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Alum split applications strengthened phosphorus fixation and phosphate sorption in high legacy phosphorus calcareous soil

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ABSTRACT

High phosphorus (P) saturation arising from historic P inputs to protected vegetable fields (PVFs) drives high P mobilisation to waterbodies. Amendment of soils with alum has shown potential in terms of fixing labile P and protecting water quality. The present 15 month pot experiment investigated P stabilisation across single alum application (Alum-1 treatment, 20 g alum/kg soil incorporated into soil before the maize was sown), alum split applications (Alum-4 treatment, 5 g alum/kg soil incorporated into soil before each crop was sown i.e. 4×5 g/kg) and soil only treatment (Control). Results showed that the Alum-1 treatment caused the strongest stabilisation of soil labile P after maize plant removal, whereas the P stabilisation effect was gradually weakened due to the transformation of soil non-labile P to labile P and the reduced active Al^{3+} in soil solution. For the Alum-4 treatment, soil labile P decreased gradually with each crop planting and was lower than the Alum-1 treatment at the end of the final crop removal, without any impairment on plant growth. The better P stabilisation at the end of Alum-4 treatment was closely correlated with a progressive supply of Al^{3+} and a gradual decrease of pH, which resulted in higher contents of poorly-crystalline Al, Fe and exchangeable Ca. These aspects were conducive to increasing the soil P stabilisation and phosphate sorption. In terms of management, growers in continuous cropping systems could utilise split alum applications as a strategy to alleviate P losses in high-P enriched calcareous soil.

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Introduction

Phosphorus (P) accumulation due to high P inputs has been a considerable issue in the arable land of China (Zhang et al., 2019). While recommended threshold soil test P (STP) values based on yield response to applied P (here these values are termed as agronomic threshold) have been identified for optimum crop production, many regions with intensive agriculture have STP concentrations above these agronomic threshold values (Gourley et al., 2015; Yan et al., 2013). Although it is questionable whether P fertiliser application needs to be continued in these intensive soils (Sharpley et al., 2013), there

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is a consensus that intensive agriculture is the main non-point source of P losses to surface waters (Giles et al., 2015; Kalkhajeh et al., 2018; Kronvang et al., 2005).

In calcareous soil which is widely distributed in the north of China, high base status and pH render most of the exogenous phosphate ion from fertiliser unavailable and transform it into various precipitated P forms, such as stable Ca-P and Mg-P (Yan et al., 2018). However, previous studies demonstrated that the proportion of the soil labile P increases abruptly when legacy P continues to accumulate in soil, specifically in soils fertilised with livestock manure (Withers et al., 2017; Yan et al., 2013). In China PVFs are utilised to spread large amounts of livestock manure (Yan et al., 2016). It was estimated that PVFs, which account for 12% of the total arable land in China, annually receive over 50% of the manure produced in China's livestock industry (Jia et al., 2018). Consequently, P losses in the dissolved as well as in the particulate form along surface and subsurface pathways were commonly reported in the soils of PVFs (Kang et al., 2018; Shi et al., 2008; Yan et al., 2016). It is reported that the STP concentrations at the depths of 60 cm in many PVFs soils still exceed the threshold STP values (Chen et al., 2019; Kalkhajeh et al., 2018; Yan et al., 2018). Best management practices (BMPs) to protect water quality involve matching crop requirements with P inputs. However, such options do not mitigate against legacy P in the soil (Withers et al., 2015). Soil amendment with P fixation materials (PFMs) has been researched and shows promise as an above baseline BMP for growers in areas of China with historically high application rates of fertiliser (Fan et al., 2020).

Alum amendment of soils has been shown to reduce P losses from the intensively fertilised horticultural soils, or soils that have received animal wastes in the last decade (Anderson et al., 2018; Fan et al., 2019; Lombi et al., 2010; Zhao et al., 2018). Peak et al. (2002) reported that at pH >6, alum precipitates out as poorly-crystalline Al hydroxides and then reacts with P via an adsorption mechanism as proven by X-ray absorption near edge structure (XANES) spectroscopy. A recent study of Fan et al. (2020) demonstrated P sorption on poorly-crystalline Al hydroxides mainly occurred through the displacement of inner-sphere Al-OH rather than a formation of $AlPO_4$ at pH 6.5. The maxima of adsorbed P on the poorly-crystalline Al hydroxides varied from 23.9 to 143 mg/g in the batch P sorption experiment (Gypser et al., 2018; Li et al., 2013; Wang et al., 2019). However, Fan et al. (2020) found that a calcareous soil amended with 20 g/kg of alum only had P sorption maxima of 0.45 mg P/g soil after 24 hrs. This raised questions about the decline of the P sorption amounts on Al hydroxides in the soil amended with alum. Batch studies exploring P sorption on the surface of Al hydroxides have identified that adsorbed P reached maxima and maintained stable after approximately 72 hr (Li et al., 2013; Wang et al., 2019). However, P cycling from soil non-labile P to labile P might be occurring to enable a new soil P balance when the soil labile P was fixed by Al hydroxides. It was reported that the time scale of P cycling operates from seconds to months from soil non-labile P to labile P (Helfenstein et al., 2018). In addition, other anions or soil colloids also react with Al hydroxides at the complicate soil system since Al also forms strong complexes with OH^-, F^- or organic substances containing carboxylate and phenolic functional groups (Arai and Sparks, 2007; Essington, 2015).

Based on the evidence put forward above, the "little and often" approach of alum applications (multiple smaller applications of alum that account for the same amount of alum applied in one single application) may be a good strategy to increase the soil P stabilisation, as "little" can diminish the reaction between other anions and Al^{3+} whilst "often" can strengthen the reaction between the soil labile P and Al hydroxides. In particular, the split alum applications approach was recommended to maximise binding efficiency and minimise risk and treatment cost on the restoration of lake eutrophication (Kuster et al., 2020). However, the higher P stabilisation efficacy of alum in soils before crops are sown needs to be validated to elucidate a more effective management strategy for growers.

