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The effects of flue gas desulfurization gypsum (FGD gypsum) on P fractions in a coastal plain soil

Kun He[1,2] · **Xiaoping Li**[1] · **Longli Dong**[1]

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Abstract
Purpose In order to explore the possibility of using FGD gypsum in controlling P loss due to agricultural runoff, the effects of FGD gypsum on the P fraction were studied in the Yangtze River Delta coastal plains. The field experiments were conducted to identify (1) different application rates of FGD Gypsum to the P losses and (2) formation of Ca-P complexes in the soil in response to FGD gypsum applications.
Materials and methods The field experiments consisted four rates of FGD gypsum (0, 15, 30, and 45 t/ha) in triplicate. FGD gypsum was obtained from a coal burning power plant. The "S" multi-point sampling method was used to collect samples of the uppermost soil interval in July and December of 2015. The total phosphorus (TP) in soil and plants was determined using the sulfuric acid-perchloric acid digestion method. The available phosphorus (AP) was determined using the sodium bicarbonate extraction-molybdenum-antimony anti-spectrophotometric method. The soluble reactive phosphorus (SRP) in the soil leachate was determined using the molybdenum-antimony anti-spectrophotometric method. The Visual MINTEQ 3.0 model was used to simulate the forms and distribution of the P fractions in the soil solution.
Results and discussion The results indicated that the soil P fractions changed with application rats of FGD gypsum while the total soil P showed no significant change. The concentrations of SRP in the leachate also decreased in average of 27.5, 41.9, and 54.5%, respectively, with increasing FGD gypsum rates. The amounts of Ca_2-P, Ca_8-P, and Ca_{10}-P of the calcium phosphates in the soil were significantly increased over the ranges of 44.3–68.6, 34.1–70.1, and 7.4–17.2%, while soil AP concentrations decreased. Visual MINTEQ modeling confirmed the speciation and fractionation of Ca-P compounds under the coastal plain soil conditions. The field experiments also showed that FGD gypsum applications did not affect the absorption of P by the vegetation.
Conclusions Experiments indicated that FGD gypsum has been shown to react with P in soil, resulting in decrease of AP and SRP and formation of insoluble Ca-P compounds and thereby decreasing the potential of P losses with surface runoff. FGD gypsum appears to be a more viable soil amendment than commercially mined gypsum to potentially achieve reductions in P losses and eutrophication of receiving waters.

Keywords Coastal plain soil · Flue gas desulfurization gypsum (FGD gypsum) · Phosphorus fractions · P loss

1 Introduction

Gypsum (calcium sulfate dihydrate) is derived from a number of sources and is commonly found worldwide in sedimentary rock formations, where it is mined or quarried. Flue gas desulfurization gypsum (FGD gypsum), which is primarily composed of $CaSO_4 \cdot 2H_2O$, is an industrial byproduct derived from the desulfurization of flue gas produced by the combustion of sulfur-containing fuels (mainly coal). In 2012, the USA produced 23 million tons of FGD gypsum, and that value increases annually, with approximately 47% effectively utilized (USGS 2013). Moreover, China's annual FGD gypsum

Responsible editor: Chengrong Chen

✉ Xiaoping Li
652755713@qq.com

[1] State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, People's Republic of China

[2] The Ecological Technology and Engineering School, Shanghai Institute of Technology, Shanghai 201418, People's Republic of China

emissions have reached nearly 100 million tons, and the effective utilization has been close to 70% (Chen et al. 2017).

Because of improvements to the quality of FGD gypsum products, the ecological safety of FGD gypsum meets the agricultural requirements without increasing the content of heavy metals in the soil; therefore, FGD gypsum has been widely applied for the improvement of agricultural soils and for the investigation and practice of mine reclamation (Chen and Dick 2011). Studies have shown that the abundant calcium ions in FGD gypsum exchange with sodium ions on the surfaces of alkaline soil colloids, thereby decreasing the soil pH (Mao et al. 2016). Thus, FGD gypsum is clearly capable of improving alkaline soils without resulting in environmental contamination (Chun et al. 2001; Chen et al. 2014; Li et al. 2014).

FGD gypsum from some coal-fired power plants may contain higher metals than some mined gypsum, but their concentrations are lower than background levels stipulated for soils (EPRI 2011; Smith et al. 2013). The environmental impacts of FGD gypsum are mostly positive, even when applied at rates at 280 Mg/ha for reclamation of abandoned coal-mined land (Chen et al. 2015), 60 Mg/ha for reclaimed tidal lands (Li et al. 2014), or 20 Mg/ha for agricultural lands (EPRI 2012). Many studies indicate that metals in FGD gypsum and their potential release to plants and water through land application are not considered to pose any serious environmental concerns (Watts and Dick 2014). Environmental releases of constituents of potential concern of FGD gypsum products are at or below relevant regulatory and health-based benchmarks for human and ecological receptors (USEPA 2014).

