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AND SOIL FERTILITY

Availability and Uptake of Phosphorus and Zinc by Maize in the Presence of Phosphate-Containing Zn-Al-LDH in a Calcareous Soil

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Abstract—In this research, the potential application of phosphate containing zinc–aluminum–layered double hydroxide (Zn-Al-P-LDH) to enhance the availability of P and Zn compared to triple superphosphate (TSP) in a calcareous soil was investigated. First, soil availability of P and Zn at two P levels (18 and 45 mg kg⁻¹) of Zn-Al-P-LDH and TSP were compared in a 70-day incubation procedure. Second, a pot experiment was performed to study the effect of these treatments on growth and on P and Zn uptake by maize. Incubation experiment showed that, in contrast to the TSP, addition of both P levels of LDH increased P availability during the incubation period. Furthermore, the soil-available Zn in LDH was significantly enhanced compared to TSP and control treatments. This observation suggested that ion exchange accompanied by partial dissolution mechanism possibility happened for studied LDH. However, the values of shoot dry weight and leaves P uptake were significantly higher for LDH than TSP treatment just at 18 mg P kg⁻¹ level probably due to its effect on adequate Zn supply along with P. Therefore, Zn-Al-P-LDH might be a candidate as dual-purpose fertilizer if its limitations in terms of high Zn content to be overcome.

Keywords: controlled release fertilizer, ion exchange, phosphorus, solubility, Zn-Al-LDH

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INTRODUCTION

Phosphorus (P) is the second most frequently limiting macronutrient for plant growth [27]. The relatively small pool of soil P is unable to supply adequate amounts of P to soil solution for satisfactory crop growth; therefore, it is the least accessible macronutrient [4]. Thus, chemical P fertilizers with high water solubility (e.g., diammonium hydrogen phosphate (DAP) and triple superphosphate (TSP)) [15] and/or organic sources of P (e.g., manure) [34] are imported into agricultural systems to increase and maintain productivity. However, due to the P reactions with soil components such as Fe-Al oxides (in acidic soil) and CaCO₃ (in calcareous soil), not all the P applied to soils is available to plants [1] and only 15–30% of it is taken up by crops in the year of its application [41]. Furthermore, due to the high demand of P fertilizers, there are concerns for the depletion of non-renewable global rock phosphate (main source of P) reserves [45]. In such situation, the expected increase of P fertilizer cost in future may impact global food security. Therefore, it is essential to develop new materials that are capable of controlled release of P to improve P fertilizer use efficiency and provide adequate food for

humans. Among materials displaying such a feature, layered double hydroxides (LDHs) are appropriate candidates. LDHs belong to a group of lamellar non-silicate compounds with positively charge [18]. The general structural formula for these compounds is $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(A^{n-})_{x/n} \cdot m(\text{H}_2\text{O})$, where M²⁺ and M³⁺ are divalent and trivalent cations, respectively. The value of x is equal to $M^{3+}/(M^{3+} + M^{2+})$ and Aⁿ⁻ is the intercalated anion [21]. Recently, LDHs have received wide-spread attention for the adsorption of different anions such as phosphate [11, 13, 28] due to the presence of positively charged brucite-like sheets, relatively weak interlayer bonding and ion-exchange properties [21]. Furthermore, there are studies that show the adsorbed phosphate by LDH is able to be released slowly into solution, thereby making them a controlled release phosphate source [23, 36, 46]. In this context, Koilraj et al. [30] investigated the effect of using directly Ni-Al-LDH as a P fertilizer on growth of green seaweed (*Ulva lactuca*) in hydroponic. Their results illustrated that when LDH were used as a source of P, growth rate of seaweed was higher than other sources of P. They attributed these results to the

Table 1. Some physical-chemical properties of the soil

Available Fe, mg kg ⁻¹	Available Zn, mg kg ⁻¹	Available K, mg kg ⁻¹	Available P, mg kg ⁻¹	N, mg kg ⁻¹	OC, %	CCE, %	EC (1 : 2), dS m ⁻¹	pH (1 : 2)	Texture
1.78	0.54	121	9.87	448	0.33	11.62	0.43	7.98	Loam

controlled release of phosphate from LDH. Everaert et al. [16] assessed the P response of barley in two acid and calcareous soils amended with a P form of Mg-Al-LDH. They found that in the acid soil, the P uptake by barley from the LDH treatment was up to 4.5 times higher than that of the KH₂PO₄ treatment, likely because of the liming effect associated with LDH dissolution. In contrast, in the calcareous soil barley P uptake in the presence of LDH was lower than KH₂PO₄ at the higher P doses and being similar at low P doses. Similarly, the positive effects of Mg-Al-LDH and Ca-Al-LDH as sources of P on growth of maize and *Bradyrhizobium elkanii*, a nitrogen-fixing symbiotic bacterium, were reported by Benício et al. [5] and Bernardo et al. [6], respectively. In addition to interlayer anion, an effective zinc (Zn) supply to barley plants following the application of Zn-doped Mg-Fe-LDH in quartz sand and in a calcareous soil has been stated by López-Rayó et al. [32]. They reported the Zn concentrations in the plants receiving LDH were between 2- and 9.5-fold higher than those in plants without Zn addition. As can be observed in most studies, P containing Mg-Al-LDH have been used as P fertilizer because of non-toxic effect of Mg and Al on plant growth in a well-managed agricultural soil (liming, soil pH > 5). However, the application of P form of Zn-Al-LDH as a fertilizer has received less attention, despite its suitability as a dual-purpose fertilizer to develop appropriate source of P and Zn in agricultural, especially, calcareous soils suffering from these plant nutrients.