In this study, the hypotheses was as follow: P fixation efficiency would increase with an increase in the P sorption capacity induced by the alum split applications. To meet the objectives, a 15 month pot study with continuous cropping of maize-celery-tomato-tomato was established to (1) investigate temporal variations in soil labile P and transformation of the soil P forms and pools across single (20 g/kg) and split (4 × 5 g/kg before each sowing period) alum amendments; (2) differentiate the dominant anions competing with P in the alum amended calcareous soil.

1. Materials and methods

1.1. Soil and alum preparation

Intensively cultivated soil, extracted to a 20 cm depth, was selected from one of the typical PVFs located in the Fangshan district (39.38°N, 116.10°E), Beijing, China, with a typical continental monsoon climate. Annual mean temperature is 11.6 °C and precipitation is 603 mm. The site has a 5-year rotation of tomato and leafy vegetables and received high application rates of chicken manure (150 m^3/ha/year) and urea (750 kg /ha/year). Soil samples were collected in April 2017. After extraction, the soil was air-dried and coarse rocks and plant residue were removed before it was sieved to 2 mm and homogenised. This silty loam soil was clarified as Calcaric Cambisol in US taxonomy with 27.1% sand, 57.8% silt, and 15.3% clay and named as brown soil in Chinese taxonomy (Brady and Weil, 2019). The bulk density of the soil was 1.32 g/kg. The pH of soil is 7.56 and soil contains 226 mg/kg Olsen-P, 11.4 g/kg organic carbon (OC), 414 mg/kg Mehlich3-P and 1.36 g/kg total P.

The alum used in this study was commercial-grade (≥ 99.8% $KAl(SO_4)_2$ on a dry basis, containing 14% Al) with pH 2.83 (W/V = 1:2.5). The specific surface area (S_{BEF}) of the sieved alum was 0.46 m^2/g, which was determined using a Quantachrome instrument at 77 K with a nitrogen adsorptive medium. Before incorporation into the homogenised soil, the amendments were dried and sieved through nylon mesh with 100 mesh number.

1.2. Experimental design and plant management

In order to compare the P stabilisation efficacy and investigate the variations of soil P forms across single (20 g/kg) and split

(4 × 5 g/kg before each sowing period) alum amendments, a 15 month pot study was conducted. The pot experiment comprised three treatments designed as follows: (1) control: no amendment; (2) Alum-1: single alum rate of 20 g/kg applied before the first crop was sown; (3) Alum-4: split alum rate of 5 g/kg before each crop was sown i.e. 4 × 5 g/kg as there are 4 crops. Therefore, the total amount of alum applied in Alum-1 treatment was equivalent to the Alum-4 treatment. For the soil treatments, 8 kg soil were thoroughly mixed with 160 g alum in the single alum application treatment (Alum-1) and with 40 g alum in the alum split applications treatment (Alum-4). Then each mixed soil was put into a pot (25 cm top diameter, 18 cm bottom diameter, 20 cm height). The equal weight of soil (8 kg) was put into the equal volume in each pot to achieve the target bulk density of 1.3 g/kg. Deionised water was added to each pot to achieve 70% of field water holding capacity (FWHC). All pots were randomly distributed inside a glasshouse for 10 days incubation. The first 7 days were under the 70% FWHC while no water was added in the last 3 days. Afterwards, maize was planted in each pot in July 2017. The soil water capacity was maintained to 50%−80% of the FWHC through the weight method during planting. As the seedling stage of crops is much more sensitive to soil P supply, the maize was collected after the seedling stage (at approximately 2 months after planting).

The remaining soil in each pot was extracted, dried and sieved through 2 mm nylon mesh. Afterwards, the dried soils in the control and Alum-1 treatments were put back into each pot accordingly, while 40 g alum was mixed thoroughly into the dried soil of the Alum-4 treatment before they were put back into the pot. These pots were randomly distributed in a glasshouse for 10 days again as described above and celery was planted in October 2017. After 2 months, the celery was collected and the soil in each pot was processed in the same way as for the maize removal. Next, tomatoes were planted twice in April 2018 and July 2018 and each planting season lasted for 2 months. Eventually, 160 g alum was mixed for the Alum-1 treatment once and four times for the Alum-4 treatment. Except for the maize, 3 g/pot urea was applied in every pot before the celery and tomatoes were sown. Each treatment in each season consisted of three replicates. A 200 g soil sample was collected from the triplicate pots of each treatment after the crop removal. Afterwards, these pots were discarded.

In a PVFs system, fruit vegetables are usually planted in the spring season, while leafy vegetables are planted in the autumn-winter season following changes in temperature. During the summer with high temperatures, some farmers choose to plant maize to uptake the nitrogen (N) and P in the deep soil (Kang et al., 2018). Therefore, to simulate such conditions, crops of maize (*Zea mays* L. cv. Tianyu No.4), celery (*Apium graveolens* L. cv. Wentula), tomato (*Lycopersicum esculentum Mill.* cv. Jiabao No.5) and tomato (*Lycopersicum esculentum Mill.* cv. Jiabao No.5) were planted.

1.3. Samples analysis

1.3.1. Plant samples

To ascertain the plant shoot dry weight (SDW), the shoots of plant were rinsed by deionised water, dried in an oven at 105 °C for 30 min and then at 75 °C to a constant weight (Yuan et al., 2017). The dried samples were ground and digested with concentrated H_2SO_4 and H_2O_2. The concentration of P, Fe, Al, Ca and Mg in the SDW were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, ICAP6300, USA). Finally, the uptake of plant total P (TP), Fe, Al, Ca and Mg contents were determined by the product of SDW and total element concentrations in shoot dry biomass.