After the application of FGD gypsum to soil, the abundant calcium ions react with excess phosphate ions, thereby converting most of the soil phosphorus to fixed phosphorus (He et al. 2008; Li et al. 2005), reducing the conversion of phosphorus to soluble fractions, and decreasing the leaching out and runoff of soluble phosphorus (Xu et al. 2013). In recent years, agricultural and environmental experts have focused on the possibility of decreasing losses of agricultural nonpoint-source phosphorus using desulfurized gypsum while applying FGD gypsum to improve soil (Stout et al. 2000; Favaretto et al. 2006; Buckley and Wolkowski 2014). To control the increasingly serious eutrophication in Lake Erie, the USA began investigating methods to control agricultural nonpoint-source P and demonstrated best management practices (BMPs) by applying FGD gypsum at the beginning of this century (Dick et al. 2013). The application of sufficient FGD gypsum can continually provide soluble Ca ions to high-phosphorus soil and effectively reduce the amount of soluble reactive phosphorus (SRP) (Brauer et al. 2005). The SRP in soil decreases markedly with increasing application of FGD gypsum (Torbert and Watts 2014). Increasing the amount of FGD gypsum in agricultural composting can reduce the total phosphorus and inorganic phosphorus in the soluble fraction (Mishra et al. 2012). In addition, FGD gypsum evidently decreases the loss of phosphorus by runoff. Experiments in the Ningxia farm region of western China indicated that with increased applications of desulfurization gypsum, the available phosphorus decreased by an average of 3.9–17.2% (Zhang et al. 2013). A column leaching experiment using coastal saline soil indicated that the loss of total phosphorus could be reduced by applying a small amount of FGD gypsum (Cheng et al. 2014). Murphy and Stevens (2010) reported that the addition of FGD gypsum to soil reduced the migration of soluble phosphates and organic phosphorus to water bodies by 14–56 and 10–53%, respectively. Torbert and Watts (2014) reported that when 8.9 Mg/ha of FGD gypsum was applied, the runoff load of total phosphorus was reduced by 51%.

Currently, most studies have focused on phosphorus losses from agricultural runoff and decreases in SRP after the application of FGD gypsum to soil. Few studies have investigated the effects of FGD gypsum on variations in phosphorus fractions, particularly variations in inorganic phosphorus. Through field experiments involving the application of various levels of FGD gypsum combined with Visual MINTEQ software modeling, the effect of FGD gypsum on the effectiveness of phosphorus nutrition and variations in inorganic phosphorus fractions in the Yangtze River Delta coastal plains was systematically investigated. The objectives were to identify the correlation between FGD gypsum application and phosphorus loss in this coastal plain soil and study the fixation effect on and variation characteristics of inorganic phosphorus in the soil in response to FGD gypsum. The results provide an economical and reliable technical approach and a theoretical method for controlling agricultural nonpoint-source pollution and for improving polluted water in the coastal plains of eastern China.

2 Materials and methods

2.1 Study site and materials

The field experiments were performed at the experimental field site (30°50′45.71″N, 121°30′49.06″E) of the Shanghai Institute of Technology, located in the inland Shanghai Fengxian District on the northern shore of Hangzhou Bay. The average rainfall and annual average temperature in the Fengxian District are 1050 mm and 15.7 °C, respectively. The experimental site consisted of land reclaimed from marshes a century ago that was a rice field before the study. The soil in the experimental site consists of yellow sandy soil that is dark yellow when wet. The FGD gypsum, which was obtained from the Shanghai Waigaoqiao Power Generation Co. Ltd., was a creamy yellow powdered solid.

2.2 Field experimental design and plant

During the field experiment, portions of the experimental field site where FGD gypsum was not applied (0 t/ha) were used as the control plots. Three rates of FGD gypsum application, i.e., 15, 30, and 45 t/ha, were replicated 3 times. Thus, there were 12 experimental plots, each of which measured 3.0-m long by 2.0-m wide and had an area of 6.0 m^2 (Fig. 1). The distance between adjacent plots was 0.5 m. The width of the ridge between plots was 30 cm, and it was covered with plastic film that was buried 40 cm deep to prevent the cross flow of water and fertilizer. On one side of the experimental plots, drainage grooves were installed to collect the soil leachate. The bottom of each plot contained two 3.0-m-long perforated PVC pipes connected to the drainage grooves. The PVC drainage pipes were buried 0.3 m deep, and the soil-covered parts had 5 holes (diameter of 5 cm) covered with filter screen, spaced at equal distances to provide drainage. The PVC pipes were placed at a slight tilt to ensure the smooth outflow of leachate. Wide-mouth containers were used to collect the leachate on one side of the drainage grooves after precipitation.

Land preparation was completed in December 2014. The same organic fertilizer was used as the base fertilizer in each treatment. Then, the FGD gypsum was homogeneously applied once to the soil surface, and then, the soil was turned to a depth of 0.3 m to ensure sufficient homogeneous mixing of the FGD gypsum and soil. Manual ditching was used to plant *Echinacea purpurea* (Linn.) Moench in February 2015. The management measures, such as irrigation and fertilization during the growth period, were the same in each experimental plot.

2.3 Monitoring method

The "S" multi-point sampling method was used to collect samples of the uppermost soil interval (0–30 cm) in July and December 2015, and this procedure was repeated 3 times in each plot. After drying and grinding the samples, they were sifted through 1.0-mm soil sieves and then subjected to an analysis of the total P and available P (TP and AP). The soil leachate was collected 4 times each in the precipitation periods of June, July, August, and September 2015, and the supernatant was collected after filtration through a 4.5-μm filter for analysis of the concentration of SRP in the leachate.

The soil TP was determined using the sulfuric acid-perchloric acid digestion method (Bao 2000). The AP was determined using the sodium bicarbonate extraction-molybdenum-antimony anti-spectrophotometric method (Olsen et al. 1954). The SRP in the soil leachate was determined using the molybdenum-antimony anti-spectrophotometric method (Pote et al. 1996). The Hg and As contents in the soil and FGD gypsum were determined using an atomic fluorescence spectrophotometer; the Cr, Pb, Ag, Se, Ni, Cu, and Cd contents in the soil and FGD gypsum were determined using an inductively coupled plasma spectrometer (Mao et al. 2016).

2.4 Sequential extraction of soil inorganic phosphorus

The inorganic phosphorus concentration was determined based on the fractionation scheme of inorganic phosphorus in calcareous soils developed by Gu and Jiang (1990) (Table 1). This method has been widely applied in investigations of the effects of soil phosphorus fractions on the response and effectiveness of fertilization in southern China (Gu and Jiang 1990; Shen et al. 2004) and western Australia (Samadi and Gilkes 1998).

