



Inhibiting effects of flue gas desulfurization gypsum on soil phosphorus loss in Chongming Dongtan, southeastern China

He Kun¹ · Li Xiaoping²

Received: 29 October 2018 / Accepted: 1 April 2019 / Published online: 22 April 2019
© Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

To explore the possibility of using flue gas desulfurization gypsum (FGDG) for inhibiting phosphorus (P) loss due to agricultural runoff, a 3-year study was performed in the farmlands of Chongming Dongtan between 2012 and 2015. Five different quantities of FGDG were used to treat the soil, and the effects of different treatments on the characteristics of soil P and crop growth were investigated. The results showed that 2 years after application of FGDG, the soil density at a depth of 0–10 cm decreased by 4.35–7.97%, the porosity increased by 1.77–11.0%, and the topsoil permeability increased by 0.87–3.81 times. Although the use of FGDG did not change the total P concentration in the soil, it decreased the concentration of sodium bicarbonate extractable P in the soil. Compared to the control, the average extractable P concentration at depths of 0–10 cm, 10–20 cm, and 20–30 cm decreased by 22.0–46.1%, 26.9–40.5%, and 22.8–34.8%, respectively. The inorganic P in the soil increased as the amount of FGDG increased, and the increase was mainly as Ca–P in the forms Ca₂–P and Ca₁₀–P. The decrease in bicarbonate extractable P and increase in inorganic P in the soil did not affect the growth of the crops, and the biomass and output of the crops increased compared to the control. Therefore, FGDG can enhance soil P immobilization, thus reducing soluble P runoff from farm fields, and improving water quality in receiving lakes and rivers while maintaining P nutrition to the crops.

Keywords Flue gas desulfurization gypsum (FGDG) · P loss · P fraction · Agricultural nonpoint source pollution

Introduction

The Yangtze River Delta has a high level of agricultural intensification. The excessive use of fertilizer has resulted in a large increase in phosphorus (P) concentration in the soil of the farms in this delta region (Yang et al. 2013). However, the efficiency of the use of P is rather low. The agricultural nonpoint source pollution is severe, which increases the risk of runoff loss of P into the water, thus affecting the water quality (Sheng et al. 2004; Ou et al. 2016). Therefore, it is imperative to investigate technologies for the interception, discharge

reduction, and inhibition of agricultural nonpoint source pollution to decrease the loss of P if agricultural activities are to continue on these lands (Yang et al. 2013; Xu et al. 2013).

A large amount of an industrial byproduct, flue gas desulfurization gypsum (FGDG) (CaSO₄·2H₂O), is produced when coal-fired power plants use the limestone-gypsum forced air oxidation process to remove sulfur from flue gas. In recent years, FGDG has been widely used in the improvement of soil, mine reclamation, and desalting and restoration of beach saline-alkali lands (Chen et al. 2008; Wang et al. 2005; Damodhara and Anita 2011; Li et al. 2015). Recent studies have shown that FGDG can improve the physical structure and chemical properties of soil and decrease the transport of nutrients, precipitates, pesticides, and other pollutions in soil to bodies of water, and it plays an important role in controlling the runoff of P from farmlands (Buckley and Wolkowski 2011; Favaretto et al. 2012; Torbert 2014). Therefore, agricultural and environmental experts have started to pay attention to the possibility of decreasing agricultural nonpoint source P loss using FGDG when it is also used to improve the soil (Watts and Torbert 2009; Warren et al. 2013; Buckley and Wolkowski 2014).