1.3.2. Soil samples

Soil $CaCl_2$-P and Olsen-P, which indicates P loss risk and plant available P in calcareous soils were determined using 0.01 mol/L $CaCl_2$ (soil/solution ratio of 1:5) and 0.5 mol/L $NaHCO_3$ (soil/solution ratio of 1:20), respectively (Olsen, 1954; Schofield, 1955). Phosphorus concentrations in the extracts were measured using the colorimetric analysis (Murphy and Riley, 1962). Generally, $CaCl_2$-P is extracting the most readily desorbable P which mainly sourced from labile P, while Olsen-P is extracting the available and readily desorbable P which includes a large proportion of labile P and a few Al-bound P and Ca-bound P. In order to examine sequential P fractionation, soil samples from all treatments were subjected to the modified method of Hedley sequential fractionation (Hedley et al., 1982; Sui et al., 1999; Tiessen and Moir, 1993). The following extractions were performed in sequence: deionised water, 0.5 mol/L $NaHCO_3$, 0.1 mol/L NaOH, 1 mol/L HCl and concentrated H_2SO_4 and H_2O_2. The P in each extract before and after autoclave persulfate digestion (0.9 mol/L H_2SO_4 and 1 g $K_2S_2O_8$) was determined by the colorimetric method (Murphy and Riley, 1962), which denoted P_i and P_t. The organic P was calculated by subtracting P_i from P_t.

In order to differentiate the variation of the Al forms in a single or split application, soil samples from all treatments, which were obtained at the end of the experiment were subjected to the sequential Al fractionation method (Dai et al., 2011). Various forms of Al were extracted by different reagents as follows: 1.0 g of soil was weighed into a 100 mL polyethylene centrifuge tube. As the first extractant 25.0 mL potassium chloride (1 mol/L KCl) were added to the centrifuge tube. After shaking for 1 hr, the suspension was centrifuged, filtered and collected. This extraction procedure was repeated sequentially with four extractants: copper chloride (20.0 mL 0.5 mol/L $CuCl_2$, pH 2.8, shaking for 2 hr), sodium pyrophosphate (80.0 mL 0.1 mol/L Na_4P_2O, pH 10, shaking for 16 hr), ammonium oxalate (50.0 mL 0.2 mol/L NH_4–Oxalate, pH 3, shaking for 4 hr in the dark) and sodium hydroxide (80.0 mL 0.5 mol/L NaOH, shaking for 16 hr). The Al contents in each fraction were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, ICAP6300, USA). It has been reported that the Al extracted by potassium chloride is considered readily exchangeable Al. Al extracted by copper chloride gives an estimate of organo-Al complexes of low to medium stability (Garcia-Rodeja et al., 2004; Juo and Kamprath, 1979) and Al extracted by sodium pyrophosphate gives an estimate of the strong stability of organically bind form (Bascomb, 1968). Finally, extraction with ammonium oxalate and sodium hydroxide provides an estimate of the non-crystalline Al and crystalline Al.

In order to examine the competition between phosphate and other anions, ion chromatography (PIC-10/10A, USA) was employed to measure the contents of the F^-, Cl^-, NO_3^-, PO_4^{3-}

and SO_4^{2-} at the end of the pot experiment. A 1:25 soil to water ratio was used in this procedure.

1.4. P sorption-desorption experiment

To examine the P sorption capacity of the soils obtained at the end of the experiment in the Control, Alum-1 and Alum-4 treatments, P sorption isotherms were constructed using the method of Pautler and Sims (2000). 2.0 g of soil in duplicate were weighed in 50.0 mL centrifuge tubes. These soil samples were combined with seven 30.0 mL solutions (0, 1, 5, 10, 15, 25, 50 mg P/L) made up by diluting KH_2PO_4 stock solution (500 mg P/L) with 0.01 mol/L $CaCl_2$. Two drops of toluene were added to restrict microbial activity which may affect the transformation between inorganic P and organic P. The suspensions were shaken (25 °C for 24 hr), centrifuged and filtered (Whatman No. 42) and the concentration of P in the solution was measured with colorimetric analysis (Murphy and Riley, 1962). The P adsorbed to the soil was calculated as the difference between the initial P concentration and final P concentration measured at equilibrium.

Afterwards, a P desorption experiment was performed as follows: each tube was filled with 30 mL of 0.01 mol/L $CaCl_2$ solution. The tubes were shaken for 24 hr (25 °C). After shaking, the suspensions were centrifuged at 4000 r/min for 8 min, and then filtered (Whatman No. 42). The final P concentration of the supernatant was measured using the colorimetric method (Murphy and Riley, 1962). The desorbed P was determined by subtracting the measured amount of P at equilibrium and the residual P in tubes.

1.5. Statistical analyses

All statistical data were analysed using Microsoft Excel 2016 and figures were made by Origin 2018. Analysis of variance (ANOVA) was used to determine the statistical significance of the treatment effects based on randomised complete block design. Multiple comparisons of mean values of $CaCl_2$-P, Olsen-P, pH, P contents in soil P fraction were performed using the Fisher's least significant difference (LSD, $P < 0.05$) amongst different treatments. IBM SPSS 19.0 software was used for all statistical tests.

The predictors of the P forms were selected using the *adonis* function (vegan package, R 3.6.2). Soil properties with significant effects ($P < 0.05$) were kept for redundancy analysis (RDA), which was performed using R software (vegan package, R 3.6.2). Finally, ANOVA was used to test the RDA model and to identify parameters which significantly explained the variance in the soil P fraction.

2. Results

2.1. Plant dry biomass and elements uptake

Compared with the control treatment, alum application treatments had no significant impairment on the SDW of maize and tomatoes during the seedling stage. Alum application even slightly increased the SDW of maize. However, the SDW
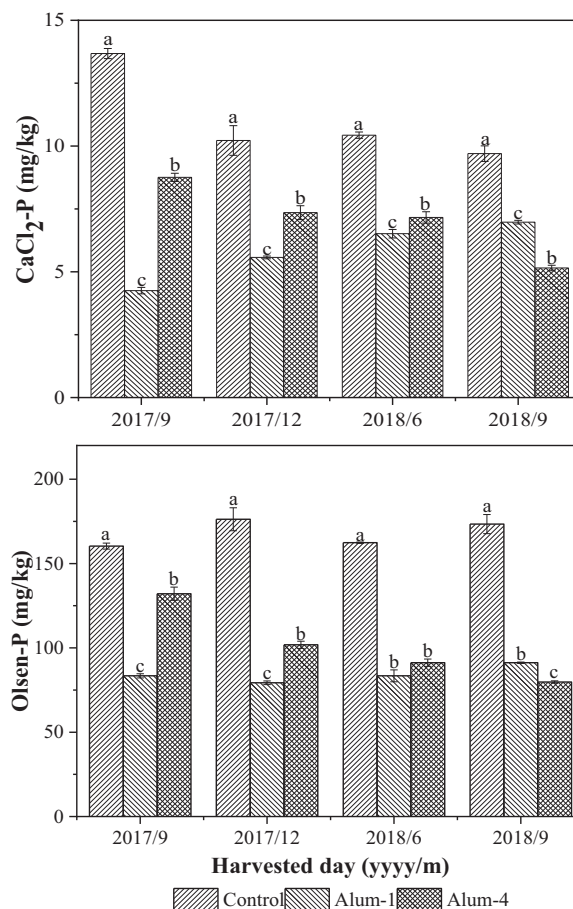

