and MIX, while total P concentration in maize under mixed fertilizer treatment decreased by 16.73% compared to DAP treatment. Compared to DAP, the MIX treatment reduced total P uptake in Chinese cabbage and maize by 45.82% and 33.41%, respectively, with no direct difference in cowpea. Soil Olsen-P and $CaCl_2$-P concentrations were highest in DAP among the different treatments. The MIX treatment significantly increased the water-soluble P in Chinese cabbage and cowpea by 5.87% and 5.23%, respectively, while the water-soluble P in maize was lower in the mixed fertilizer treatment than in the DAP treatment. In addition, mixed fertilizer significantly increased soil pH and soil phosphatase activity compared to DAP. This result suggested that among the three treatments of struvite, DAP, and MIX, struvite had the weakest effect on crop growth. In addition, among the three crops, Chinese cabbage, cowpea, and maize, the compatibility between struvite and maize was the highest. These results provide valuable insights for the future application of struvite in agricultural production for achieving stable yields while mitigating environmental risks.

Keywords: struvite; phosphorus availability; Chinese cabbage; maize; cowpea

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1. Introduction

Phosphorus, as an essential component for crop growth [1], is also a non-renewable and scarce resource. The excessive use of phosphate fertilizers in agriculture poses a threat to sustainable agricultural development and the scarcity of phosphorus resources. This raises concerns about the affordability of phosphate fertilizers, particularly in countries with limited or no phosphate reserves [2]. Studies have shown that 29% of the world's arable land is deficient in soil phosphorus (particularly in South America, the northern United States, and Eastern Europe), while 71% has a surplus (including most of East Asia, much of Western and Southern Europe, and the coastal United States) [3]. Inefficient phosphorus utilization in most countries leads to its accumulation in soil, causing environmental problems such as eutrophication, red tide outbreaks, and threats to aquatic ecosystems [4,5].

At the same time, the limited availability of P fertilizers in other regions has contributed to prolonged P deficits that can deplete soil P and limit crop yields [6].

Struvite is a recently developed slow-release fertilizer that exhibits several advantageous characteristics, including prolonged fertilizer efficiency, high nutrient utilization rates, and environmental compatibility. It has been demonstrated to promote crop growth and is considered an ideal slow-release composite fertilizer [7]. In the context of agricultural applications, struvite can be employed as an alternative to conventional fertilizers, offering a source of phosphorus, nitrogen, and magnesium [8]. Martens demonstrated that the application of struvite enhances wheat grain yield, shoot phosphorus concentration, and phosphorus accumulation [9]. Furthermore, the application of struvite to forage resulted in an approximate 8% increase in yield compared to commercial ammonium phosphate fertilizers [10]. Additionally, the application of struvite led to a notable enhancement in pepper fruit yield and leaf growth [11]. Beyond its benefits in agricultural production, struvite has demonstrated substantial advantages in mitigating phosphorus-related environmental concerns.

Antonini examined the solubility of struvite from six distinct wastewater sources and discovered that the solubility of three of them in water was only 1%, significantly lower than the 70–74% solubility of phosphates in water-soluble phosphate fertilizers [12]. A previous study examined the nutrient release cycle of struvite from various sources and discovered that, when extracted from phosphorus-containing wastewater, its release cycle in soil could extend up to 63 days, in comparison to just 18 days for water-soluble phosphorus [13]. Further results indicated that the utilization of recycled slow-release fertilizers, such as struvite, could synergistically facilitate efficient production and resource recycling, offering a sustainable option for agricultural development [14].

The roots of different crops employ distinct mechanisms for phosphorus absorption. For instance, Chinese cabbage (*Brassicaceae*) enhances phosphorus absorption efficiency by excreting a substantial amount of citrate [15]. As the solubility of struvite in water is considerably lower than in acid [16], the release of citrate from the root of Chinese cabbage can improve the utilization of phosphorus in struvite. Maize (*Zea mays* L.), which is also a mycorrhizal crop, improves phosphorus utilization efficiency by enhancing root morphology and yield [17], establishing a symbiotic relationship with arbuscular mycorrhizal fungi (AMF). The extensive rhizomycelium in the soil enhances the uptake of immobile nutrients such as phosphorus (P) and zinc (Zn) by host plants [18]. Cowpeas (*Leguminosae*) obtain sufficient nitrogen through rhizobia, which makes phosphorus a crucial limiting factor for legume growth [19]. The slow-release property of struvite may limit the growth of cowpeas at the seedling stage. The incorporation of struvite with highly water-soluble conventional P fertilizers could potentially provide sufficient early-season P. Consequently, struvite exhibits differential responses across diverse crops, underscoring the necessity for further research on the responses of different crops to struvite.

In recent years, slow-release fertilizers containing phosphorus have become increasingly prevalent due to their high nutrient content and sustainability. Nevertheless, limited research exists on the mechanisms by which struvite impacts the efficient uptake of phosphorus by different crops through their roots. Therefore, this study selected three different types of crops: Chinese cabbage (*Brassicaceae*), cowpea (*Leguminosae*), and maize (*Zea mays* L.) to investigate the response mechanisms of root morphology and rhizosphere processes to the struvite, DAP, and mixed fertilizer. Two hypotheses were formulated: (1) The mixed fertilizer exhibits inconsistent effects compared with the application of struvite and DAP. (2) The combination of struvite and DAP fertilizer can support the growth of maize and cowpea while exhibiting inhibitory effects on Chinese cabbage. The objective was to elucidate the effects of the application and reveal the physiological mechanisms underlying the coupling of soil, roots, and fertilizer for the efficient transformation of soil phosphorus and the uptake of phosphorus by roots. In conclusion, an effective application strategy for struvite was established, providing theoretical support for the formulation of efficient plans for the application of phosphate fertilizer across a range of crops.