Previous research on synthesized Zn-Al-LDH with Zn/Al molar ratios of 2 and 3 by general (Zn_{2G}-Al and Zn_{3G}-Al) and modified (Zn_{2M}-Al and Zn_{3M}-Al) urea hydrolysis methods [12, 25] showed high phosphate adsorption capacity, as well as phosphate controlled release in Zn_{2G}-Al, Zn_{2M}-Al and Zn_{3M}-Al [23]. Among these LDHs, phosphate form of Zn_{2G}-Al (Zn_{2G}-Al-P) was selected for further experiments due to the higher dry solid production compared to the other LDHs. Therefore, this study was setup to compare the effects of Zn_{2G}-Al-P and TSP application on availability of P and Zn over time (incubation experiment) and on P and Zn uptake by maize in a calcareous soil.

OBJECTS AND METHODS

Synthesis of Zn_{2G}-Al-P. To synthesis of Zn_{2G}-Al-P, firstly a general urea hydrolysis method was used to produce nitrate containing Zn_{2G}-Al and then anion exchange method was employed to substitute phosphate

with nitrate anions, described by Hatami et al. [23]. For such a replacement, a known weight of nitrate containing Zn_{2G}-Al or volume of 0.05 M aqueous solution of KH₂PO₄ were reacted under stirring for 12 h condition at room temperature (solid-to-solution ratio of 5 g L⁻¹ and pH = 7) and then the precipitates were collected by centrifugation. The saturation process was repeated three times to achieve the maximum loading of phosphate on the LDH. Afterward, synthesized Zn_{2G}-Al-P were collected by Whatman 42 filter paper and dried at 70°C for 18 h. The specimens of <0.5 mm in diameter were used for the experiments. The total amounts of Zn and P in Zn_{2G}-Al-P were measured by atomic absorption spectroscopy (PG 900) and molybdate methods [35], respectively, after digestion in 1 M H₂SO₄ [47]. Characterization of studied LDH (X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR)) before and after phosphate adsorption have been shown elsewhere [23].

Samples collection. Surface sample (0–20 cm) of a calcareous soil collected from Mashhad, northeastern Iran (36.27° N 59.60° E) was used for incubation and pot experiments. The soil sample was air-dried and ground to pass through a 2 mm sieve before use. Some general soil properties (Table 1) were determined according to the standard methods including soil texture by the hydrometer method [20], soil organic carbon using modified Walkley and Black method [48], pH at 1 : 2 soil/water ratio using a glass electrode (Metrohm-632), electrical conductivity (EC) in the water extract of 1 : 2 soil/water ratio (Jenway-4510), total nitrogen (N) by digestion with sulfuric acid and Kjeldahl distillation [7], available potassium (K) extracted by 1 M ammonium acetate at pH 7 [29], available P extracted by 0.5 M sodium bicarbonate at pH 8.5 [37], available Fe and Zn extracted with diethylene triamine pentaacetic acid-triethanolamine (DTPA-TEA) solution at pH 7.3 [31] and calcium carbonate equivalent (CCE) by neutralization with acid [3].

Incubation and pot experiments design. For the incubation experiment, 50-g samples of air-dried of soil were treated with two sources of P (Zn_{2G}-Al-P and TSP) with two levels (18 and 45 mg P kg⁻¹ soil which were named C₁ and C₂, respectively) in three replications. Furthermore, three 50-g samples of air-dried of soil which were not treated with Zn_{2G}-Al-P and TSP sources as control. These samples were incubated at 25°C for up to 70 days and maintained at field capacity by weight calibration. At the end of each incubation time, soil destructive samples for each period were