2.5 Assessment of bioavailable phosphorus

The diagonal sampling method was used to collect five plants in the seedling and flowering stages from each plot in June 2016 and October 2016, respectively. After the plants were rinsed, they were grinded and sifted through 1-mm sieves. The sulfuric acid-perchloric acid digestion method was used to determine the TP in the plants (Bao 2000).

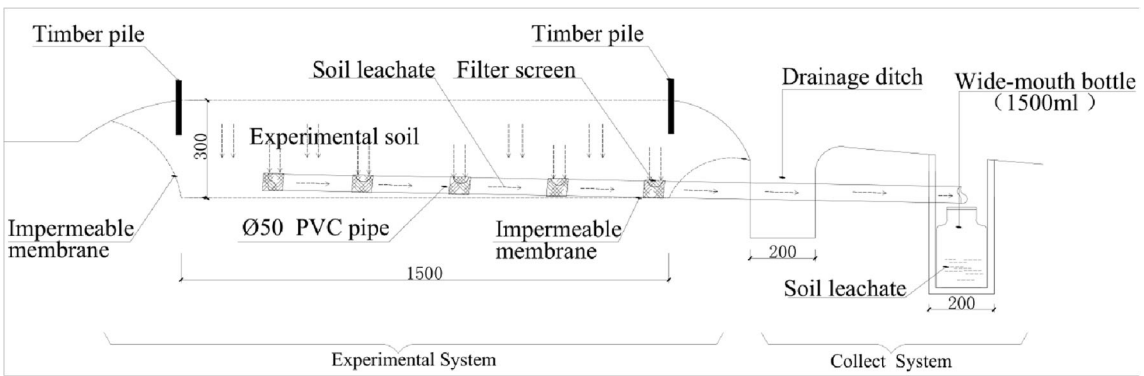


Fig. 1 Schematic illustration of the experimental setup (dimensions are in mm). Note: the arrows represent the flowing direction of the soil leachate. After the rainfall infiltrating the soil, the leachate deep into the PVC pipe through the tube hole, and ultimately pool into wide-mouth bottle

Table 1 Extraction steps for the analysis of inorganic P fractions (Gu and Jiang 1990)

Step	Extraction procedure	Extracted P form (and notation)
1	One gram of soil added to a 50 ml of 0.25 M $NaHCO_3$ (pH 7.5) solution and shaken for 1 h.	Surface complex of P on calcite or discrete dicalcium phosphate (Ca_2-P)
2	Residue washed twice with 95% alcohol, added to 50 ml of 0.5 M NH_4COO (pH 4.2), left soaking for 4 h, and shaken for 1 h.	Octacalcium phosphate (Ca_8-P)
3	Residue washed twice with saturated NaCl, added to 50 ml of 0.5 M NH_4F, and shaken orbitally for 1 h.	Amorphous aluminum phosphate (Al-P)
4	Residue washed twice with saturated NaCl, added to a 1:1 ratio 0.1 M NaOH and 0.1 M Na_2CO_3 solution (pH 8.2) and shaken again for 2 h.	P adsorbed on surface of iron oxides (Fe-P)
5	Residue washed twice with saturated NaCl, added to 40 ml of 0.3 N Na-citrate plus 1 g of Na-dithionate and heated at 80 °C for 15 min.	P incorporated, trapped in iron oxide coatings, or amorphous iron oxide P(O-P)
6	Residue added to 50 ml of 0.5 M H_2SO_4 and shaken for 1 h.	Hydroxylapatite (Ca_{10}-P)

Table 2 Chemical properties of tested the flue gas desulfurization gypsum

Material	pH	Moisture (%)	$CaSO_3$ (%)	$CaSO_4$ (%)	$Ca(OH)_2$ (%)	Others (%)	CA (%)	S (%)	P (‰)
FGDG	7.2	5.0	0	90.0	6.0	4.0	24.3	18.5	< 0.001

FGDG flue gas desulfurization gypsum

2.6 Statistical analysis

Excel 2010 and SPSS17.0 software were used for the statistical analysis of the experimental results. Duncan's test was used to verify the statistical significance of each treatment. The Visual MINTEQ3.0 model developed by the US EPA was used to simulate the forms and distribution of P fractions in the soil solution at equilibrium at various pH values and Ca ion concentrations.

3 Results and discussion

3.1 Basic characteristics of the soils and FGD gypsum

Tables 2 and 3 present the main physical and chemical indexes of the FGD gypsum and the experimental soils. The main composition of the FGD gypsum was $CaSO_4 \cdot 2H_2O$, which contains two essential beneficial mineral nutrients for plants, S and Ca. The P concentration was less than 0.001‰. The soil in the experimental plots consisted of coastal saline soil with a density of 0.92–1.22 g/cm^3, a water content of 31.3–41.4%, and medium alkalinity. Because a large amount of P fertilizer was used in the prior rice cultivation, high soil P fractions were measured (soil TP of 1050 mg/kg, AP of 19.2 mg/kg). Qu et al. (2016) reported that the change point of soil AP, which is related to the field water TP concentration above soil surface, was 19.0 mg/kg. The amount of P lost with runoff water, leaching water, or sediment exceeded the critical concentration of water body eutrophication in the neighborhood (Qian et al. 2010). Because of high precipitation, a large amount of the P might be lost to surrounding water bodies. Except for Hg, the concentrations of heavy metals in the FGD gypsum were all less than those in the soil (Table 4). In addition, the index concentrations of various heavy metals in the soil reached and satisfied the grade II criteria (pH > 7.5) of GB15618-1995 (Administration SEP 1995).

The physical and chemical properties of soil affect the absorption and fraction distribution of P (Mehmood et al. 2015).