Responsible editor: Zhihong Xu

✉ Li Xiaoping
652755713@qq.com

He Kun
hekun@sit.edu.cn

¹ The Ecological Technology and Engineering School of Shanghai Institute of Technology, Shanghai 201418, China

² State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China

There have been no systematic studies in China to investigate how the use of FGDG decreases soil runoff and how FGDG impacts P fractions in soil, particularly the inorganic P form (IPF). Specific engineering practices using FGDG have also been rare. On the basis of a laboratory study and field study (Chen et al. 2017; He et al. 2017), we performed a project demonstration for P-rich soil on the plain farmlands of eastern Shanghai by applying different levels of FGDG (1) to determine and optimize the effects of FGDG on the physical and chemical properties of soil and on the loss of soil P and (2) to explore the effect of FGDG on the change in soil P forms, particularly the forms of inorganic P at different soil depths and on the growth and output of drought-resistant rice. The results provide a reliable and economic technical means and theoretical method for the interception and discharge reduction in agricultural nonpoint source pollution of P to improve polluted rivers and bodies of water in the river network region of the Yangtze Plain as well as provide a new way for recycling industrial byproducts.

Material and method

Experiment site

The experiment site was located in the farmlands of the eastern Chongming district of Shanghai. The Chongming district of Shanghai belongs to the subtropical monsoon climate, where the annual mean rainfall is 1025 mm. The area of the experimental field was 0.2 ha, with planting area for crops of 0.15 ha. The experimental time of the demonstration project spanned from Nov. 2012 to Oct. 2015.

Experimental materials

The FGDG used in this study was from the Waigaoqiao Power Generation Co., Ltd. in Shanghai. The main composition of the FGDG was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which contains two essential beneficial mineral nutrients for plants, S and Ca. The P concentration was less than 0.001%. The soil used in the experiment had total P concentration of 922 mg/kg and a pH of 8.36.

The “Zaoyuxiangjing” rice planted in the experimental fields was a water-saving and drought-resistant variety that possesses properties such as good growth at low fertility and lodging resistance. Its growth period is approximately 125 days.

Experimental design

A randomized experimental design was used in the demonstration project. A total of 20 experimental plots, each $10 \times 10 \text{ m}^2$, were developed. The plots were separated by deep

ditches. The land preparation and application of FGDG were completed in the winter of 2012. First, the land was leveled, and it was then tilled for approximately 30 min by rotary tillage. The FGDG and the surface soil were completely mixed. The application amounts of FGDG were 0, 15, 30, 45, and 60 Mg/ha, and these treatments were replicated four times. Management measures such as irrigation and fertilization were the same for each treatment.

The drought-resistant rice seedlings were planted by hand. The spacing in the rows was 30 cm, and the spacing between rows was 15 cm. The rice seedlings were planted on May 15, 2015, and the plants were manually reaped on Nov. 20. According to the S-type sampling method, three quadrats with a size of $1.0 \text{ m} \times 1.0 \text{ m}$ were harvested from each treated plot.

Sample collection and measurement

Two years after the application of FGDG, soil samples at depths of 0–10 cm, 10–20 cm, and 20–30 cm were collected from each plot. The soil density, saturated water content, soil total P (TP), sodium bicarbonate extractable P (EP), and inorganic P (IP) were measured.

The soil TP was determined using the sulfuric acid-perchloric acid digestion method (Bao 2000). The EP was determined using the sodium bicarbonate extraction-molybdenum-antimony anti-spectrophotometric method (Olsen et al. 1954). The soil IP was determined using the inorganic P fractionation (IPF) classification scheme for calcareous soils proposed by Jiang and Gu (1989) (Table 1). The soil density was determined using ring shear testing; the soil porosity was determined using the soil saturated water-holding capacity method.

After maturation, five plants of the drought-resistant rice were randomly collected from the quadrats in different treatment plots. In the lab, Vernier calipers were used to measure the total height and the height above ground for each plant. Then, the plant root was cut, and the root analysis system WinRHIZO was used to measure the total length of the root. Moreover, the tiller number, spike number, grain number per spike, total grain weight, and 1000 grain weight were measured and calculated for each plant. After drying in an oven, the biomasses of the drought-resistant rice plant above and below ground were measured.