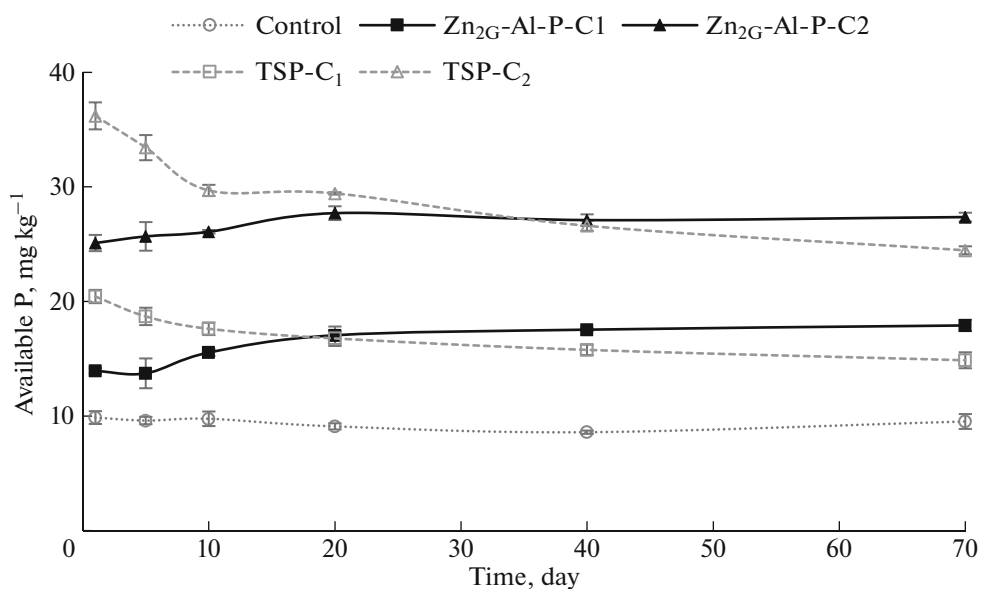


Fig. 1. Changes in available P as a function of time after amendment with different levels of Zn₂G-Al-P and TSP. Vertical bars indicate standard deviation ($n = 3$).

removed, air-dried and analyzed for available P and Zn using the methods as described earlier.

To assess the application effects of Zn₂G-Al-P and TSP on growth and availability of P and Zn to maize, a greenhouse experiment was carried out in a completely randomized design in three replications with five treatments (control, Zn₂G-Al-P-C₁, Zn₂G-Al-P-C₂, TSP-C₁ and TSP-C₂). The recommended dose of N, K and Fe were applied based on soil testing results as follows: 72 mg N, 35 mg K and 15 mg Fe per kg of soil using CO(NH₂)₂, K₂SO₄ and FeSO₄·7H₂O, respectively. The black plastic pots were filled with 5 kg of treated soil and covered with 150 g coarse sand. The pots were watered daily to maintain the moisture contents at 80% of field capacity by observing daily weight loss. In each pot, five maize seeds (*Zea mays* L.) were initially sown and finally two plants per pot were maintained. Sixty days after planting, the plants were harvested for recording plant height. The shoots were oven dried at 70°C and the dry weight was measured. Additionally, the dry leaves were crushed, ashed at 450°C and extracted in 0.1 M HCl [17] solution to determine the content of P and Zn by procedures described earlier. Furthermore, soil within the pots was air dried, crushed gently and analyzed for determination of EC, pH and the available P and Zn, after harvesting. Statistical analyses were performed with MSTATC 1.42 and the means were compared by Duncan's test at $p < 0.05$.

Agronomic indices. The agronomic indices including partial factor productivity (PFP), agronomic P-use efficiency (AE) and partial nutrient balance (PNB) [14] were used to investigate the P efficiency of Zn₂G-Al-P and TSP on production of shoot dry weight and P

content of maize plant. These indices were shown in Eq. 1, 2 and 3, respectively:

$$\text{PFP} = Y_P / F_P, \quad (1)$$

$$\text{AE} = (Y_P - Y_0) / F_P, \quad (2)$$

$$\text{PNB} = U_P / F_P, \quad (3)$$

where Y_P and Y_0 (both mg kg⁻¹) were yield (shoot dry weight) in P fertilizer and control treatments, respectively. F_P (mg kg⁻¹) was quantity of P fertilizer input and U_P (mg kg⁻¹) was P content of harvested portion of the maize.

RESULTS

Elemental analysis of Zn₂G-Al-P. Chemical analysis of Zn₂G-Al-P showed that total amount of P and Zn were 89.91 (±0.31) and 305.45 (±5.55) mg g⁻¹. After three times saturation, the amount of P in Zn₂G-Al-P became very close to the measured and theoretical anion exchange capacity in Zn₂G-Al which were obtained in the previous study [23].

Effect of Zn₂G-Al-P and TSP treatments on soil available P and Zn during incubation time. In incubation experiment, application of various levels of Zn₂G-Al-P and TSP significantly increased available P compared to the control (Fig. 1). However, the rate of changes of available P in two sources was different. In both levels of TSP, the amount of available P was higher than the control and equivalent to P levels in Zn₂G-Al-P at the early stages of the incubation (10 days) but slowed down with time, so that it decreased up to 14.87 (±0.70) and