2. Materials and Methods

2.1. Soil and Materials

The soil utilized in the pot experiment was red soil, which was collected from the field soil of Kunming, Yunnan Province, in June 2023. The soil had a pH of 6.8 (water:soil = 2.5:1), a total organic carbon (TOC) content of 20.2 g C/kg (Walkley–Black method) [20], 2.4 mg N/kg NH_4^+-N (0.01 M $CaCl_2$), 42.7 mg N/kg NO_3-N (0.01 M $CaCl_2$) [21], available phosphorus content of 22 mg/kg (Olsen-P) [22], and available potassium content of 65 mg K/kg (1 N NH_4COOH) [23]. Struvite had a pH of 6.8, 42 g N/kg, 63 g P/kg, water-soluble phosphate 41 g/kg, and 38 g K/kg. Diammonium phosphate had a pH of 2.3, 123 g N/kg, 157 g P/kg, and 114 g K/kg. After collection, the soil was air dried and passed through a 2 mm sieve before being stored for future use.

The Chinese cabbage variety utilized in the experiment was Fengkang 70, while the maize variety chosen was Zhengdan 958, and the cowpea variety selected was Chongqing Erba. On 26 May 2023, Chinese cabbage seedlings were cultivated in the laboratory using the paper culture method. Subsequently, on June 29th, when the seedlings reached the six-leaf stage, the requisite uniformity criteria were met, allowing for the selection of three plants for transplantation into pots. Concurrently, three maize and cowpea seeds were distributed uniformly within each pot at a depth of approximately one centimeter. Throughout the growth period, the soil moisture content was maintained at approximately 70% of the field water holding capacity.

2.2. Experimental Design

A pot experiment was established in the solar greenhouse at the National Purple Soil Monitoring Station in Beibei, Chongqing, China (29°48′ N, 106°24′ E) during June to August 2023. The test pots were constructed using plastic material, featuring an inner diameter of 40 cm. Each pot was filled with 4 kg of soil. The experimental design included four treatments for each of Chinese cabbage, cowpea, and maize: a control group without phosphorus fertilizer (CK), as well as three different phosphorus treatments: struvite, diammonium phosphorus (DAP), and a mixed fertilizer of 40% struvite and 60% diammonium phosphate (MIX). Each treatment was replicated four times, containing phosphorus at a rate of 200 mg P/kg, nitrogen at a rate of 200 mg/kg (as N), and potassium at a rate of 150 mg/kg (as K_2O).

2.3. Sample Collection and Analysis

Samples of Chinese cabbage, cowpea, and maize were collected in early September. The aboveground part of the plant was collected and subsequently dried at 105 °C for 30 min to remove terminated enzymatic activity. Further drying was conducted at 65 °C until a constant weight was achieved. The dry weight measurements were used to determine biomass. Subsequently, the biomass samples were crushed for elemental analysis testing. The soil from each pot was meticulously poured onto kraft paper, and all roots within the soil were gathered and placed into self-sealing bags. After washing with deionized water, the roots were dried at 65 °C until a constant weight was reached. The dry weight of the roots was measured to calculate their biomass. Furthermore, root–soil and soil samples were separately collected using self-sealing bags after air drying and removal of impurities. Subsequently, these samples underwent grinding, screening, and mixing processes before being stored for subsequent determination of Olsen-P content, pH, and phosphorus fractions.

The crop biomass was quantified through gravimetric analysis. Total phosphorus content in plant tissues was assessed by pulverizing dried samples from various plant parts and subsequently digesting them with a mixture of HNO_3-H_2O_2 employing an Auto Digiblock S60UP system. Quantification of total phosphorus content utilized ICP-OES (5110 SVDV), based on its ability to perform spectral emission analysis. Soil Olsen-P and $CaCl_2$-P concentrations were extracted by 0.5 $mol \cdot L^{-1}$ $NaHCO_3$ (pH 8.5, soil–water ratio 1:20) and 0.01 $mol \cdot L^{-1} CaCl_2$ (soil–water ratio 1:5), respectively, and determined by the molybdovanado phosphatase method [24]. Soil pH was determined by the potentiometric method (1:2.5 *w*/*v* in water) (Mettler Toledo FiveEasy Plus FE28, Shanghai, China). Soil acid phosphatase (ACP) and alkaline phosphatase (ALP) were determined using the colorimetric method of disodium benzene phosphate. To categorize soil P fractions, we followed the sequential extraction method proposed by Tiessen and Moir [25], which divided P into nine forms [26], including Resin-P, $NaHCO_3$-P (P_o and P_i), NaOH-P (P_o and P_i), Dil. HCl-P_i, Conc. HCl-P (P_o and P_i), and Residual-P.

2.4. Data Analysis and Statistics

The following formula was used to calculate plant P accumulation [27] and P concentration:

Plant P accumulation = Aboveground biomass ∗ Aboveground P concentration + Root biomass ∗ Root P concentration

Total P concentration = total P accumulation/total plant biomass

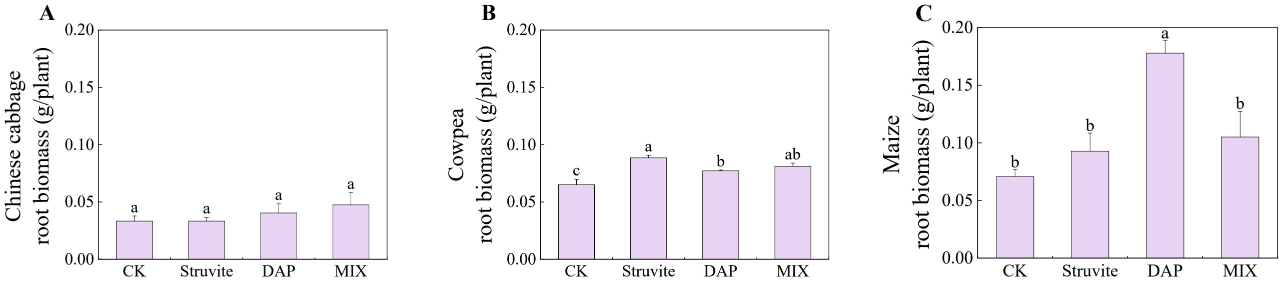
All data were analyzed by one-way ANOVA using SPSS 26. In cases where the ANOVA indicated significance, we compared means using the LSD test at a significance level of $p < 0.05$. All figures in this study were generated using Origin 2023.