Statistical analysis

The experimental data were processed and analyzed using SPSS 17.0 and Excel. The analysis of variance for the P index between the different FGDG treatments was performed at a significance level of $P < 0.05$ and compared using the Duncan multiple comparison method.

Table 1 Extraction steps for the analysis of inorganic P fractions by Jiang and Gu

Step	Extraction procedure	Extracted P form (and notation)
1	1 g 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 ₄ COO (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 ₄ F, 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 ₂ CO 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 ₂ SO ₄ and shaken for 1 h.	Hydroxylapatite (Ca ₁₀ -P)

Results and analysis

Effect of FGDG on the physical structures of the soil

The solubility of FGDG allows the transport of Ca and S from the soil surface to the root regions, thus improving the physical and chemical properties of the soil, promoting soil aggregation, and increasing soil permeability and water movement in the soil (Chen and Dick 2011; American Coal Ash Association 2013). Two years after the application of FGDG, changes in the soil density, porosity, saturated water-holding capacity, and soil permeability occurred to different degrees (Table 2). Compared to the control, the soil density at a depth of 0–10 cm decreased by 4.35–7.97%, and the porosity increased by 1.77–11.0%; the soil density at a depth of 10–20 cm decreased by 4.25–11.3%, and the porosity increased by 3.17–12.7%; and the soil density at a depth of 20–30 cm decreased by 1.41–12.7%, and the porosity increased by 1.77–11.00%. The results indicate that FGDG decreases the soil density, increases the total porosity, and improves the structure of soil, thus benefiting the soil biological activities and the growth of crop roots.

Soil permeability is an important physical property because it reflects the movement and storage of water in soil. The soil treated with FGDG exhibited a significant increase in the soil infiltration rate compared to the control (Table 2). This trend

increased as the application rate of FGDG increased. The maximum infiltration rate was 32.7 mm/h, which was 3.81 times higher than that of the control group. This result indicates that the application of FGDG improves the physical states of water in the soil and increases the soil permeability. Therefore, it can decrease farmland runoff and decrease the possibility of P loss in soil because of surface runoff.

Effect of FGDG on the soil total P and change in the sodium bicarbonate extractable P

Two years after the application of FGDG to the soil, in which no change in the soil TP was observed (Fig. 1). There was also no significant difference ($P > 0.05$) in the soil TP at different depths between the control and the plots treated with different amounts of FGDG.

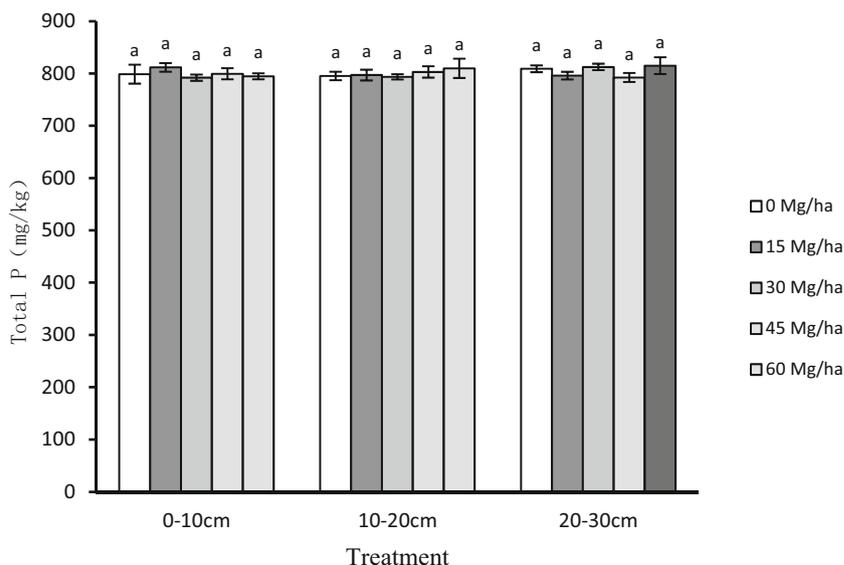
EP can reflect the availability of soil phosphorus. Research has shown that the measured values of soil P by this method are positively correlated with soluble P in calcareous soils or in surface/subsurface runoff (Bu and Magdoff 2003). Figure 2 shows that the EP concentration decreased significantly after the application of FGDG and continued to decrease as the amount of FGDG increased. For the soil between 0 and 10 cm, there was no significant difference in the EP concentration between the 15 Mg/ha treatment and the control. However, the difference was significant between the 30, 45,