Fig. 1 – Changes of soil $CaCl_2$-P and Olsen-P contents in calcareous soils receiving different splitting methods of alum applications in pot experiment from 2017 to 2018 ($n = 3$). Means followed by different letters denote significant differences amongst soil treatments for each season ($P < 0.05$).

of the celery in the Alum-1 treatment was lower than the control treatment (Table 1).

Generally, alum applications decreased the P and Ca uptake, whilst they increased the Fe and Al uptake. Compared with the control treatment, the plant TP in the Alum-1 treatment decreased by 30, 35.4, 56.9 and 32.9% during the first to the fourth crop planting, respectively. The plant TP in the first, second and third crops in the Alum-4 treatment were greater than the Alum-1 treatment, but was lower in the fourth crop (Table 1).

2.2. Soil test P, P forms and P sorption-desorption

2.2.1. Soil $CaCl_2$-P and Olsen-P
Alum applications significantly decreased the soil $CaCl_2$-P and Olsen-P relative to the control treatment (Fig. 1). It can be seen that the alum split applications had lower soil $CaCl_2$-P and Olsen-P contents in comparison with the single application at the end of the experiment. It was noticeable that the soil

Table 1 – The shoot dry weight and uptake of P, Fe, Al, Ca and Mg in the shoot of four seasonal harvested crops receiving different splitting methods of alum applications in pot experiment from 2017 to 2018 ($n = 3$).

Treatment	Shoot dry weight (g/pot)	P (mg/pot)	Fe (mg/pot)	Al (mg/pot)	Ca (mg/pot)	Mg (mg/pot)
First season (Maize)						
Control	21.9[a]	72.6[a]	7.1[b]	4.2[b]	186.4[a]	96.2[a]
Alum-1	24.0[a]	53.0[a]	7.0[b]	4.0[b]	105.5[b]	82.6[a]
Alum-4	27.2[a]	67.7[a]	15.0[a]	9.0[a]	208.0[a]	111.9[a]
Second season (Celery)						
Control	12.4[a]	33.3[a]	8.6[a]	7.0[a]	206.5[a]	68.6[a]
Alum-1	8.3[b]	21.5[b]	11.1[a]	9.3[a]	94.9[b]	41.1[a]
Alum-4	10.5[ab]	29.9[ab]	15.3[a]	13.9[a]	211.3[ab]	55.2[a]
Third season (Tomato)						
Control	20.5[a]	47.8[a]	12.0[a]	7.4[a]	572.7[a]	211.0[a]
Alum-1	15.2[a]	20.6[b]	9.8[a]	5.5[a]	397.2[a]	235.2[a]
Alum-4	15.3[a]	25.4[b]	8.6[a]	5.4[a]	385.4[a]	228.1[a]
Fourth season (Tomato)						
Control	5.0[a]	16.1[a]	3.1[a]	1.9[a]	155.5[a]	50.2[a]
Alum-1	4.9[a]	10.8[ab]	3.4[a]	2.1[a]	115.9[a]	50.5[a]
Alum-4	4.2[a]	7.3[b]	3.1[a]	1.8[a]	72.7[a]	39.4[a]

Control: no alum application; Alum-1: alum application rate at 20 g/ kg; Alum-4: split alum for four times and the application rate at 5 g/kg each season.
Different letters within each column at each season indicate significant differences amongst the treatments according to the least significant difference test at $P < 0.05$.

$CaCl_2$-P increased progressively after the first season in the Alum-1 treatment.

2.2.2. Hedley P fractionation

Sequential P fractionation recovered 101%−106% of the soil P_t amongst the treatments (Table 2). The dominant fraction of P in this soil was HCl-P, which accounted for 55.9%−66.4% of P_t. As compared with the control treatment, alum applications substantially decreased the proportion of labile P (H_2O-P + $NaHCO_3$-P) while increasing the moderately labile P (NaOH-P). More importantly, the moderately labile P at the third and fourth season in the alum split applications treatment had been significantly higher than that in the single alum application treatment.

2.2.3. Soil P sorption-desorption

Examination of the graphical isotherm data strongly suggested a higher P sorption capacity of the alum applications treatments as evidenced by the rapid elevated P sorption amounts (Fig. 2). In addition, the tendency of the P adsorbed amounts at equilibrium in the alum split applications treatment increased relative to the single alum application treatment.

The P desorbed amounts in the control treatment increased when the P adsorbed amounts increased (Fig. 2). The P release (proportion of desorbed P in adsorbed P) varied from 26.8%−33.7% in the control treatment, with the P adsorbed amounts ranging from 35.1–124.8 mg/kg (Table 3). This proportion increased abruptly up to 59.0% when the P adsorbed amount reached 184.4 mg/kg in the control treatment. On the contrary, P desorbed amounts in the alum application treatments decreased although more P was adsorbed. It was found that P release maintained approximately 10% and 8% in the Alum-1 and Alum-4 treatments respectively.

2.3. Variation of soil Al forms and main anions

2.3.1. Soil Al fractionation

Sequential Al fractionation recovered 93.2% and 96.2% of added Al in the Alum-1 and Alum-4 treatments (Table 4). The dominant Al fraction in the control treatment was poorly-crystalline Al. Alum applications significantly increased all of the Al contents and the organic bind Al (sum of the weakly and strongly organic bind Al) became the main Al fraction as compared with the control treatment. Generally, alum split applications contributed to the formation of weakly organic bind Al and poorly-crystalline Al, whereas single application facilitated the transformation of exchangeable Al, strongly organic bind Al and crystalline Al.