3. Results

3.1. Crop Biomass

The application of phosphorus (P) fertilizer significantly increased the biomass of crops (Figure 1). While struvite and MIX had no effect on the biomass of Chinese cabbage and maize compared to the CK, struvite significantly promoted the underground biomass of cowpeas, which was 1.15 times higher than that under DAP treatment. The application of struvite and MIX resulted in a significant increase in the aboveground biomass of maize by 63.40% and 72.91%, respectively, in comparison to the control (CK) treatment. Conversely, no significant effect was observed on the aboveground biomass of Chinese cabbage and cowpea. Due to the large proportion of aboveground mass, there was a consistent trend in total crop biomass changes among all treatments. Notably, DAP application significantly improved total crop biomass with a remarkable promotion effect on the root biomass of maize, increasing it by 151.27% compared to CK treatment.

The application of struvite resulted in a notable increase in the root-to-shoot ratio of cowpea, with a 27.94% enhancement compared to the control treatment without phosphorus (Table 1). However, no statistically significant change was observed in the root-to-shoot ratio of Chinese cabbage and maize among different P treatments. Specifically, in comparison to struvite, DAP was observed to decrease the root-to-shoot ratio by 46.01% for Chinese cabbage and 9.64% for cowpea, while it increased by 28.91% for maize.



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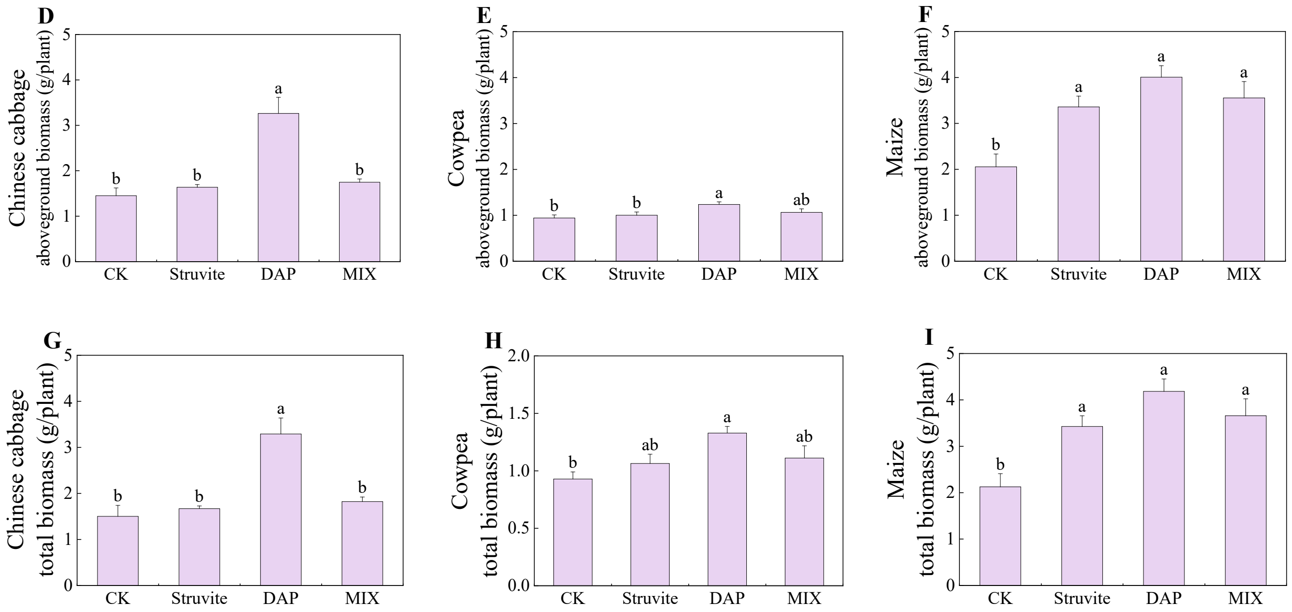

Figure 1. Root, aboveground, and total biomass of Chinese cabbage (**A**,**D**,**G**), cowpea (**B**,**E**,**H**), and maize (**C**,**F**,**I**) under different phosphate fertilizers. Error bars represent standard error, and the different lowercase letters represent significant differences between treatments at ($p < 0.05$) levels.

Table 1. Effects of different phosphate fertilizers on the root–shoot ratio of Chinese cabbage, cowpea, and maize.

Treatment	Chinese Cabbage	Cowpea	Maize
CK	0.023	0.069	0.034
struvite	0.020	0.088	0.028
DAP	0.012	0.062	0.044
MIX	0.027	0.076	0.030

3.2. Crop P Uptake

Different phosphorus application treatments exerted varying effects on crop phosphorus uptake (Figures 2 and 3), with DAP having the most significant impact by markedly enhancing both below-ground and above-ground phosphorus accumulation in crops. In comparison to CK, struvite and MIX treatments did not significantly affect root phosphorus concentration in any of the three crops. While struvite treatment significantly increased aboveground phosphorus accumulation in maize by 62.5% compared to CK, it had no notable effect on the aboveground parts of Chinese cabbage and cowpea. The combined application of DAP and struvite significantly promoted aboveground phosphorus accumulation in all crops, with no significant difference observed between this treatment and struvite. Under struvite treatment, total phosphorus accumulation increased by 61.01% for maize, 54.98% for Chinese cabbage, and 25.74% for cowpea compared to CK. Also, DAP application resulted in a substantial increase in phosphorus accumulation across all three crops: 167.82% for maize, 53.19% for Chinese cabbage, and 73.21% for cowpea. Compared to CK, struvite showed no significant effect on phosphorus concentration in Chinese cabbage, cowpea, and maize. However, both DAP and MIX treatments significantly increased phosphorus concentration across all three crops. In comparison to the DAP treatment, the total phosphorus concentration levels in Chinese cabbage and cowpea remained unaltered under struvite treatment.