Table 2 Changes in the characteristics of the soil physical structure

Treatment	Volume weight (g cm ⁻³)			Porosity (%)			Infiltration rate (mm min ⁻¹) 0–30 cm
	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm	
0 Mg/ha	1.38a	1.41a	1.42a	50.9a	50.4a	48.6a	6.80a
15 Mg/ha	1.32b	1.35b	1.40a	51.8a	52.0a	51.6a	12.7b
30 Mg/ha	1.30b	1.30c	1.28b	52.7a	52.5a	52.2a	18.5c
45 Mg/ha	1.28b	1.26d	1.27b	57.2b	55.9b	55.1b	30.6d
60 Mg/ha	1.27b	1.25d	1.24b	56.5b	56.8b	55.7b	32.7d

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

Fig. 1 Change in total phosphorus in soil under different FGDG application rates



and 60 Mg/ha treatments and the control ($P < 0.05$). The mean EP concentrations decreased by 22.0–46.1%. For the soil between 10 and 20 cm and between 20 and 30 cm, there was a significant difference in the EP concentration between all treatments and the control, and the mean EP concentration decreased by 26.9–40.5% and 22.8–34.8%, respectively. These results indicate that FGDG exhibits a more pronounced effect of decreasing the EP in soil near the top compared to the soil further down. When the amount of FGDG was the greatest, i.e., 60 Mg/ha, the EP content of the topsoil decreased to the minimum of approximately 9.50 mg/kg. Therefore, the application of FGDG inhibits the availability of soil P, which is in agreement with the results of a previous laboratory study (Bao 2000).

For the same treatment, the EP concentration also varied at different depths and decreased as the depth increased in our study (Fig. 2). This behavior occurs because there is an

obvious change in the soil texture as the depth increases. The deeper the soil is, the larger the density. Higher soil density prevents easy adsorption of the available P. The EP is mainly HPO_4^{2-} and PO_4^{3-} , which can be adsorbed into the soil aggregate but cannot dissociate into the soil solution. Therefore, a loose aggregate structure is more favorable to the adsorption of P (Wang et al. 2010).

Effect of FGDG on soil IP

Among the forms of soil IP, the Ca–P concentration was highest, followed by the O–P content (Table 3). Two years after the application of FGDG, the total soil IP increased as the amount of applied FGDG increased. All values were higher than the control. Among the tested combinations, the total soil IP increased by 206 mg/kg for the 60 Mg/ha treatment. The increase in Ca–P was the most significant of the

Fig. 2 Change in sodium bicarbonate extractable P in soil under different FGDG application rates