2.3.2. Variation of anions

The contents of soil F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} at the end of experiment are presented in Table 5. Results showed the concentrations of NO_3^- and SO_4^{2-} in the Alum-1 and Alum-4 treatments increased significantly while the PO_4^{3-} notably decreased with respect to the control treatment. The results showed the PO_4^{3-} concentration significantly decreased by 41.0% while the SO_4^{2-} concentration increased by 14.0% in the Alum-4 relative to the Alum-1 treatment.

2.4. Correlation analyses of the P stabilisation with soil properties

The change of the soil pH is illustrated in Fig. 3. Clearly, soil pH decreased once alum was applied and gradually increased in the Alum-1 treatment during the following planting season. The soil pH in the Alum-4 treatment decreased progressively from the first to fourth planting season. For the current study, no significant differences were determined for the effect of alum on organic matter for the control and alum amendment

Table 2 – Hedley soil P sequential fractionation in calcareous soils receiving different splitting methods of alum applications in pot experiment from 2017 to 2018 ($n = 3$).

Treatment	Recovery of P_t (%)	H_2O-P (mg/kg)		NaHCO$_3$- P (mg/kg)		NaOH-P (mg/kg)		HCl-P (mg/kg)	Residual P (mg/kg)	Labile P (mg/kg)	Moderately labile P (mg/kg)	Stable P (mg/kg)
		P_i	P_o	P_i	P_o	P_i	P_o					
First season (Maize)												
Control	105[a]	70.4[a]	15.5[a]	285.6[a]	28.7[a]	18.4[c]	13.8[b]	875.9[a]	187.1[a]	400.2[a]	32.2[c]	1063[a]
Alum-1	104[a]	27.6[c]	6.5[c]	208.8[b]	13.2[b]	51.5[a]	25.1[a]	899.5[a]	195.6[a]	256.1[c]	76.6[a]	1095[a]
Alum-4	106[a]	58.3[b]	12.7[b]	264.7[a]	16.5[b]	29.6[b]	23.5[a]	887.7[a]	186.6[a]	352.2[b]	53.1[b]	1074[a]
Second season (Celery)												
Control	102[a]	69.3[a]	22.1[a]	298.3[a]	27.5[a]	19.0[b]	16.7[a]	847.9[b]	185.2[a]	384.0[a]	35.7[b]	1033[a]
Alum-1	103[a]	29.2[c]	7.2[b]	206.6[b]	15.6[b]	45.7[a]	21.3[a]	932.0[a]	178.1[a]	245.4[c]	67.0[a]	1110[a]
Alum-4	106[a]	40.7[b]	8.8[b]	232.7[b]	14.6[b]	49.0[a]	20.2[b]	951.1[a]	184.2[a]	281.1[b]	69.2[a]	1135[a]
Third season (Tomato)												
Control	101[a]	63.4[a]	21.0[a]	286.4[a]	29.6[a]	20.5[c]	21.3[a]	793.3[a]	183.3[a]	424.9[a]	41.8[c]	977[a]
Alum-1	103[a]	29.1[b]	15.8[b]	199.9[b]	16.4[b]	49.8[b]	20.7[a]	898.0[a]	191.3[a]	252.9[c]	70.5[b]	1089[a]
Alum-4	104[a]	30.1[b]	12.4[b]	209.6[b]	13.7[b]	78.2[a]	25.8[a]	929.0[a]	181.9[a]	265.8[b]	103.0[a]	1111[a]
Fourth season (Tomato)												
Control	106[a]	62.1[a]	17.7[a]	262.5[a]	27.4[a]	19.0[c]	15.7[a]	911.3[a]	180.5[a]	369.7[a]	37.4[c]	1092[a]
Alum-1	106[a]	33.5[b]	15.5[b]	209.6[b]	22.0[b]	51.2[b]	24.8[b]	927.5[a]	170.1[a]	280.6[b]	70.5[b]	1098[a]
Alum-4	102[a]	25.4[c]	11.5[c]	170.0[c]	17.1[c]	101[a]	32.0[c]	933.4[a]	189.9[a]	224.1[c]	133.1[a]	1123[a]

Recovery of P_t: the sum of total P concentrations in all fractions relative to total P concentration measured by perchloric acid digestion.

P_t: total P; P_i: inorganic P; P_o: organic P, the difference between P_t in solution (determined by digestion) and P_i.

Different letters within each column at each season indicate significant differences amongst the treatments according to the least significant difference test at $P < 0.05$.

Labile P = H_2O-P + NaHCO$_3$-P; moderately labile P = NaOH-P; stable P = HCl-P + residual P.

Table 3 – Phosphorus sorption-desorption data, exchangeable Ca and amorphous Fe in the soils obtained at the end of the pot experiment in 2018 after receiving the same rate of alum with one single time (Alum-1) or four times splitting applications (Alum-4).

Treatment	P concentration (mg/L)	P adsorbed (mg/kg)	P desorbed (mg/kg)	P release (%)	Exchangeable Ca (mg/kg)	Amorphous Fe (mg/kg)
Control	0	−14.2	5.9	NS	1779[c]	1100[c]
	1	−2.1	6.8	NS		
	5	35.1	11.8	33.7		
	10	69.3	18.5	26.8		
	15	89.4	25.8	28.8		
	25	124.8	36.3	29.1		
	50	184.4	108.8	59.0		
Alum-1	0	−8.3	3.4	NS	3543[b]	1333[b]
	1	4.6	4.0	NS		
	5	54.2	8.3	15.4		
	10	111.8	12.5	11.2		
	15	164.1	16.0	9.8		
	25	265.8	23.4	8.8		
	50	443.3	45.8	10.3		
Alum-4	0	−6.3	2.4	NS	3710[a]	1430[a]
	1	7.3	3.2	NS		
	5	59.4	5.2	8.8		
	10	120.8	8.9	7.3		
	15	179.3	13.7	7.6		
	25	286.5	20.5	7.2		
	50	486.5	38.4	7.9		

P concentrations: the initial P concentrations used in the P sorption experiment.