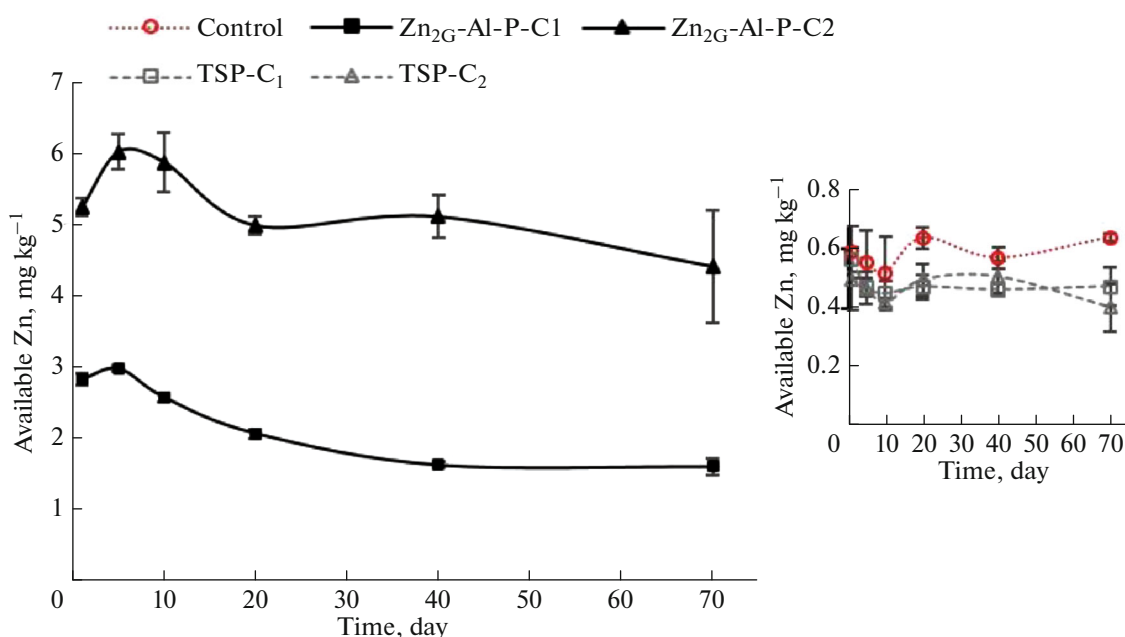


Fig. 2. Changes in available Zn as a function of time after amendment with different levels of Zn₂GAl-P and TSP (inset). Vertical bars indicate standard deviation ($n = 3$).

24.47 (± 0.35) mg kg⁻¹ for TSP-C₁ and TSP-C₂, respectively after 70 days. In contrast, not only P did not reduce over time in both levels of Zn₂G-Al-P, but also it significantly increased with incubation time. Furthermore, by excluding the available P value originating from the control, the maximum values of available P in Zn₂G-Al-P-C₁ and Zn₂G-Al-P-C₂ treatments were 47 and 40% of total P which was present at each levels, respectively. While, these values were 61 and 60% for TSP-C₁ and TSP-C₂, respectively. Hence, it seems that increase of available P remained more stable in the presence of Zn₂G-Al-P compared to TSP during the time.

Unlike TSP and the control treatments that did not show significant changes in available Zn throughout the incubation period, this labile Zn significantly was improved by the application of both Zn₂G-Al-P levels (Fig. 2). However, available Zn in Zn₂G-Al-P-C₁ and Zn₂G-Al-P-C₂ treatments initially increased up to 5 days and then diminished to 1.61 (± 0.11) and 4.42 (± 0.23) mg kg⁻¹, respectively, at the end of the experiment. On the other hand, the maximum values of available Zn in Zn₂G-Al-P-C₁ and Zn₂G-Al-P-C₂ were 4% of total Zn, which were very lower than the above mentioned values for available P in Zn₂G-Al-P treatments.

Effect of Zn₂G-Al-P and TSP treatments on maize plant growth. Height and shoot dry weight of maize plants as affected by different treatments have been presented in Fig. 3. Based on Fig. 3a, although C₁ and C₂ levels of both sources had significant effect on height

of maize, there was no statistically difference between Zn₂G-Al-P and TSP treatments. In contrast to the TSP treatments, no remarkable differences were observed between the shoot dry weight values of Zn₂G-Al-P treatments (Fig. 3b). Both TSP-C₂ and Zn₂G-Al-P-C₂ treatments showed higher shoot dry weight with no difference between them. However, there was statistically difference between shoot dry weights of Zn₂G-Al-P-C₁ and TSP-C₁ and it was 20.57% higher for Zn₂G-Al-P-C₁ than TSP-C₁.

The largest P concentration of maize leaves was obtained in Zn₂G-Al-P-C₂ which was significantly higher than TSP-C₁, TSP-C₂ and Zn₂G-Al-P-C₁ (Table 2). In line with this, there was no difference between leaves P concentration of Zn₂G-Al-P-C₁ and TSP-C₂. To compare P content of the treatments, P uptake of maize leaves were calculated (Table 2). Similar to leaves P concentration results, Zn₂G-Al-P-C₂ revealed the greatest leaves P uptake being 41, 8 and 16% higher than TSP-C₁, TSP-C₂ and Zn₂G-Al-P-C₁, respectively. Furthermore, there was no difference between leaves P uptake of Zn₂G-Al-P-C₂ and TSP-C₂ treatments while, leaves P uptake of Zn₂G-Al-P-C₁ was significantly more than TSP-C₁. These results were similar with shoot dry weight observation (Fig. 3b).