Table 3 Chemical properties of the tested soil

Material	pH	Total saline (mg/kg)	ESP (%)	SOM (%)	EC/ (mg/kg)	TN (mg/kg)	TK (mg/kg)	TP (mg/kg)	AP (mg/kg)
Soil	8.64	$0.23*10^3$	15.5–18.0	2.52	0.23×10^3	600	1.27×10^4	1050	19.2

ESP exchangeable sodium percentage, *SOM* soluble organic matter

Table 4 Concentrations of heavy metals in the soil and flue gas desulfurization gypsum (mg/kg)

Material	As	Cr	Pb	Hg	Ag	Se	Ni	Cu	Cd
Soil	10.5	75.2	24.3	0.09	0.42	< 5.0	50.4	17.2	0.20
FGDG	5.1	0.47	14.7	0.20	< 0.47	< 5.0	15.0	11.5	n.d.

n.d. the value was not determined

3.2 Effects on TP, AP, and SRP in the runoff and leachate

Table 5 shows that the application of FGD gypsum did not change the TP in the soil after 0.5 and 1 year. Statistically significant differences were not observed in the TP between the control and treated plots receiving different amounts of FGD gypsum ($p > 0.05$). One year after the application of the FGD gypsum, the TP was less in all the control and treated plots than that after 0.5 years, although the difference was not significant ($p > 0.05$).

Table 5 Changes in total P and available P in soil (mg/kg) at various application rates of FGD gypsum

Treatment	FGD gypsum (0 t/ha)	FGD gypsum (15 t/ha)	FGD gypsum (30 t/ha)	FGD gypsum (45 t/ha)
Time (years)		TP		
0.5 year	1083 ± 14a	1051 ± 12a	1097 ± 41a	1099 ± 41a
1 year	1056 ± 27a	1029 ± 23a	1076 ± 20a	1080 ± 34a
Time (years)		AP		
0.5 year	19.8 ± 0.8a	18.6 ± 0.5a	17.4 ± 0.5b	15.9 ± 0.3c
1 year	19.2 ± 0.5a	18.0 ± 0.7b	17.4 ± 0.6bc	15.6 ± 0.3c

Results with the same letter in the same row within the same sampling time are not significantly different at $p < 0.05$

TP total soil phosphorus, *AP* available phosphorus

The effectiveness of P is controlled by the free iron, reactive calcium carbonate, pH, and many other factors (Rayan et al. 1985). The precipitation and dissolution of insoluble P in alkaline soil are one of the main mechanisms controlling the concentration of SRP (Zhang et al. 2014). In addition, in alkaline soil, calcium ions in FGD gypsum exchange with sodium ions on the surfaces of alkaline soil colloids, thereby decreasing the soil pH and alkalinity. However, calcium ions remain abundant in the soil in an exchangeable form and react with the enriched phosphates in the soil (Chen et al. 2014).

During growth, plants need to absorb a large amount of AP from soil, and this concentration reflects the supply capacity of P in the soil and the release rate of P after the application of FGD gypsum to soil (Li et al. 2005). Table 5 shows that after application of the FGD gypsum, the concentration of AP decreased markedly with increasing application rates of the FGD gypsum. Six months after the application, the amount of AP in

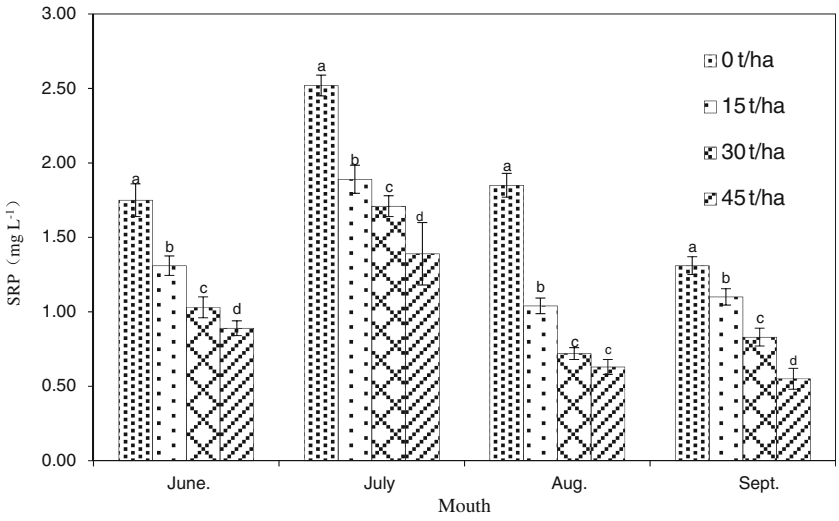


Fig. 2 Leachate SRP with different application rates of FGD gypsum. *SRP* soluble reactive phosphorus

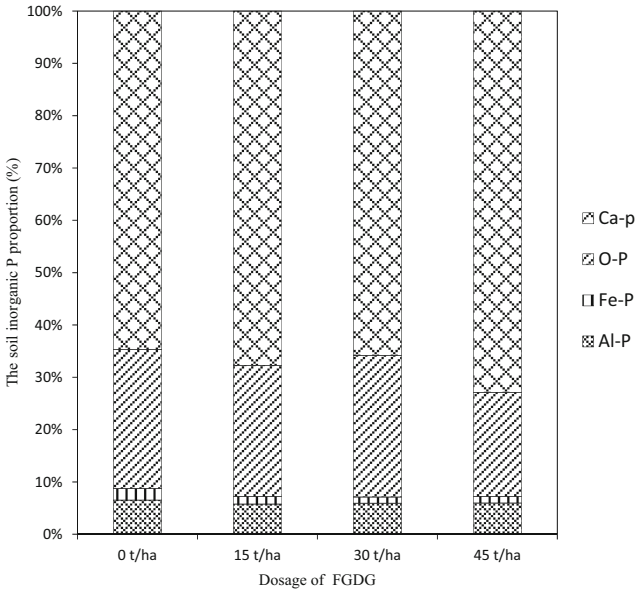


Fig. 3 Variations in the fractions of soil inorganic P with different application rates of FGD gypsum