P release: proportion of desorbed P in adsorbed P.

NS: data were not shown as P released in the P sorption experiment.

Exchangeable Ca: calcium extracted by the 1 mol/L KCl; Amorphous Fe: ion extracted by the 0.2 mol/L acid ammonium oxalate.

Table 4 – Soil Al sequential fractionation in calcareous soils obtained at the end of the pot experiment in 2018 after receiving the same rate of alum with one single time (Alum-1) or four times splitting applications (Alum-4).

Treatment	Exchangeable Al (mg/kg)	Weakly organic bind Al (mg/kg)	Strongly organic bind Al (mg/kg)	Poorly-crystalline Al (mg/kg)	Crystalline Al (mg/kg)	Added Al (g/kg)	Recovery of Al
Control	0.4[c]	65.0[c]	112.2[b]	376.4[c]	103.1[c]	0	0
Alum-1	3.3[a]	381.8[b]	557.3[a]	609.2[b]	167.5[a]	1.14	93.2%
Alum-4	2.5[b]	413.8[a]	533.1[a]	673.2[a]	130.8[b]	1.14	96.2%

Exchangeable Al: the following extractions were performed in sequence to denote exchangeable Al, weakly organic bind Al, strongly organic bind Al, non-crystalline Al and crystalline Al: 1 mol/L KCl, 0.5 mol/L $CuCl_2$, 0.1 mol/L $Na_4P_2O_7$, 0.2 mol/LNH_4–Oxalate (pH=3) and 0.5 mol/L NaOH. Different letters within each column indicate significant differences amongst the treatments according to the least significant difference test at $P < 0.05$.
The added Al in the soil was calculated as the product of the Al proportion in the alum and the applied rate of 20 g/kg.
Recovery of Al was calculated as the increment contents of the Al (calculated by subtracting the total Al concentration in the control treatment from the Alum-1 or Alum-4 treatment) to added Al.

Table 5 – Soil anion contents in calcareous soils obtained at the end of the pot experiment in 2018 after receiving the same rate of alum with one single time (Alum-1) or four times splitting applications (Alum-4).

Treatment	F^- (cmol/kg)	Cl^- (cmol/kg)	NO_3^- (cmol/kg)	PO_4^{3-} (cmol/kg)	SO_4^{2-} (cmol/kg)
Control	NS	100.6[c]	111.0[b]	17.2[a]	29.9[c]
Alum-1	NS	109.1[ab]	155.3[a]	8.3[b]	707.8[b]
Alum-4	NS	121.0[a]	153.9[a]	4.9[c]	806.9[a]

Anion were determined by the chromatography method with a 25:1 ratio of water to soil.
NS: data was below the limit of detection.
Different letters within each column indicate significant differences amongst the treatments according to the least significant difference test at $P < 0.05$.

treatments. The *adonis* test showed that soil pH, exchangeable Ca, amorphous Fe and Al, and crystalline Al had significant effects on the P composition ($P < 0.05$) in the soil amended with alum. The first two axes of the RDA explain 84.2% of the total variance observed in the P forms in this soil (Fig. 4).

3. Discussion

3.1. Acceptability of alum application on agronomic impacts

The use of alum within a PVFs involved the soil and plant health (Mukherjee et al., 2014). Incorrect management may lead to problems for growers and therefore an optimised system must be developed at field scale. Other studies have shown negative aspects pertaining to alum amendment. For example, Zhao et al. (2018) reported that a decrease in the plant dry biomass in 18 out of 35 cases was found after land application of alum amendment. In the current study, the plant dry biomass of maize showed a descending order of Alum-4>Alum-1>Control. This result was in line with the findings of Mahdy et al. (2009), who reported a significant increase of the maize yield in the alkaline soils with increasing alum amendment application rate. It was explained that the elevated maize yield was mainly attributed to the increase of the soil water holding capacity after alum amendment (Mahdy et al., 2009). However, the dry biomass of celery was substantially decreased in the Alum-1 treatment (Table 1). Lombi et al. (2010) indicated that a detrimental ef-

fect on leafy vegetables growth induced by alum amendment was attributed to the reduction of plant available P. In the present study, the plant available P (denoted by Olsen-P) in the Alum-1 treatment was higher than the agronomic threshold of 60 mg/kg (Fig. 1) and the P concentration in celery tissue exceeded 2500 mg/kg. Thus, the decrease of the dry mass of celery was not correlated with P deficiency.

Aluminium phytotoxicity also is a critical factor with respect to the acceptability of alum application. Previous studies (e.g. Ippolito et al., 1999 and Sloan et al., 1995) demonstrated that Al would not likely pose any toxic problem if the soil pH is >6. In addition, it was reported that the adverse effects of Al on plants are generally associated with an extractable Al concentration of > 60 mg/kg (Sloan et al., 1995). The extractable Al (extracted by KCl) in this calcareous soil amended with alum was below 3 mg/kg (Table 4) and the soil pH was >6.5 after alum application. Thus, it would not result in toxic impacts on the soil-plant system.