Zn concentrations of maize leaves for Zn₂G-Al-P-C₁ and Zn₂G-Al-P-C₂ (62.98 (± 3.52) and 79.90 (± 0.99) mg kg⁻¹, respectively) were significantly more than TSP and control treatments (Table 2). Furthermore, Zn concentration of maize plant increased by increasing doses of the LDH. Similarly, Zn uptake

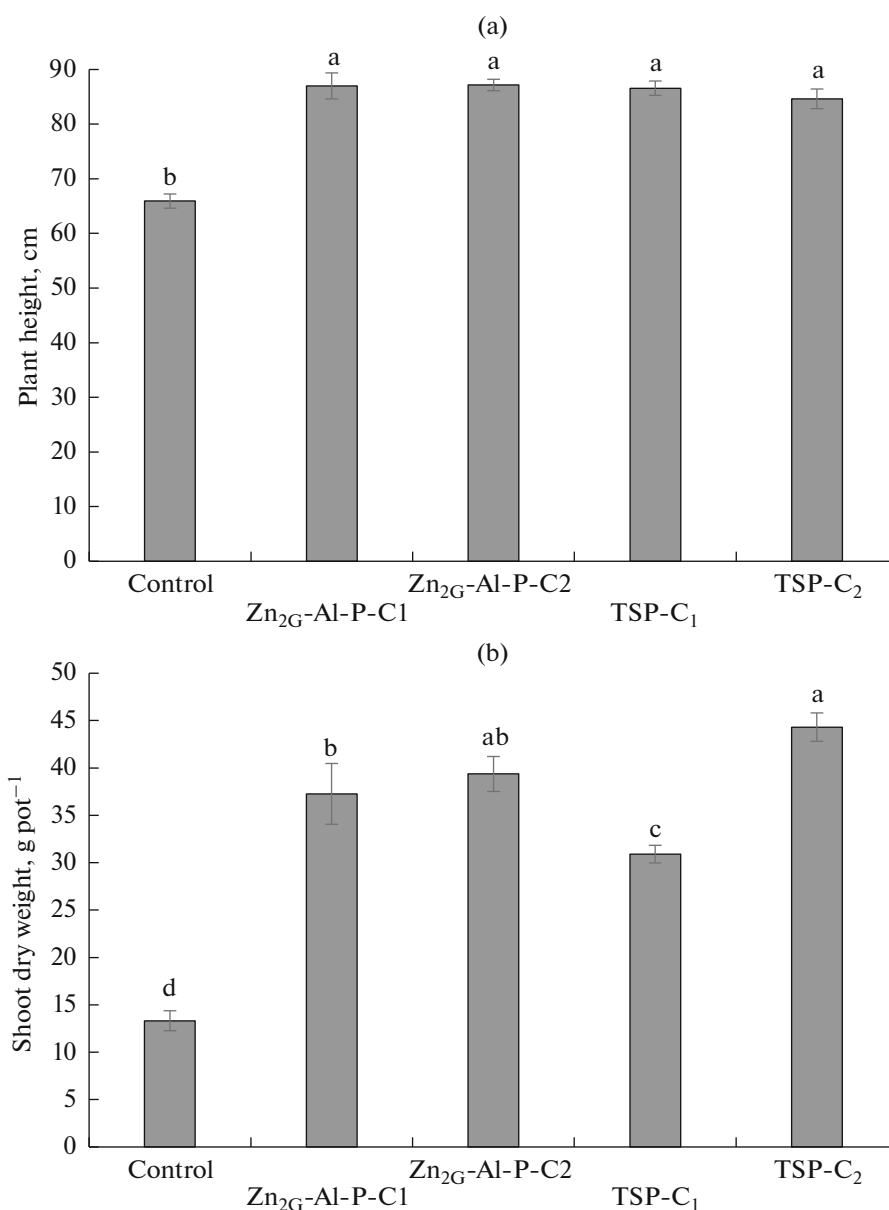


Fig. 3. Height (a) and shoot dry weight (b) of maize plants as affected by different doses and sources of P applied. Vertical bars indicate standard deviation ($n = 3$). For any one measured parameter, the treatments followed by similar letters are not statistically different at $p < 0.05$ level.