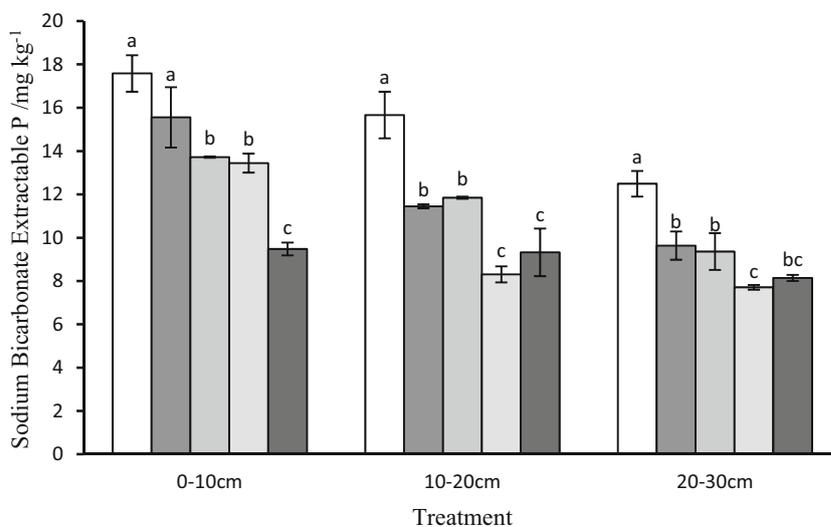


Table 3 Change in each IP fraction with different FGDG application levels at the soil surface mg/kg

Treatment	Al-P 0.5 mol/LNH ₄ F	Fe-P 0.1 mol/LNaOH- Na ₂ CO ₃	O-P 0.3 mol/LNa ₂ C ₆ H ₅ O ₇ •2H ₂ O-Na ₂ S ₂ O ₄	Ca-P Table 5	Total IP	Total P
0 Mg/ha	7.41 ± 0.41a	31.0 ± 12.3a	36.6 ± 6.46a	427 ± 27.6a	502 ± 46.3a	801 ± 15.8a
15 Mg/ha	10.4 ± 0.71b	46.1 ± 8.21b	50.3 ± 7.45b	467 ± 11.9b	574 ± 25.0b	801 ± 7.26 a
30 Mg/ha	21.3 ± 3.72c	47.7 ± 9.52b	49.7 ± 8.87b	491 ± 42.6c	609 ± 51.7b	799 ± 9.26 a
45 Mg/ha	26.1 ± 4.67c	42.9 ± 6.62b	81.0 ± 9.89c	526 ± 24.8 cd	676 ± 35.6c	798 ± 14.4 a
60 Mg/ha	24.0 ± 2.56c	42.4 ± 1.91b	75.3 ± 6.48c	564 ± 43.4d	708 ± 40.3c	806 ± 8.65 a

various IP forms. The total soil Ca-P of the 60 Mg/ha treatment increased by 137 mg/kg compared to the control, and the increase accounted for 66.5% of the total IP increase. Therefore, as the applied FGDG increased, mainly the calcium phosphate fractions of the soil IP increased. This result is consistent with the experimental results from laboratory and field plots (Chen et al. 2017; He et al. 2017). The O-P concentration in the farmland soil applied with FGDG also increased as the amount of FGDG increased, and the concentration increased by 37.4–106% compared to the control. The Al-P and Fe-P concentrations in the farmland soil, in contrast, first increased and then decreased as the application rate increased, but all increased more than the control; the increase occurred from 40.4 to 224% and from 36.8 to 48.7% for the Al-P and Fe-P concentrations, respectively.

For the soil at a depth of 0–10 cm, both the Al-P and O-P concentrations increased, while the Fe-P concentration first increased and then decreased as the application rate increased (Table 4). For the soil at a depth of 10–20 cm, the Al-P, Fe-P, and O-P concentrations first increased and then decreased. For the 20–30-cm soil, both the Al-P and O-P concentrations increased, while the Fe-P concentration first increased, then decreased and finally increased. These trends occurred even though the IP concentration of the treatments increased compared to the control at different depths.

The increase in the various IP in the soils at different depths was further analyzed. Take the 60 Mg/ha FGDG treatment as an example. For the 0–10-cm soil, the Al-P concentration increased by 2.43 times compared to the control, and for the 20–30-cm soil, the Al-P concentration increased by 2.76

times compared to the control. Thus, the increase in the Al-P concentration in the bottom (20–30 cm) soil layer was higher than that in the top (0–10 cm) soil. The increase in the Fe-P and O-P concentrations also exhibited the same behavior, further indicating that FGDG has a greater impact on the change in IP in the deeper soil layers.