3.2. Phosphorus cycling indirectly enhanced P fixation of the alum split applications

The soil used in this study is representative of soils in the PVFs in the north of China (Yan et al., 2013). Indeed, the P inputs in the PVFs rarely follow a P management regime which involves "build up and maintenance". This is due to the fact that farmers mostly focus on economic crops such as vegetables believed that increased fertiliser input leads directly to high yield (Zhou et al., 2019). Kalkhajeh et al. (2017) demonstrated that the dissolved reactive P mobilisation increased rapidly in
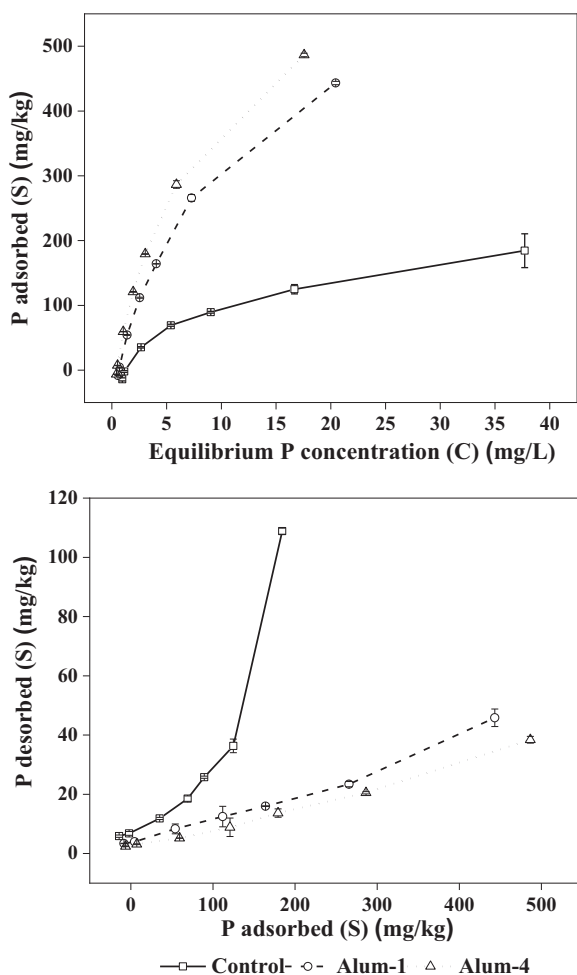
Fig. 2 – The P sorption isotherms and desorption amounts of the soils obtained at the end of the pot experiment in 2018 after receiving the same rate of alum with one single time (Alum-1) or four times splitting applications (Alum-4). The initial P concentrations in the P sorption experiments were supplied at 0, 1, 5, 10, 15, 25, 50 mg/L.
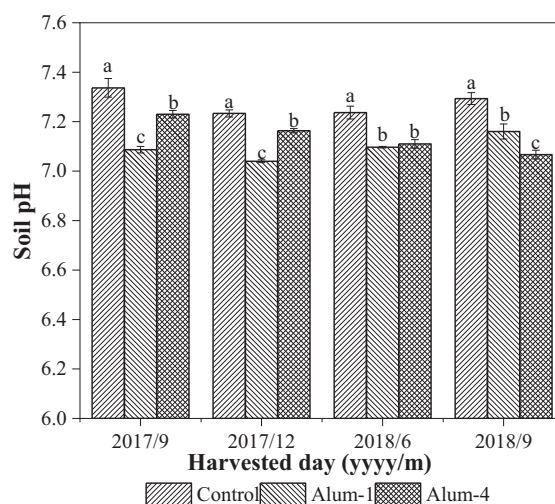

Fig. 3 – Changes of soil pH in calcareous soils receiving different splitting methods of alum applications in pot experiment from 2017 to 2018 ($n = 3$). Means followed by different letters denote significant differences amongst soil treatments for each season ($P < 0.05$).
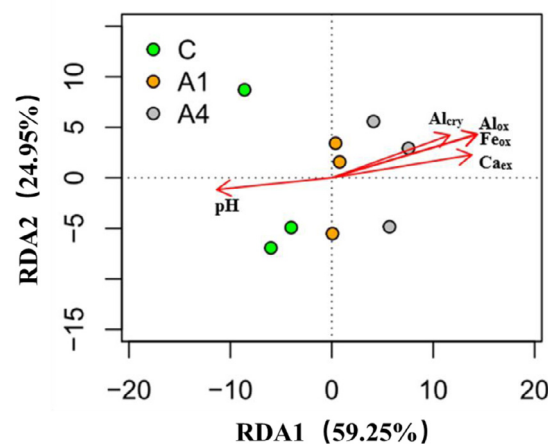

Fig. 4 – Redundancy analysis (RDA) showing the relationships between the soil properties and P fractionations for the calcareous soils obtained at the end of the pot experiment in 2018 after receiving the same rate of alum with one single time (Alum-1) or four times splitting applications (Alum-4). C, Control treatment: without alum application; A1, Alum-1 treatment: receiving the alum in one single application; A4, Alum-4 treatment: receiving the same amount of alum in four times. Al_{cry}, NaOH extractable Al; Al_{ox}/Fe_{ox}, Oxalate extractable Al/Fe; Ca_{ex}, KCl extractable Ca.

the PVFs when the soil Olsen P value was over 41 mg/kg. Given the Olsen-P value over 150 mg/kg in this study, it was obvious that the soil was at high risk to lose substantial amounts of P to the aqueous environment.

In the present study, the soil $CaCl_2$-P in the control treatment reduced gradually from the first to the fourth planting season due to the plant P uptake (Fig. 1). The alum application rate at 20 g/kg in one single application substantially decreased the soil $CaCl_2$-P and Olsen-P by 68.9% and 47.9% in the first season. With P fractionation, alum applications significantly decreased the amounts of both P_i and P_o of the labile P (sum of H_2O-P and $NaHCO_3$- P, Table 2), while increasing the moderately labile P (NaOH-P). This indicated the potentially positive impact of alum application in calcareous soil regarding P mobilisation from arable lands to water (Huang et al., 2018; Yan et al., 2013), which was in accordance with many previous studies (Anderson et al., 2018; Brennan et al., 2011; Fan et al., 2019; O' Flynn et al., 2018). However, the values of soil $CaCl_2$-P and Olsen-P in the Alum-1 treatment increased

gradually after the first season. Soil solution P is identified as the most reactive soil P (Kruse et al., 2015), which is therefore preferential to be stabilised in the soil amended with alum. However, the dynamic P cycling from adsorbed or precipitated P would occur to compensate for the reduction of the solution P after alum amendment. Helfenstein et al. (2018) confirmed the time scale for the P transformation between adsorbed P

and exchangeable P was within 3 months using the sequential P extraction method coupled with P K-edge X-ray absorption spectroscopy and isotopic methods (^{33}P and ^{18}O in phosphate). Therefore, it can be expected that a single alum application would result in P fixation at the initial stage, but the continuous increase in soil solution P sourced from adsorbed or precipitated P, would occur after this period. This assertion was also backed up by the progressively enhanced H_2O-P in the Hedley P fractionation in the Alum-1 treatment after the first season (Table 2). However, this newly transformed soil solution P was prone to stabilise if the alum was split applied. Hence, it can be expected that the soil $CaCl_2$-P and Olsen-P values in the Alum-4 treatment were lower than the Alum-1 treatment after four planting seasons (Fig. 1). Additionally, the alum application rate at 20 g/kg in one single application, which was nearly impossible in reality, still did not reduce the soil Olsen-P below the proposed 90 mg/kg for vegetable production (Liang et al., 2013) after four seasons (Fig. 1). However, the approach of splitting alum applications gradually decreased the soil Olsen-P values and achieved the target of Olsen-P values between 60 and 90 mg/kg after the fourth season.