Table 2. Leaf concentration and uptake of P and Zn of maize as affected by different doses and sources of P applied

Treatments	Leaf P concentration, mg kg ⁻¹	Leaf P uptake, mg pot ⁻¹	Leaf Zn concentration, mg kg ⁻¹	Leaf Zn uptake, mg pot ⁻¹
Control	1216.93 (±74.08) ^d	10.67 (±1.36) ^c	12.37 (±1.62) ^c	0.11 (±0.02) ^c
Zn ₂ G-Al-P-C ₁	2943.78 (±50.59) ^b	58.86 (±4.93) ^a	62.98 (±3.52) ^b	1.13 (±0.04) ^b
Zn ₂ G-Al-P-C ₂	3117.39 (±64.44) ^a	68.37 (±1.38) ^a	79.90 (±0.99) ^a	1.78 (±0.05) ^a
TSP-C ₁	2705.03 (±176.19) ^c	48.60 (±2.48) ^b	11.17 (±0.98) ^c	0.22 (±0.01) ^c
TSP-C ₂	2845.57 (±114.12) ^b	63.45 (±3.86) ^a	10.43 (±1.07) ^c	0.23 (±0.03) ^c

Data are the means ± standard error ($n = 3$). For each measured parameter, means without common letter are significantly different (at $p \leq 0.05$), according to Duncan test.

Table 3. EC, pH, available P and Zn in soil as affected by different doses and sources of P applied after harvesting

Treatments	EC, dS m ⁻¹	pH	Available P, mg kg ⁻¹	Available Zn, mg kg ⁻¹
Control	0.47 (±0.01) ^b	8.04 (±0.50) ^a	6.65 (±0.46) ^e	0.59 (±0.03) ^c
Zn _{2G} -Al-P-C ₁	0.63 (±0.02) ^a	7.99 (±0.01) ^a	13.30 (±1.09) ^c	8.90 (±0.50) ^b
Zn _{2G} -Al-P-C ₂	0.66 (±0.03) ^a	7.97 (±0.03) ^a	20.18 (±0.87) ^a	15.03 (±1.95) ^a
TSP-C ₁	0.60 (±0.04) ^{ab}	7.87 (±0.01) ^b	10.64 (±0.92) ^d	0.81 (±0.03) ^c
TSP-C ₂	0.60 (±0.03) ^{ab}	7.84 (±0.02) ^b	17.00 (±0.19) ^b	0.90 (±0.08) ^c

Data are the means ± standard error ($n = 3$). For each measured parameter, means without common letter are significantly different (at $p \leq 0.05$), according to Duncan test.

for Zn_{2G}-Al-P-C₁ and Zn_{2G}-Al-P-C₂ was absolutely higher than other treatments (Table 2). However, there was no difference between Zn concentration and uptake of TSP treatments and control.

Effect of Zn_{2G}-Al-P and TSP treatments on some chemical characteristics of studied soil. The values of pH, EC, available P and Zn of soil samples were investigated after harvesting (Table 3). The results indicated that compared with the control, soil pH showed no and small reduction (around 0.2 unit) by the addition of various P levels of Zn_{2G}-Al-P and TSP, respectively. Unlike the soil pH, EC values for LDH treatments tended to be greater by around 0.2 unit while, TSP treatments did not present any effect on EC values.

After harvesting, the maximum soil available P (20.18 (±0.87) mg kg⁻¹) was recorded for Zn_{2G}-Al-P-C₂ which was 3.03, 1.52, 1.90 and 1.19 times more than control, Zn_{2G}-Al-P-C₁, TSP-C₁ and TSP-C₂, respectively. Moreover, the values of soil available P were significantly greater for Zn_{2G}-Al-P treatments than TSP treatments receiving equal amounts of P (Table 3). Likewise, Zn_{2G}-Al-P-C₂ provided a higher amount of soil available Zn (15.03 (±1.95) mg kg⁻¹) and it was significantly more than other treatments. Using of TSP treatments did not significantly influence the values of soil available Zn after harvesting (Table 3).

Agronomic indices. Agronomic indices including PFP, AE and PNB for Zn_{2G}-Al-P-C₁, Zn_{2G}-Al-P-C₂,

and TSP-C₁ and TSP-C₂ treatments are shown in Table 4. The PFP index that shows the production of shoot dry weight per unit of P applied was larger for Zn_{2G}-Al-P-C₁ than TSP-C₁, while it became a little lower for Zn_{2G}-Al-P-C₂ than TSP-C₂. The same trend was observed for AE index, that indicates the increase in plant yield per unit of P applied. Therefore, relative increase of shoot dry weight per unit of P was more when the P sources was Zn_{2G}-Al-P-C₁. Moreover, the values of PFP and AE decreased by increasing P level in both sources. Unlike the PFP and AE indexes, PNB that expresses the content of P exported by maize leaves per unit of P input, was higher for Zn_{2G}-Al-P than TSP in both P levels. However, the maximum PNB value was recorded for Zn_{2G}-Al-P-C₁.