the soil did not differ significantly between the control and the treated plots receiving 15 t/ha; however, the difference was significant between the treated plots receiving 30 and 45 t/ha and the control ($p < 0.05$). Compared with the control, the average concentration of AP in the soil decreased by 12.1–19.7%. One year after the application, the concentration of AP in the soil in the treated plots receiving 15, 30, and 45 t/ha differed significantly from that in the control, showing decreases of 6.3, 9.4, and 18.8%, respectively. In the plots where the application rate of FGD gypsum was 45 t/ha, the AP in the soil decreased to the minimum value of 15.6 mg/kg after 1 year. These results indicate that the application of FGD gypsum inhibited the effectiveness of P in the soil, which is consistent with the findings reported by Li et al. (2005) and Misra et al. (2007).

Figure 2 shows that after the application of FGD gypsum, the SRP concentrations in the soil leachate in different months significantly decreased with increasing application rate of FGD gypsum. Specifically, the SRP in the soil leachate collected from the treated plots in June, July, August, and September was 25.1–49.1, 25.0–44.8%, 43.7–65.9, and 16.0–58.1% lower, respectively, than that in the control plots. Compared with the control, the SRP in the leachate from the different treated plots decreased by an average of 27.5, 41.9, and 54.5%. These results indicate that after a certain time following the application of FGD gypsum, the effect on P fixation started to emerge, and the effect on the SRP in the soil leachate was much greater than that on the AP, indicating the small effect of the application of FGD gypsum on the AP and the larger effect on the easily lost P (water-soluble P).

The SRP in the soil flows underground because of leaching from precipitation and irrigation, and this leached SRP can pollute groundwater and then enter water bodies, thus exacerbating eutrophication (Murphy and Stevens 2010). In the present study, after the application of FGD gypsum, the AP and SRP in the leachate exhibited a decreasing trend. Therefore, the risk of excess P fractions migrating to water bodies through surface runoff and eluviation was markedly reduced. In addition, the application of FGD gypsum could also increase the permeability of soil, which could further decrease agricultural runoff and the risk of soil P migration to water bodies via runoff (Murphy and Stevens 2010).

3.3 Effects on P fractions in soil

Figure 3 shows that the concentration of calcium phosphate in inorganic P (Ca-P) was the highest and accounted for more than 60% of the TP. The second highest fraction was occluded P (O-P), and the concentrations of amorphous aluminum phosphate (Al-P) and iron-bound phosphate (Fe-P) were relatively low. The total concentration of Al-P and Fe-P in the inorganic P decreased further after the application of FGD gypsum. The concentration of Ca-P in the treated plots exceeded that in the control. The ratio of Ca-P to total inorganic P concentration in the 45 t/ha treatment was the highest and was 10% greater than that in the control.

Table 6 Variations in soil inorganic P fractions with different application rates of FGD gypsum

Treatment	Al-P 0.5 mol/L NH_4F	Fe-P 0.1 mol/L NaOH-Na2CO3	O-P 0.3 mol/L $Na_2C_6H_5O_7{\cdot}2H_2O$-$Na_2S_2O_4$	Ca-P Table 4	Total Pi
FGDG (0 t/ha)	46 ± 5a	15 ± 2a	185 ± 4a	473 ± 16a	720 ± 37a
FGDG (15 t/ha)	47 ± 1a	12 ± 1b	204 ± 24b	549 ± 16b	814 ± 13b
FGDG (30 t/ha)	53 ± 4b	10 ± 3b	242 ± 27c	589 ± 27b	895 ± 57c
FGDG (45 t/ha)	52 ± 3b	11 ± 1b	208 ± 19b	618 ± 25c	888 ± 43c

Note: in a given column, the same letter indicates no significant differences ($p \geq 0.05$); same as below

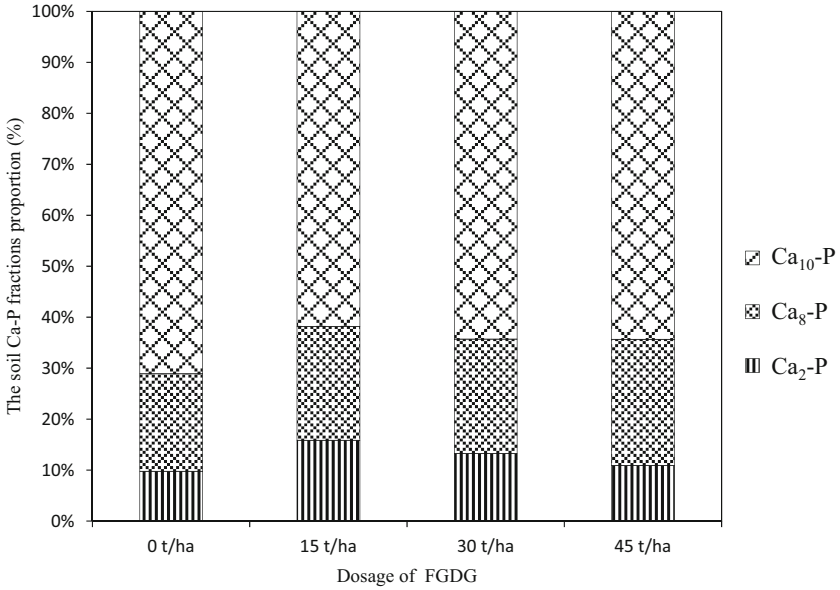


Fig. 4 Variations in the soil Ca-P fractions with different application rates of FGD gypsum

Table 6 shows that the application of FGD gypsum significantly affected the composition of soil inorganic phosphorus and increased the total inorganic concentration in the soil. One year after applying the FGD gypsum, the total inorganic P in the soil was significantly higher in all treated plots than in the control. Among the plots, the total inorganic P has the maximum value of 895 mg/kg in the plot receiving 30 t/ha, which represented an increase of 24.3% compared with the control. At the treatment rate of 45 t/ha, the total inorganic P was slightly lower but was still significantly higher than that in the control.