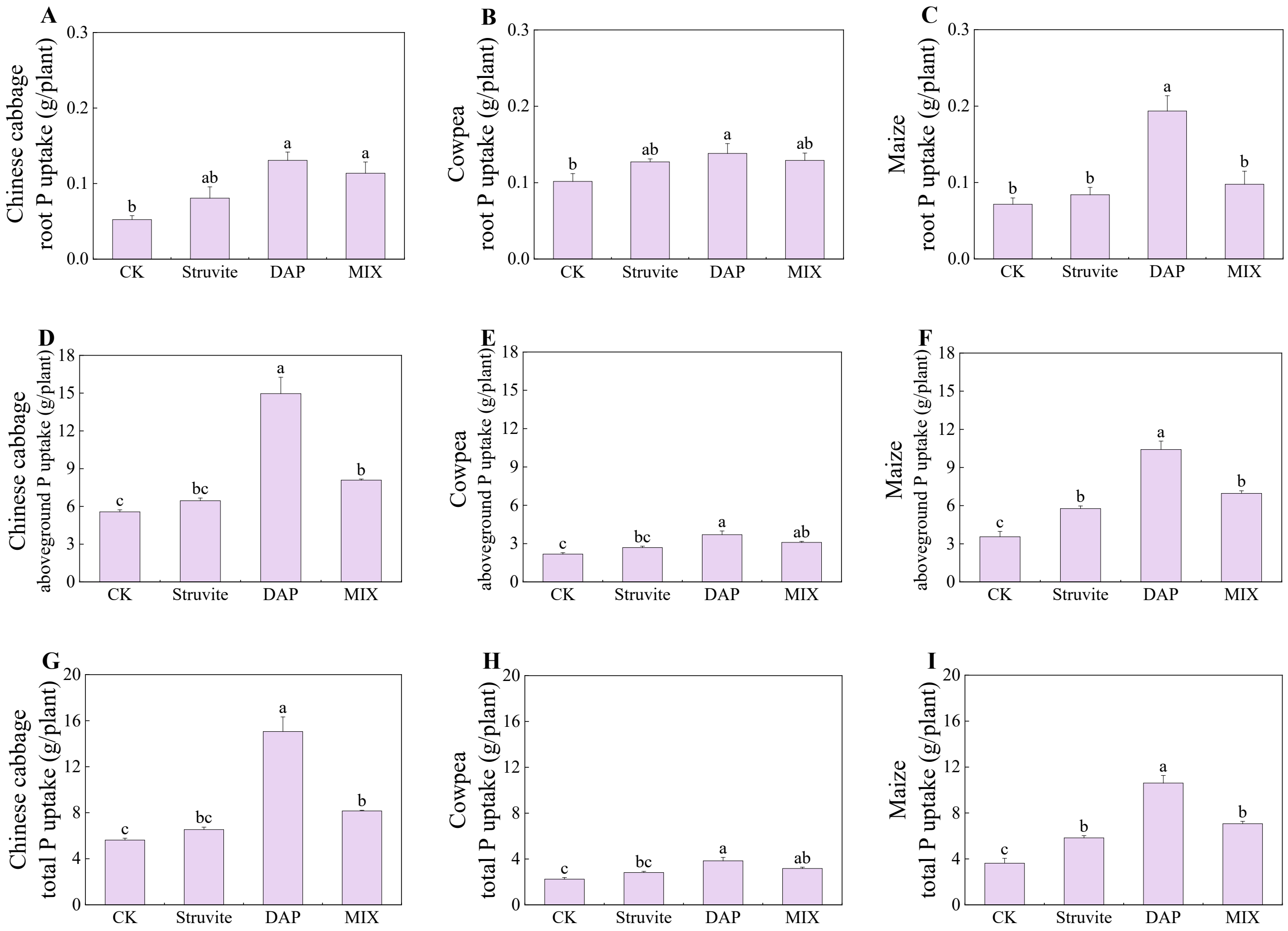

Figure 2. Root, aboveground, and total P uptake of Chinese cabbage (**A**,**D**,**G**), cowpea (**B**,**E**,**H**), and maize (**C**,**F**,**I**) under different phosphate fertilizers. Error bars represent standard error, and the different lowercase letters represent significant differences between treatments at ($p < 0.05$) levels.

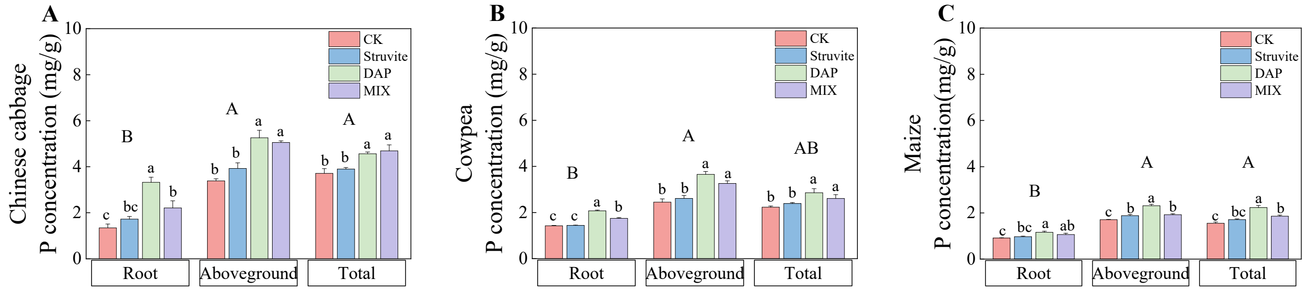

Figure 3. P concentration of Chinese cabbage (**A**), cowpea (**B**), and maize (**C**) under different phosphate fertilizers. Error bars represent standard error, and the different lowercase letters represent significant differences between treatments at ($p < 0.05$) levels. The different uppercase letters represent significant differences between treatment groups at ($p < 0.05$) levels.