DISCUSSION

Incubation experiment. Under incubation conditions, the reduction of P availability in TSP treatments was foreseeable due to the possibility of calcium-phosphate precipitation [24] based on the amount of CCE in studied soil (Table 1). This behavior of P fertilizers in calcareous soils were reported in other studies [10, 19]. However, no decrease of P availability in Zn_{2G}-Al-P treatments was probably because of the slow release of phosphate ions from the LDH resulting in less adsorption of P onto soil surfaces. This result was in agreement with finding of Everaert et al. [16] who indicated a clear slow release of P for Mg-Al-P-LDH compared to KH₂PO₄ and TSP during equilibration with a zero sink for P. In addition to P, the controlled release of organic and inorganic sources such as nitrate, 2,4-D, 2-methyl-4-chlorophenoxy acetic acid, picloram and terbutylazine into soil environment have also been reported for Mg-Al-LDHs [8, 9, 22].

As mentioned earlier, the available Zn in Zn_{2G}-Al-P treatments was enhanced along with the P levels and achieved to 1.61 (±0.21) and 4.42 (±0.23) mg kg⁻¹ for Zn_{2G}-Al-P-C₁ and Zn_{2G}-Al-P-C₂ treatments, respectively; these values were higher than Zn critical value in Iranian soils for corn (1.50 mg kg⁻¹ DTPA-extractable Zn) [49]. Therefore, although ion exchange and ion exchange accompanied by dissolution mecha-

Table 4. Effect of different P levels of Zn_{2G}-Al-P and TSP on Partial factor productivity (PFP), Agronomic efficiency (AE) indices

P dose	PFP	AE	PNB
Zn _{2G} -Al-P			
C ₁	414.05	266.02	0.65
C ₂	174.96	115.75	0.30
TSP			
C ₁	343.40	195.37	0.54
C ₂	196.95	137.73	0.28

C₁ and C₂ are the levels of 18 and 45 mg P kg⁻¹ soil, respectively.

nisms have been suggested for release of P from LDH in neutral and acid-weathered soils, respectively [16], it seems that the mixing of ion exchange and partial dissolution of Zn_{2G} -Al-P mechanisms took place in the present study. The solubility of LDH may be due to the complexity of soil environment affecting the stability of these compounds. For example, decrease in crystallinity degree of Zn_{2G} -Al-P by adsorption of inorganic and organic anions in soil may be one of the factors involved in the LDH solubility [22]. Increasing the solubility of LDHs after nitrate, sulfate and phosphate adsorption has been reported by Allada et al. [2], Tsujimura, et al. [44] and Seida and Nakano [38]. Moreover, the solubility of LDHs has been influenced by the pH that is controlled by surface [26]. Therefore, the particle size may be considered as another reason for the LDH solubility. Torres-Dorante et al. [43] showed that the stability of Mg-Al-LDH mineral applied in powder form into the soil was less than its granular form. Hence, using of larger particles probably would be more appropriate in soil applications of LDHs.

Pot experiment. Based on pot experiment results, application of Zn_{2G} -Al-P treatments did not improve plant height and shoot dry weight compared to TSP treatments (except Zn_{2G} -Al-P- C_1 for shoot dry weight). These results were in disagreement with the study of Benício et al. [5] reporting higher height and shoot dry weight of maize for Mg-Al-LDH than TSP treatments at all P levels. The difference in the type of utilized LDH could be as one of the important reason for our different results. We used Zn_{2G} -Al-P, as its effect on increasing of soil Zn content could be the main factor for such a discrepancy. Therefore, P and Zn uptake in the maize leaves (Table 2) as well as soil available P and Zn after harvesting (Table 3) may provide helpful information about the possibility of reasons that resulting in such a difference.

The results of leaves P uptake showed that only at low fertilizer dose (C_1), Zn_{2G} -Al-P performed better than TSP (Table 2). Everaert et al. [16] illustrated that in an acidic soil increase of Mg-Al-P-LDH does lead to increase of shoot P uptake and yield of barely compared to KH_2PO_4 . On the contrary, in their calcareous soil, this trend showed reverse trend at the highest P dose of Mg-Al-P-LDH (100 mg P kg^{-1}). They related this observation to sulfur (S) deficiency in soil due to the SO_4^{2-} sorption on the LDH phase. In our study, S deficiency could not be the case because of the application of K_2SO_4 and $FeSO_4 \cdot 7H_2O$ during the greenhouse experiment before planting and also possibility of Zn_{2G} -Al-P solubility. According Table 2, the control and TSP treatments showed insufficient leaves Zn concentration ($10.43 (\pm 1.07)$ – $12.37 (\pm 1.62) \text{ mg kg}^{-1}$) which were below the critical level required in maize leaves (12 – 14.2 mg kg^{-1} , [40]) while, Zn content increased up to $62.98 (\pm 3.52)$ and $79.90 (\pm 0.99) \text{ mg kg}^{-1}$