Effect of FGDG on the change in soil calcium phosphate

The soil calcium phosphate concentration increased as the application of FGDG increased, and the difference between each treatment was significant (Table 5). Among the calcium phosphate components, the Ca₁₀-P concentration was the highest and accounted for approximately 90% of the total calcium phosphate; the next highest concentration was Ca₈-P. The Ca₂-P and Ca₁₀-P concentrations increased as the amount of FGDG increased by 58.9–286% and 6.49–26.8%, respectively, compared to the control. Except for the 45-Mg/ha treatment, the Ca₈-P concentration also increased as the amount of FGDG increased. The Ca₈-P content increased by 26.9–80.5% compared to the control. The experimental results show that the exchangeable calcium ions react with the phosphate ions in the soil, which results in a universal increase in concentration of each calcium phosphate. For each FGDG treatment, the Ca-P concentration exhibited an increase at different depths compared to the control, which agrees with the trends in Al-P and Fe-P.

In terms of the availability to plants, there is a significant difference between the different forms of IP. Al-P and Ca₂-P

Table 4 Change in each IP fraction with different FGDG application levels at different depths mg/kg

Treatment	Al-P			Fe-P			O-P		
	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
0 Mg/ha	7.61a	7.45a	6.78a	47.9a	26.3a	18.8a	45.3a	35.3a	39.2a
15 Mg/ha	11.3b	10.0b	9.78a	57.5b	41.8b	38.8b	56.7b	54.1b	39.7a
30 Mg/ha	26.1c	20.7a	17.0b	60.0b	46.3c	36.8b	60.3b	48.2b	40.7a
45 Mg/ha	31.8c	26.4d	20.1c	44.3a	50.3c	34.2b	80.2a	93.6d	69.2b
60 Mg/ha	26.1c	20.4c	25.5d	47.1a	43.2b	42.9c	66.2b	81.2c	78.5c

Table 5 Change in the various Ca–P with different FGDG application levels at the soil surface mg/kg

Treatment	Ca ₂ –P 0.25 mol/LNaHCO ₃	Ca ₈ –P 0.5 mol/LNH ₄ Ac	Ca ₁₀ –P 0.5 mol/LH ₂ SO ₄	Total Ca–P
0 Mg/ha	5.11 ± 2.33a	30.8 ± 8.61a	385 ± 24.78a	424 ± 27.6a
15 Mg/ha	8.12 ± 1.60b	39.1 ± 11.1b	410 ± 3.23a	457 ± 11.9b
30 Mg/ha	11.1 ± 2.62c	43.0 ± 13.2b	437 ± 44.1b	491 ± 42.6c
45 Mg/ha	16.6 ± 4.90d	41.4 ± 3.22b	468 ± 16.9c	526 ± 24.8 cd
60 Mg/ha	19.7 ± 8.42e	55.6 ± 11.9c	488 ± 25.1c	564 ± 43.4d

have the best availability in addition to excellent sustainability; Ca₈–P possesses some availability and is thus a potential slowly available phosphorus source. In neutral or basic solutions, Ca₁₀–P is the most stable form among all calcium phosphates and is nearly impossible to be absorbed by crops (He et al. 2017). In the present study, the concentrations of various types of Ca–P in the soil all increased, which indicates that the majority of P can be fixed by FGDG to rather stable forms. However, during the growth of plants, P can be released from the fixed form as an available P source Al–P/Ca₂–P and slow-releasing Ca₈–P to satisfy the requirements of the crops (Wang et al. 2010).

Effect of FGDG on the growth and development of plants

For the treatments with different amounts of FGDG, the biomass, total root length, and plant height of the drought-resistant rice during maturity were all greater than that of the control (Table 6). However, the amount of FGDG applied affected the growth and development of drought-resistant rice to different degrees. When the FGDG application amount was 45 Mg/ha, the plant height and root length of the plant were a maximum. The grain number per spike and the total grain weight are important indices for the output of drought-resistant rice. The tiller number of the rice plant and the number of spikes per plant increased after the farmland soil was improved by applying FGDG. Compared to the control, the number of grains per spike and the dry weight of the total grain also significantly increased. The dry weight of the total grain was highest when the FGDG application amount was 30 Mg/ha.