3.3. Soil Olsen-P and P Fractions

Compared to CK, DAP demonstrated the highest ability to enhance soil Olsen-P content (Figure 4), with all treatments showing a significant increase, notably higher than other treatments. While struvite had no discernible impact on overall Olsen-P content, it significantly increased the available phosphorus content in the rhizosphere soil of Chinese cabbage by 81.56%. Under mixed fertilizer, the Olsen-P content in the soil of Chinese cabbage, cowpea, and maize increased by 37.76%, 89.25%, and 225.64%, and the rhizosphere soil Olsen-P content increased by 105.46%, 102.74%, and 44.61%, compared to CK.

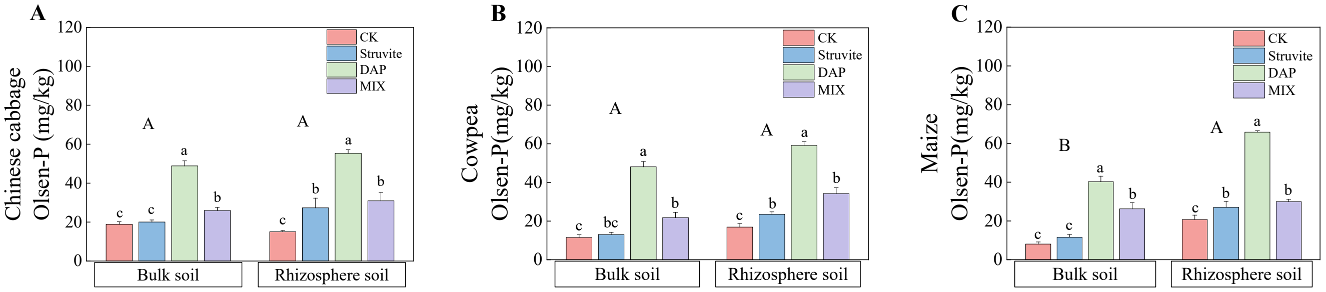

Figure 4. Soil Olsen-P content of Chinese cabbage (**A**), cowpea (**B**), and maize (**C**) under different phosphate fertilizers. Error bars represent standard error, and the different lowercase letters represent significant differences between treatments at ($p < 0.05$) levels. The different uppercase letters represent significant differences between treatment groups at ($p < 0.05$) levels.

Struvite and MIX significantly elevated $CaCl_2$-P concentration in maize soil by 17.11% and 71.71%, compared to CK (Figure 5A), but did not have a significant effect on Chinese cabbage or cowpea. Among all treatments, the application of DAP led to a substantial increase in both available phosphorus concentration and $CaCl_2$-P concentrations. Figure 5B shows that with the increase in $CaCl_2$-P concentration, the total biomass of the three crops increased. Among them, Chinese cabbage and maize were greatly affected by the concentration of $CaCl_2$-P, and the rising trend was remarkable.

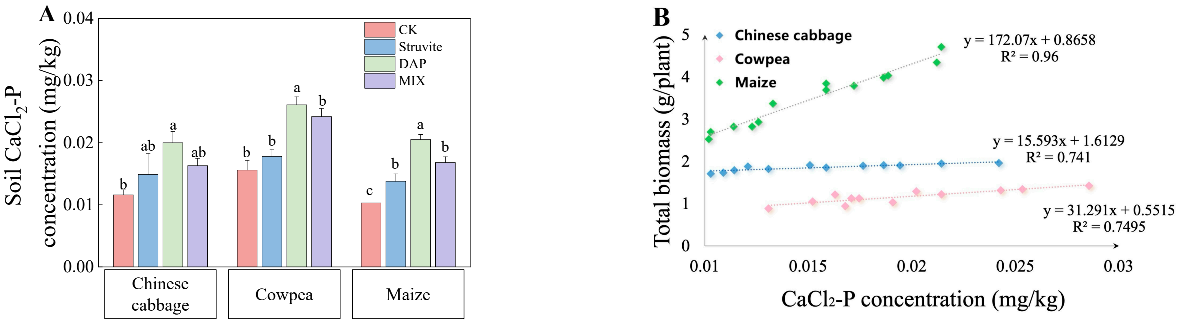

Figure 5. Soil $CaCl_2$-P concentration of Chinese cabbage, cowpea, and maize under different phosphate fertilizers (**A**) and the correlation of $CaCl_2$-P and crops' total biomass (**B**). Error bars represent standard error, and the different lowercase letters represent significant differences between treatments at ($p < 0.05$) levels.

Phosphorus fertilization significantly influenced the fractions of soil phosphorus (Figure 6). The concentrations of Resin-P and $NaHCO_3$-P_i gradually increased with the application of available phosphate fertilizer, while the concentrations of $NaHCO_3$-P_o remained unaffected. Compared to the CK, DAP increased the concentrations of Resin-P and $NaHCO_3$-P_i in cowpea and maize by 1.5 to 12.5 times and 1.2 to 2.4 times, respectively. Among the three crops under MAP treatment, maize soil exhibited a 29.59% increase in Resin-P concentration and a 17.84% increase in $NaHCO_3$-P_i concentration compared to CK levels. The concentrations of NaOH-P_i and dilute HCl-P_i increased with the amount of applied phosphate fertilizer, while the concentration of NaOH-P_o remained unaffected. Additionally, the concentrations of concentrated HCl-P_i and HCl-P_o also increased with the amount of applied phosphate fertilizer.