in Zn_{2G} -Al-P- C_1 and Zn_{2G} -Al-P- C_2 treatments, respectively. Furthermore, the values of soil available Zn after harvesting in Zn_{2G} -Al-P- C_1 and Zn_{2G} -Al-P- C_2 treatments ($8.90 (\pm 0.50)$ and $15.03 (\pm 1.95) \text{ mg kg}^{-1}$, respectively) were quite greater than TSP and control treatments (Table 3). Takkar and Mann [42] reported that Zn concentrations greater than 81 mg kg^{-1} for plant and higher than 11 mg kg^{-1} for soil (DTPA-extractable Zn) were toxic in maize and its yield reduced markedly. Since, the values of leaves Zn concentration and soil available Zn after harvesting for Zn_{2G} -Al-P- C_2 were very close and greater than values for maize and soil toxicity, respectively, it seems that the absence of a statistically difference between leaves P uptake (and shoot dry weight) of Zn_{2G} -Al-P- C_2 and TSP- C_2 may be because of Zn toxicity in Zn_{2G} -Al-P- C_2 treatment. On the other hand, these values in Zn_{2G} -Al-P- C_1 treatment were less than above mentioned values for maize and soil toxicity. Therefore, in this treatment adequate Zn supply in addition to P for maize was probably one of the reasons for its significant effect on dry matter yield compared to TSP- C_1 treatment. It is worth mentioning that although the amounts of soil available Zn in LDH treatments increased in both incubation and pot experiments (Fig. 2 and Table 3), these values were entirely higher in pot trail. Hence, these results suggested that application of Zn_{2G} -Al-P in the soil-plant system led to increase of Zn release probably due to rhizosphere acidification enhancing the LDH solubility. A positive effect of Zn-doped Mg-Fe-LDH on Zn uptake by barley as a consequence of rhizosphere pH decrease following root excretion of low molecular weight organic acids was reported by López-Rayó et al. [32].

The second reason for no difference between leaves P uptake (and shoot dry weight) of Zn_{2G} -Al-P- C_2 and TSP- C_2 may be due to the plant's ability for P uptake. In other words, both treatments (Zn_{2G} -Al-P- C_2 and TSP- C_2) were capable of supplying the adequate leaves P concentration for optimal growth of maize plant (2.5 – 3.5 g kg^{-1}) [33] and thereby no significant difference was observed among them for shoot dry weight and P uptake. This hypothesis could be supported by the values of soil available P after harvesting (Table 3) as the amounts of available P for Zn_{2G} -Al-P- C_2 and TSP- C_2 treatments were significantly higher than Zn_{2G} -Al-P- C_1 , TSP- C_1 and control treatments. This means that the greater values of P have not been taken up by these treatments despite the presence of available P in the soil.

According to pot experiment result, it seems that the positive effect of Zn_{2G} -Al-P on growth and P uptake of maize were more noticeable at lower P dose. This result was confirmed by the measured agronomic indices values which were larger for Zn_{2G} -Al-P- C_1 than other treatments (Table 4). As reported in Table 4, the values of PFP and AE decreased by increasing P level in

both sources which was probably due to the Mitscherlich law, the law of diminishing returns [5]. Similar result were reported by Shehu [39].

The absence of negative effect of Zn_{2G}-Al-P on soil pH and EC was another advantageous aspect of this compound (Table 3). Although, due to the acidifying and alkalizing effect of TSP and Zn_{2G}-Al-P, decreasing and increasing pH effects were expected after their applications, respectively. However, no appreciable changes in pH could be related to the buffering capacity of the study calcareous soil. The similar results were reported for application of Mg-Al-LDH in calcareous soils by Halajnia et al. [22] and Everaert et al. [16].

It is worth mentioning that although in the current study the content of Al in maize plant and soil was not investigated, as the possibility of Al toxicity was low due to the high pH in the study calcareous soil. Benício et al. [5] stated that when soil pH is 5.7 or higher, there is no Al left in the soil solution that would cause any harm to plants. This is probably due to the formation of amorphous Al(OH)₃ which it is not toxic [16].

CONCLUSIONS

The results of this study illustrated that, in contrast to the TSP treatments, the rate changes of soil available P for Zn_{2G}-Al-P were slower during the incubation time. Moreover, application of Zn_{2G}-Al-P enhanced soil available Zn compared to other treatments. However, in the presence of maize plant, using of Zn_{2G}-Al-P only at the level of 18 mg P kg⁻¹ was more effective in higher shoot dry weight and leaves P uptake compared to TSP treatment supplying equivalent P. This result might be due to the gradual release of P from the LDH as well as its effect on providing Zn content at adequate level for maize. It appears that incapability of Zn_{2G}-Al-P at the level of 45 mg P kg⁻¹ for effective increase of biomass yield and P uptake compared to equivalent TSP treatment was likely because of Zn toxicity and plant's ability for taking up P. Therefore, it seems that Zn_{2G}-Al-P at low level may have a good potential to be utilized as a convenient dual-purpose fertilizer in calcareous soils. However, P supply of the LDH may not be adequate based on conventional P demand of some crops. On the other hand, the increase in the amount of soil Zn following application of LDH may be high in comparison to regular crop requirement for Zn; therefore, the possibility of Zn toxicity may be applicable. Thus, further research is required to be focused on changing the components of Zn_{2G}-Al-LDH, making it higher P contents and lower Zn values.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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