After applying FGD gypsum, the concentrations of Al-P and Ca-P increased in all the treated plots as the concentration of FGD gypsum increased, and the values were 2.1–15.2 and 16.1–30.6% greater, respectively, than those in the control. In contrast, the Fe-P concentration in the soil decreased significantly by 20.0–26.7%. However, variations between the treatments were not significant. The O-P concentration first increased and then decreased with increasing application rate of FGD gypsum and reached a maximum with the treatment of 30 t/ha, which showed an increase of 30.8% compared with the control. The Ca-P concentrations showed the most pronounced increase by 145 mg/kg in the plot treated with 45 t/ha versus the control, and this increase accounts for at least 80% of the total inorganic P. Therefore, with the increased application of FGD gypsum, calcium phosphate was primarily responsible for the increase in inorganic P in the soil.

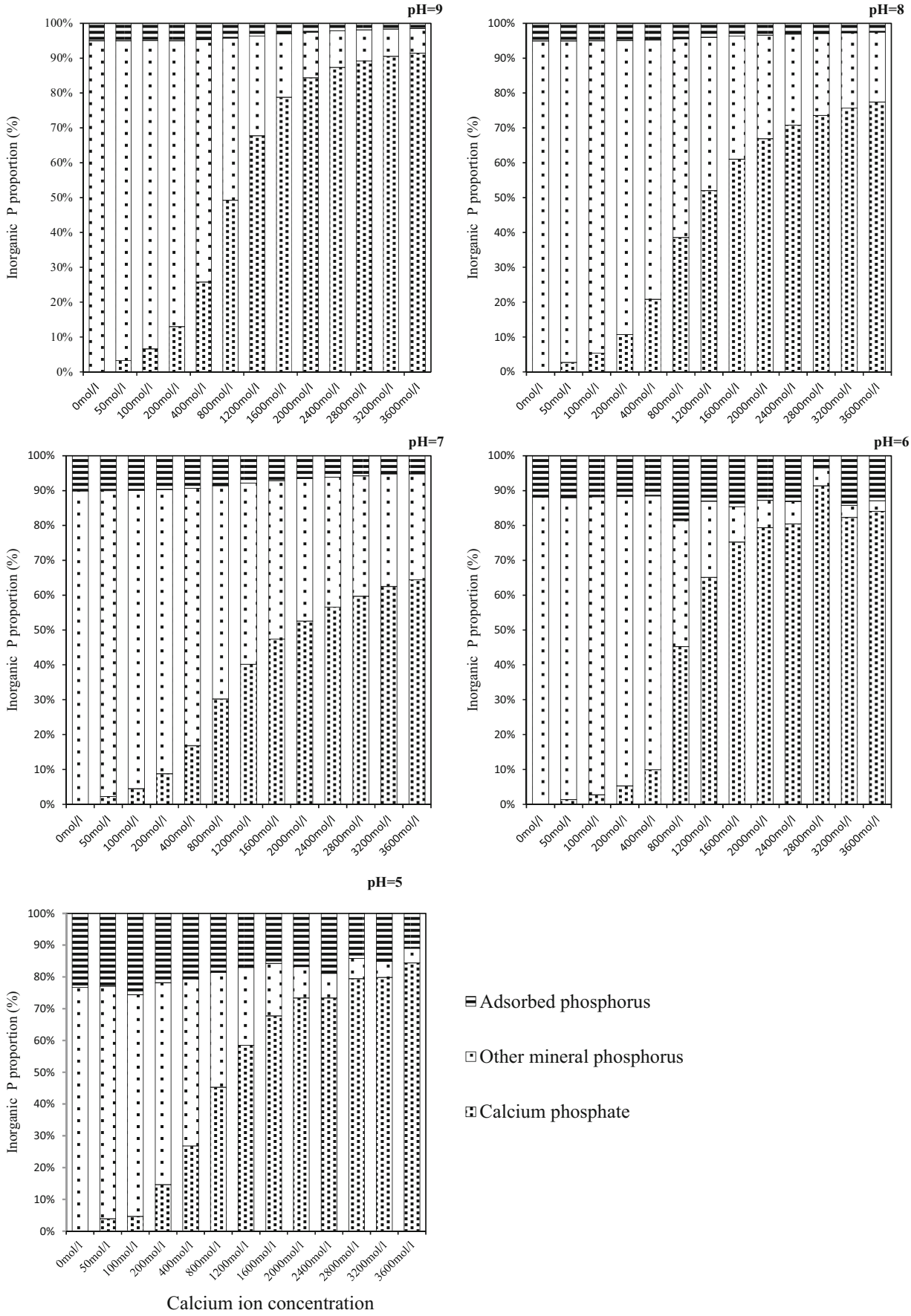
3.4 Effects on Ca-P speciation

Figure 4 shows that the concentration of Ca_{10}-P was the highest among the phosphates in the soil, accounting for at least 60% of the total amount of phosphate. The concentration of Ca_8-P was the next highest. After the application of FGD gypsum, the ratio of Ca_{10}-P among the phosphates decreased, although significant differences were not observed between the treatments. The ratios of Ca_2-P and Ca_8-P to phosphate increased compared with those in the control, and the increase of the Ca_8-P fraction was significant.