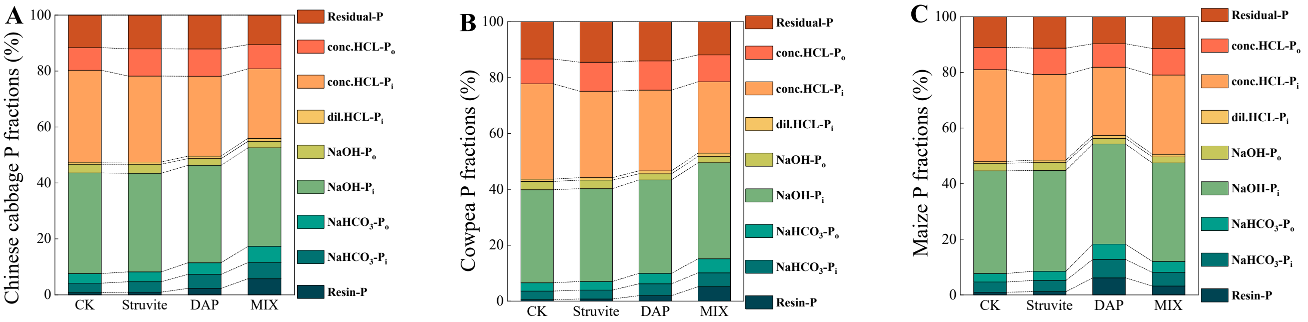

Figure 6. Effect of different phosphate fertilizers on phosphorus fractions of soil of Chinese cabbage (**A**), cowpea (**B**), and maize (**C**). Note: Resin-P_i, resin-extracted inorganic phosphorus; conc.HCl-P_i, concentrated hydrochloric-acid-extracted inorganic phosphorus; conc.HCl-P_o, concentrated hydrochloric-acid-extracted organic phosphorus; dil.HCl-P_i, 1 mol·L^{-1} HCl-extracted inorganic phosphorus; NaOH-P_o, 0.1 mol·L^{-1} NaOH-extracted organic phosphorus; NaOH-P_i, 0.1 mol·L^{-1} NaOH-extracted inorganic phosphorus; $NaHCO_3$-P_o, 0.5 mol·L^{-1} $NaHCO_3$-extracted organic phosphorus; $NaHCO_3$-P_i, 0.5 mol·L^{-1} $NaHCO_3$-extracted inorganic phosphorus; Residual-P, residual phosphorus.

3.4. Soil pH and Soil Phosphatase Activity

Among the three crops, maize had the lowest average soil pH (Figure 7). The application of DAP can mitigate soil acidification caused by fertilization, particularly in cowpeas, where the soil pH remains similar to that of soil without phosphate fertilizer when compared to struvite. However, in the case of Chinese cabbage, struvite resulted in a greater decrease in soil pH than the DAP treatment.

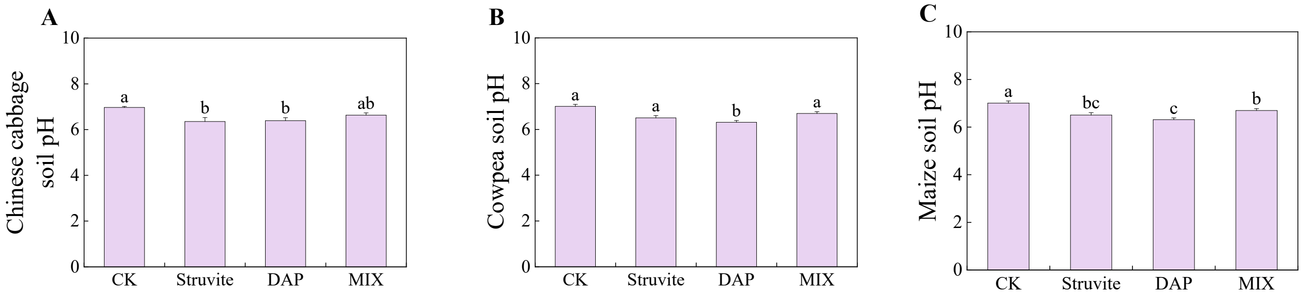

Figure 7. Soil pH of Chinese cabbage (**A**), cowpea (**B**), and maize (**C**) under different phosphate fertilizers. Error bars represent standard error, and the different lowercase letters represent significant differences between treatments at ($p < 0.05$) levels.

The application of DAP led to a significant reduction in ACP activity (Figure 8), while no correlation was observed between ALP activity and different P fertilizer treatments. Compared to the CK, ACP activity in the soil of Chinese cabbage, cowpea, and maize decreased by 57.98%, 48.56%, and 71.42%, respectively, under DAP treatment. Additionally, ACP activity in rhizosphere soil decreased by 38.37%, 86.83%, and 36.86% for Chinese cabbage, cowpea, and maize, respectively, under DAP treatment. Compared to DAP treatment, the application of struvite significantly increased soil ACP activity by 73.21%, 60.99%, and 169.21% for Chinese cabbage, cowpea, and maize soil samples, respectively, as well as increasing rhizosphere soil ACP activity by 49.96%, 219.69%, and 56.75%, respectively. The effect of the mixed application of DAP and struvite on ACP activity in soils was similar to that of struvite.