3.3. Alum split applications directly induced higher P stabilisation efficacy

At the end of the experiment, split alum applications decreased more H_2O-P and $NaHCO_3$-P while increasing more P_i and P_o contents of NaOH-P relative to the single alum application treatment (Table 2). Considering the same amounts of alum addition while different P fixation efficacy in the Alum-1 and Alum-4 treatments, it was speculated here that the Al transformation and forms involved in the alum application approaches might be closely linked with the P fixation. Thus, a soil Al fractionation using the soil samples obtained at the end of the experiment was conducted to further explain the relationship between P fixation and Al forms. The results showed that the dominant Al form in the control treatment is the poorly-crystalline Al, which was responsible for 57.3% of the total Al (Table 4). After alum application, the sum of weakly and strongly organic bind Al became the dominant Al fraction. This was consistent with the findings of Alvarez et al. (2009), which indicated that the function of the organic matter to bind Al was presumably to offset the acidic effect caused by alum application.

More importantly, the current study found that compared with single alum application, alum split applications alleviated the transformation of Al^{3+} toward crystalline Al and strongly organic bind Al, but favoured the formation of poorly-crystalline Al. It has been validated that the poorly-crystalline Al has higher P adsorption capacity than other Al forms because of its greater surface area (Maher et al., 2015; Ronkanen et al., 2016). Previous studies reported poorly crystalline Al was prone to form at pH 6–8 (Cooke et al., 1993; Fan et al., 2019). The soil pH varied in this range after alum application in the present study (Fig. 3), which was in favour of the formation of the poor-crystalline Al hydroxides. Anderson et al. (2018) demonstrated that the gradual decline of the soil pH favoured the transformation of poorly-crystalline Al, which was similar to the change of soil pH of

the alum split applications in this study (Fig. 3). In addition, the present study found the soil exchangeable Ca (extracted by KCl) and poorly-crystalline Fe (extracted by oxalate and ammonia oxalate) in the Alum-4 treatment were greater than the Alum-1 treatment (Table 3), which further increased the P fixation. This finding is in accordance with a recent P adsorption experiment on water treatment residual conducted by Zohar et al. (2018), in which it was reported that P had high affinity for Al surfaces, but also associated with Ca. The RDA analysis of the relationship between soil properties and the P fractions also indicated that the changes of soil pH and the according variation of the poorly-crystalline Al/Fe and exchangeable Ca dominated the changes in the soil P forms (Fig. 4), in which the contribution of the poorly-crystalline Al, soil pH and exchangeable Ca to the changes of the soil P fractions were 59.3%, 24.3% and 10.0% respectively. Although many studies reported the competition effect between phosphate and SO_4^{2-} or F^- etc. (Essington, 2015; Liu et al., 2012), the results of this study confirmed the anions had a marginal effect with respect to the Al^{3+} binding effect of organic matter (Table 5).

Considering the P sorption after equivalent alum application, it can be seen that in contrast to the control treatment, the P adsorbed amounts in soils amended with alum increased noticeably. This suggested the relatively high P sorption capacity of the alum-transformed compounds in calcareous soils (Fig. 2). Additionally, the increase of the amorphous Al/Fe and exchangeable Ca in the alum split applications treatment all induced the increase in P sorption amounts. More importantly, P desorbed amount and P release (proportion of desorbed P in adsorbed P) decreased in the alum split applications treatment. Fan et al. (2020) reported the significant increase Ca bind P and inner-sphere P sorption on poorly-crystalline Al were the dominant reasons of the elevated P sorption amounts and the decline of the P release. Therefore, it can be expected that when equivalent alum is applied, alum split applications could stabilise more P and therefore mitigate more P losses in terms of the quite heavy P fertiliser inputs in the PVFs systems. However, it should be noticed that although the soil labile P in the fourth season in the Alum-4 treatment was lower relative to Alum-1 treatment, alum split applications might be posing more total P losses during the whole planting season. If the intervals of alum split applications could be shortened or the incidental losses of P due to rainfall or heavy irrigation could be mitigated, the split applications would be beneficial to the reduction of total P losses. Therefore, from the point of optima for both of plant available P and P losses, split alum applications is better for the sustainable P management.

4. Conclusion

To protect against leached P losses in continuous cropping systems (e.g. maize-celery-tomato-tomato) alum can be applied to calcareous soils as a single rate before the first crop is sown or as smaller split rates before each crop is sown. The present study examined how these two contrasting approaches affected the plant growth and labile P contents in a P-enriched calcareous soil. Compared with single alum appli-

cation, alum split applications provided greater potential in terms of plant growth and protection from P losses in the soluble phase. The mechanisms involved for this were attributed to the following reasons. Firstly, plant growth was less impacted in the alum splits application due to the temperate variation of the soil pH. Secondly, the labile P was quickly fixed after each alum application. Thirdly, the formation of poorly-crystalline Fe/Al and exchangeable Ca was facilitated in the alum split applications treatment due to the gradually decreased soil pH, which further favoured P adsorption. In addition, the hypothesis of competition of sorption sites between phosphate and organic matter was identified, while competition with other anions was excluded. In summary, split alum applications could be used as a strategy to decrease the P loss risk to surface and ground water in high legacy P calcareous soil of China. Future research should examine a split management regime at field scale and examine temporal P load losses over longer periods.

Acknowledgments

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