Table 7 shows that the Ca_2-P concentration first increased and then decreased with increasing application rate of FGD gypsum. The maximum concentration of 78 mg/kg occurred in the plot treated with 30 t/ha, and the concentrations in all treated plots exceeded those in the control, representing increases of 41.3–68.6%. As the application rate of FGD gypsum increased, the Ca_8-P and Ca_{10}-P concentrations increased gradually FGD gypsum by 34.1–70.1 and 7.4–17.2%, respectively, compared with the control. The increase in Ca_8-P was the most significant. The average increases in the phosphate fractions were ranked as follows: Ca_8-P > Ca_{10}-P > Ca_2-P. The

Table 7 Variations in soil Ca-P fractions (mg/kg) with different application rates of FGD gypsum

Treatment	Ca_2-P 0.25 mol/L $NaHCO_3$	Ca_8-P 0.5 mol/L NH_4Ac	Ca_{10}-P 0.5 mol/L H_2SO_4	Total Ca-P
FGDG (0 t/ha)	46 ± 6a	91 ± 3a	337 ± 23a	473 ± 16a
FGDG (15 t/ha)	65 ± 6b	122 ± 15b	362 ± 17b	549 ± 16b
FGDG (30 t/ha)	78 ± 3c	132 ± 12b	378 ± 31b	589 ± 27b
FGDG (45 t/ha)	68 ± 7b	155 ± 24c	395 ± 27b	618 ± 25c


pH=9
pH=8
pH=7
pH=6
pH=5
Inorganic P proportion (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0mol/l
50mol/l
100mol/l
200mol/l
400mol/l
800mol/l
1200mol/l
1600mol/l
2000mol/l
2400mol/l
2800mol/l
3200mol/l
3600mol/l
Calcium ion concentration
Adsorbed phosphorus
Other mineral phosphorus
Calcium phosphate

◀ **Fig. 5** Results of Visual MINTEQ modeling of inorganic P fractions in soil solutions with different pH values

results indicated that exchangeable calcium ions reacted with phosphate ions, which resulted in consistent increases of various calcium P in the soil. The various inorganic phosphorus fractions differ greatly in their beneficial effects on plants, and Ca_2-P is the most beneficial and exhibits excellent persistence. Ca_8-P displays a certain effectiveness and is a potential slow-release P source (Wang et al. 2010). In neutral and alkaline solutions, Ca_{10}-P is the most stable fraction among calcium phosphates and almost unabsorbable by vegetation (Gu and Jiang 1990). In the present study, the increase in Ca-P in soil was primarily attributed to Ca_8-P and Ca_{10}-P, indicating that most of the P was converted to stable forms by the FGD gypsum. However, during plant growth, the available P in Ca_2-P and the slow-release Ca_8-P can also be released to satisfy plant growth needs.

3.5 Distribution of different P fractions modeled using the MINTEQ program

The inorganic P in soil primarily exists as adsorbed P, mineral P, and water-soluble P. The mineral P is referred to as the insoluble phosphate produced from the reaction of soluble P with iron, aluminum, and calcium compounds in the soil (Xiang et al. 2004). Among these compounds, calcium phosphate is the important fraction. Based on the pH and the measured ionic strength of the original soil leachate, Visual MINTEQ was used to calculate the concentration of each ion and the chemical equilibrium of compounds in the soil solution. The modeling results in Fig. 5 show that the amount of calcium phosphate in the mineral P increased as the calcium ion concentration in the soil solution increased. However, the increase in calcium phosphate differed at different pH levels. Under alkaline conditions, the increase in calcium phosphates was primarily in the form of $CaPO4^-$ and $CaHPO4^+$, and the concentration of $CaPO4^-$ gradually increased with increasing pH. Under acidic conditions, the increase in calcium phosphates was primarily in the form $CaH_2PO_4^+$ and $CaHPO_4^+$, and the concentration of $CaH_2PO_4^-$ gradually increased with decreasing pH. Simultaneously, the concentration of adsorbed P decreased markedly. The concentration of other mineral inorganic P compounds also gradually decreased.

The changes in inorganic P fractions simulated by the model essentially match the experimental results. With the increased application rate of FGD gypsum, the Ca and PO_4 in the soil formed a series of water-soluble calcium phosphate compounds, and the ratio of these compounds to the TP increased with increasing calcium ion concentration (i.e., the amount of FGD gypsum). The results also show that the concentration of calcium phosphates also gradually increased with increasing or decreasing pH, i.e., the solubility of the calcium phosphate was even higher, which is consistent with the changes in various inorganic P fractions reported by Kuroda and Okido (2012).

3.6 Effects on P in plants

Figure 6 shows that the TP in the plants during the seedling stage first increased and then decreased with increasing

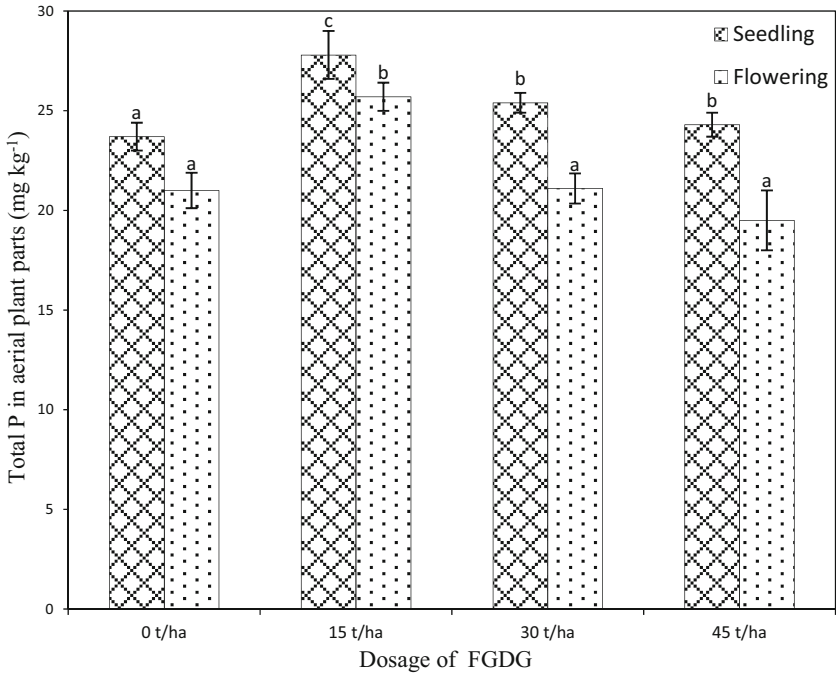


Fig. 6 Variations in the total P content in the aerial plant parts with different application rates of FGD gypsum