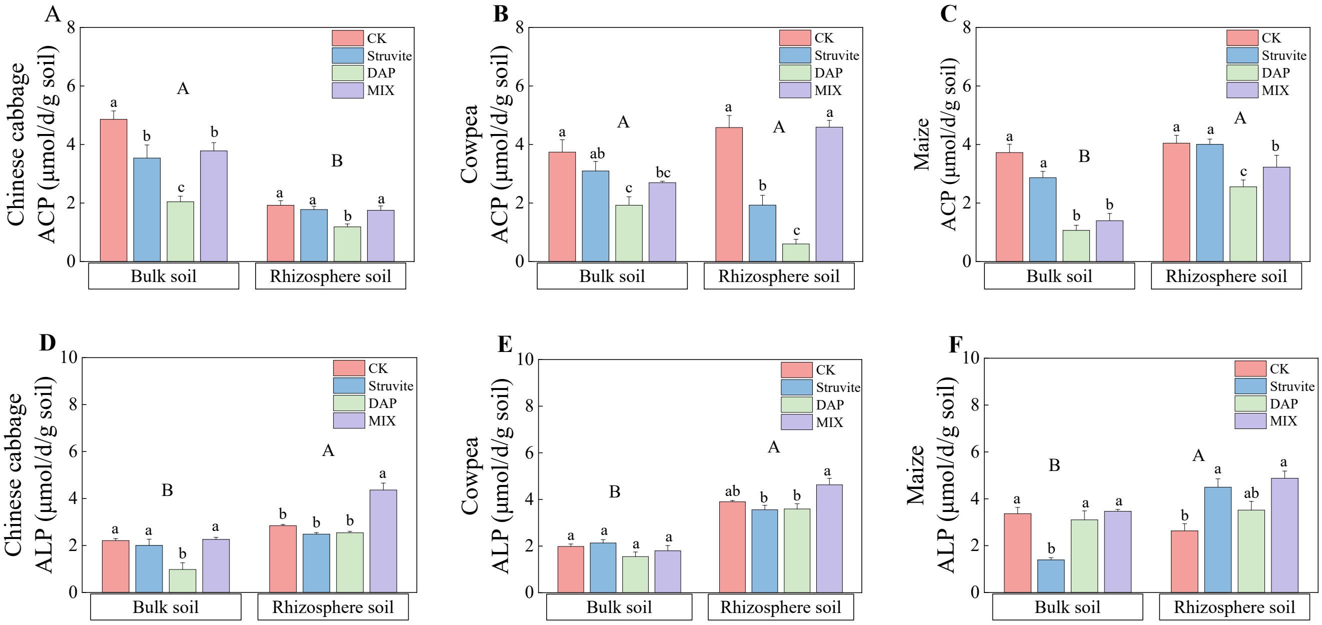

Figure 8. Soil acid phosphatase and alkaline phosphatase activity of Chinese cabbage (**A**,**D**), cowpea (**B**,**E**), and maize (**C**,**F**) under different phosphate fertilizers. Error bars represent standard error, and the different lowercase letters represent significant differences between treatments at ($p < 0.05$) levels.

4. Discussion

4.1. Crop Biomass and Phosphorus Accumulation

The application of phosphorus fertilizer significantly enhanced plant biomass compared to the CK [28,29]. In this experiment, struvite resulted in a significant increase in total biomass for cowpea and maize, with increments of 13.52% and 61.23%, respectively, compared to the control group. The increase in maize biomass was greater than that of cowpea, which is consistent with previous studies [30]. However, no notable change was observed in Chinese cabbage biomass following the application of struvite in comparison to the control group. This finding aligns with previous studies by Wen, which demonstrated that single superphosphate had superior effects on cabbage growth compared to struvite [31]. Ryu's findings also support these results, showing that complex fertilizers were more effective than struvite in promoting Chinese cabbage growth [32]. Based on the analysis of the results of this study, it can be postulated that the gradual release of phosphorus following the application of struvite may not have been sufficient to meet the nutritional requirements of Chinese cabbage. This issue can be alleviated by applying ammonium magnesium phosphate fertilizer or adjusting the available phosphorus ratios accordingly. Furthermore, under struvite treatment, all three crops displayed improved root-to-shoot ratios due to slower phosphorus release compared to DAP. It has been demonstrated that plants are able to absorb greater quantities of phosphorus under conditions of low phosphorus stress, thereby enhancing their tolerance to such stressors and resulting in an increased allocation of photosynthetic products to the roots [33].

In this experiment, a significant disparity in crop phosphorus concentration was observed among different phosphate fertilizer treatments, which deviated from previous studies. Kataki analyzed 20 crops (Chinese flowering cabbage with soil pH 6.2, maize in the field, White lupin in pots, etc.) and found no notable distinction in crop phosphorus concentration between conventional phosphate fertilizer and struvite treatment, possibly due to insufficient growth and development time of the crops [34]. Variations in phosphorus accumulation under struvite treatment were observed across different crops, with Chinese cabbage and maize exhibiting similar values. Struvite possesses unique physical properties, such as low solubility in water and increased solubility in acid. Consequently, the absorption of phosphorus from struvite is influenced by the diverse root exudates released by various crops [28,29]. The organic acids secreted by Chinese cabbage roots effectively enhance the dissolution of struvite, subsequently promoting the release of phosphorus. Maize, being a grass crop with high root density, efficiently facilitates the uptake of phosphorus from magnesium ammonium phosphate [14]. Studies have demonstrated that under low phosphorus stress, maize and other gramineous crops exhibit significant alterations in root morphology: an increase in the number and density of lateral roots, a reduction in the length of primary roots, an elevation in root growth angle, and enhanced distribution of roots in the upper soil layer to acquire more phosphorus [35]. Additionally, arbuscular mycorrhizal fungi form symbiotic associations to expand the root absorption area, thereby facilitating phosphorus uptake. Research has indicated that the application of a mixture containing struvite and diammonium phosphate on spring wheat yields optimal early- and late-stage phosphorus absorption while improving overall phosphorus utilization efficiency [14]. Furthermore, cowpea's higher efficiency in absorbing root phosphorus is not directly correlated with increased biomass production, which aligns with previous findings [7,36].

4.2. Soil P and P Fractions

According to the analysis of experimental results, the application of phosphate fertilizer can enhance soil Olsen-P content, consistent with previous research findings [37]. In this experiment, struvite promoted an increase in available phosphorus content in Chinese cabbage, cowpea, and maize soils, which was also reflected in the corresponding crop biomass. The struvite treatment significantly increased the Olsen-P content in the rhizosphere soil of Chinese cabbage. As a member of the cruciferous family and a typical non-mycorrhizal plant, Chinese cabbage uses organic acid secretion as a crucial mechanism for efficient phosphorus utilization. The secretion of a large number of organic acids reduces soil pH and further facilitates phosphorus release from magnesium ammonium phosphate. However, it should be noted that the effect of struvite on increasing soil Olsen-P content is weaker than that of DAP, and their combination effectively increases soil Olsen-P content. Among the three crops, maize showed the highest increase in $CaCl_2$-P concentration after struvite application, accompanied by an increase in biomass but a decrease in the root-to-shoot ratio. An Olsen-P value of 40 mg/kg has been widely recognized as a critical level associated with an elevated risk of phosphorus leaching loss [38]. Under struvite treatment, the Olsen-P content consistently remained below 40 mg/kg, whereas under DAP treatment, the Olsen-P content exhibited a significant increase, surpassing this threshold. Among all treatments, soil treated with DAP exhibited the highest concentration of Olsen-P and consequently had the highest risk of phosphorus loss, while struvite was beneficial for reducing phosphorus loss. To predict soil phosphorus leaching potential, a leaching change-point index was proposed and evaluated by Heckrath [39] and Hesketh and Brookes [40]. When the Olsen-P content is less than the "change-point" value, phosphorus leaching will not occur. Otherwise, leaching occurs. The available data from this experiment are insufficient to substantiate the identification of this change point, which could be addressed in future investigations.

Crops primarily depleted Resin-P and $NaHCO_3$-P_i fractions, which are considered highly available to plants [25], while accumulating Residual-P and $NaHCO_3$-P_o fractions. In this study, acid purple soil primarily relied on NaOH-P_i and conc. HCl-P_i as the main source of phosphorus. As the application amount of available phosphorus increased, NaOH-P_i became the dominant source, while conc. HCl-P_i gradually transformed into a potential source. Similarly, research has shown that maize and broad bean intercropping systems mainly utilize Resin-P and $NaHCO_3$-P_i as highly utilizable forms of phosphorus for plants [25,41]. In this experiment, the DAP application significantly increased the concentrations of Resin-P and $NaHCO_3$-P_i in the soil, followed by the MIX application. In contrast, struvite application had minimal impact on the levels of these two components.

4.3. Effect of Different Phosphate Fertilizers on Soil pH and Soil Phosphatase Activity

The alteration in soil phosphatase activity is significantly influenced by the physicochemical and biological properties of the soil, directly reflecting the direction and intensity of soil biochemical processes. Key enzymes involved in phosphorus solubilization, such as acid and alkaline phosphatase [42], facilitate the liberation of organic phosphate [43], thereby ensuring the release of phosphorus for plant utilization. Due to the solubility of struvite in acidic solutions, acid phosphatase plays a crucial role in plant growth processes in this experiment. Acid phosphatase acts as a hydrolase that promotes organic phosphate mineralization in soils. In the context of low phosphorus stress, soil microbes are capable of accessing organic phosphorus through the increased production of phosphatase enzymes, thereby overcoming bio-geochemical phosphorus limitations [44]. Under normal circumstances, there is minimal secretion of acid phosphatase from plant roots into the rhizosphere. However, under phosphorus deficiency conditions, plants increase their secretion of acid phosphatase to enhance the rhizosphere's available phosphorus content [45]. In this experiment, the application of phosphate fertilizer resulted in varying degrees of reduction in soil acid phosphatase activity. The markedly higher phosphatase activity in the low fertilizer application treatments indicates possible stimulation of microbial activity to supplement phosphorus demands for cowpeas [46]. However, in comparison to DAP fertilizer, struvite demonstrated a comparatively limited impact on acid phosphatase activity, maintaining levels that were largely consistent with the original measurements.

The application of DAP resulted in a markedly greater increase in crop biomass and phosphorus accumulation compared to struvite. However, significant soil acidification problems were observed due to the substantial decrease in soil pH under the DAP treatment. The decline in soil pH was particularly pronounced in Chinese cabbage across all treatments, which can be attributed to the higher secretion of organic acids by Chinese cabbage roots relative to the other two crops. This ultimately led to a significant drop in soil pH. Similarly, cowpeas and maize exhibited a certain degree of soil acidification following the application of phosphorus fertilizers. However, both biomass and phosphorus accumulation demonstrated an increase in comparison to the no-fertilizer treatment, aligning with the findings of previous research [28].

5. Conclusions

The impact of struvite and diammonium phosphate on crop biomass and phosphorus absorption exhibited notable discrepancies. Generally, DAP had a stronger promoting effect compared to struvite. The MIX showed intermediate effectiveness between the two single fertilizers and was also superior to using only struvite. Among the three crops, maize exhibited the highest response to struvite, followed by cowpea and Chinese cabbage. Additionally, in terms of organic acids secreted by roots and nutrients obtained from mycorrhizal fungi, Chinese cabbage and maize demonstrated better utilization of active components from struvite compared to cowpea. The application of struvite did not significantly improve the soil's available phosphorus content. However, it effectively reduced the risk of soil phosphorus loss compared to DAP treatment. This reduction was further enhanced by the root activities of Chinese cabbage and maize. Struvite significantly reduced soil pH changes compared to DAP treatment. It effectively alleviated soil acidification while maintaining acid phosphatase activity. Among the three crops, struvite exhibited the best compatibility with maize, as it not only met the plant's phosphorus requirements but also maintained soil pH levels and acid phosphatase activity. It is important to note that this study specifically investigated the seedling stage of crop growth. However, it is essential to recognize that the process of phosphorus release and uptake by roots in struvite occurs over an extended period. Future research should therefore focus on understanding the activation of phosphorus in struvite over time and the residual effect of phosphorus on crop growth.

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