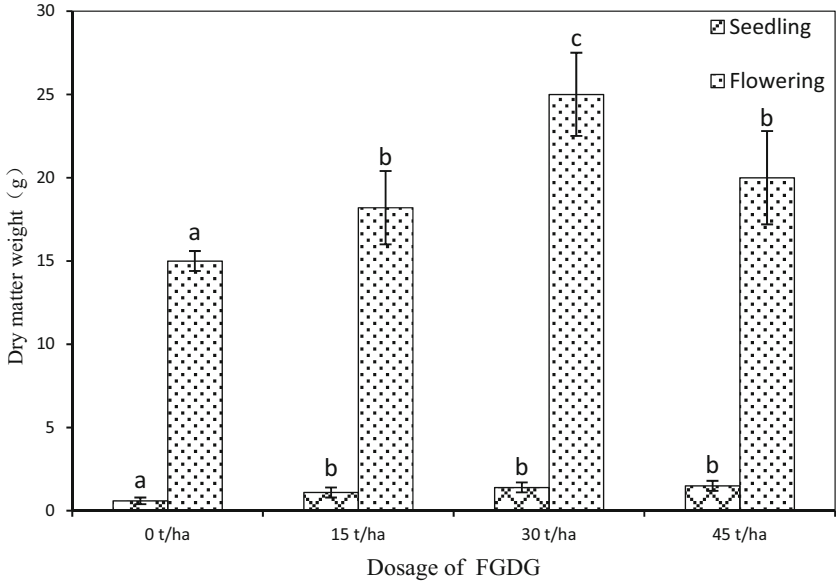


Fig. 7 Variations in the dry matter weight in the aerial plant parts with different application rates of FGD gypsum

application rate of FGD gypsum. The TP was higher in the plants growing in the treated plots than in the control. In addition, there were significant differences between the plots receiving 15, 30, and 45 t/ha and the control plots ($p < 0.05$). During the flowering stage, because of the decreased nutrient absorption capacity and material transport, the total P in the plants was generally less than that in the seedling stage, although some variation occurred in different growth stages. The T P in the plants treated with 45 t/ha was less than that in the control without significant difference statistically. Figure 7 shows that the dry matter weight in the plants during the seedling stage and flowering stage were higher in the treated plots than in the control with increasing in the application rate of FGD gypsum.

The decrease in AP and the increase in inorganic P in the soil did not significantly affect the absorption of P by the plants. The dry matter weight during the seedling stage and flowering stage was higher in the treated plots than in the control. This observation is consistent with the results reported by Stout and Sharpley (2003) and Zhang et al. (2013), where the dry matter weight of *ryegrass* and *Hibiscus moscheutos* was not affected by the FGD gypsum treatment. Chhabra et al. (1981) showed that the concentration of AP and the transport capability in alkaline soil decreased significantly with the application of desulfurized gypsum, although the absorption of P by plants was not affected. In addition, the results showed that the O-P and Ca_2-P in inorganic P reached maximum values in the treatment with 30 t/ha but were less in the treatment with 45 t/ha and that the TP of the plants in the treatment with 45 t/ha was less than that in the control. These findings indicate that the application of FGD gypsum had a marginal effect on the P fixation and that the changes after excess application were not significant. Therefore, further studies are required to investigate how the application rate of FGD gypsum controls the loss of soluble P.

4 Conclusions

The findings indicate that the application of FGD gypsum did not have a significant effect on the TP in the coastal plain soils. However, the AP in the soil and the SRP in the leachate decreased with increases in the application rate of FGD gypsum. The concentration of inorganic P in the soil gradually increased as the application rate of FGD gypsum increased. The increased inorganic P primarily consisted of water-insoluble calcium phosphate. Within this fraction, the increased calcium phosphate was primarily Ca_8-P and Ca_{10}-P, and Ca_2-P initially increased and then decreased with increasing FGD gypsum application. Although the increased Ca-P is not easily absorbed by vegetation, it is still a potential P source. The decrease in AP and SRP in the soil and the increase in soil insoluble inorganic P did not significantly affect the absorption of P by the vegetation. The Visual MINTEQ modeling results confirmed the field experimental results. With a gradual increase in the application rate of FGD gypsum, the soluble P in the soil was gradually fixed to insoluble calcium phosphates. This research achieved the expected purpose of enhancing soil P immobilization in a coastal plain soil using FGD gypsum, thus reducing soluble P runoff from farm fields and improving the water quality in receiving lakes and rivers.

FGD gypsum has a higher $CaSO_4 \cdot 2H_2O$ content, fewer impurities than commercially mined gypsum. Our experiments indicated that FGD gypsum has been shown to react with P in soil, resulting in decrease of AP and SRP and

formation of insoluble Ca-P compounds and thereby decreasing the potential of P losses with surface runoff. Therefore, it is very suitable for large-scale agricultural non-point source pollution control. At present, the eutrophication of water bodies was becoming more and more serious all over the world. FGD gypsum which was treated as solid waste in the traditional sense could widely be used in coastal plain soil with rich phosphorus and has a wide application prospect in water quality improvement.

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