The soil of the demonstration field exhibited weak alkalinity. Research has already shown that calcium ions in FGDG can displace sodium ions in saline soil, which decreases the soil salinity and increases the biomass of the plants (Li et al. 2010). In addition to the displacement of sodium ions, calcium ions also react with P to convert sodium bicarbonate EP to inorganic P in the soil. However, the decrease in soluble P in soil or in surface/subsurface runoff and the increase in IP do not impact the growth and maturation or the final output of the crops.

Discussion

Effect of FGDG on the improvement of the physical structures of soil

Research has shown that the mechanism by which FGDG controls P loss from farmland runoff is through increased soil permeability, decreased farmland runoff and increased absorption precipitation of P by the soil, which decreases the P loss of TP and soluble P (Brauer et al. 2005; Torbert and Watts 2014). The calcium ions in FGDG can displace the sodium ions on the soil gels. As a result, a soil aggregate structure forms a stable soil structure, which ensures an appropriate porosity inside soil, thereby improving the soil air/water permeability, which is beneficial to the entry and discharge of water (Chen and Dick 2012; Chen et al. 2017).

FGDG also improves soil physical properties as manifested by the decrease in soil density, improvement in porosity and saturated water-holding capacity, and improvement in the soil permeability by 0.87–3.81 times. P in the topsoil enters into the farmland runoff through desorption and leaching, and it is discharged into the surrounding bodies of water, thus causing water contamination. An increase in the soil permeability leads to an increase in the infiltration of runoff; consequently, the soluble P in the soil is infiltrated into the soil and is slowly adsorbed or fixed by the crops. This process decreases the probability of the loss of soluble P to surrounding water bodies with surface runoff.

Effect of FGDG on farmland soil TP and EP

The soil TP exists mainly as slow-release forms. AP refers to the P components that can be absorbed by plants that include all water-soluble P and some organic P. AP is an index for the level of soil P nutrition and can reflect the storage and supply capacity of P in soils (Sheng et al. 2004). The sodium bicarbonate extraction method that is commonly used to determine AP was also used in this study. The results indicate that FGDG does not cause a significant change to the TP in the soil. However, as the FGDG proportion increases, the EP in the soil at different depths decreases. In addition, with the application of a large amount of FGDG, the decrease in EP was very significant. The content for the 60 Mg/ha FGDG

Table 6 Effect of the different amounts of FGDG on the growth and development of plant

Treatment	Biomass				Output			
	Underground biomass/g ⁻¹	Total root length/cm	Aboveground Biomass/g ⁻¹	Plant height/cm	Tiller number/ea	Spike number/ea	Grain number per spike/ea	Dry weight of total grain/g
0 Mg/ha	0.30 ± 0.07a	299 ± 15.1a	3.21 ± 0.26a	67.1 ± 5.74a	3.30 ± 1.04a	3.61 ± 0.79a	198 ± 37.9a	2.93 ± 0.50a
15 Mg/ha	0.32 ± 0.15a	308 ± 10.1a	3.65 ± 0.45a	68.9 ± 6.23a	4.04 ± 0.76b	3.82 ± 0.22a	233 ± 10.3b	3.16 ± 0.23a
30 Mg/ha	0.41 ± 0.45b	339 ± 23.6b	4.36 ± 0.68b	73.2 ± 4.56a	4.28 ± 0.28b	4.18 ± 0.32b	321 ± 23.9c	4.15 ± 0.15c
45 Mg/ha	0.47 ± 0.23b	338 ± 56.2b	5.12 ± 0.78b	83.6 ± 7.56b	4.09 ± 1.29b	4.40 ± 1.28b	301 ± 36.5c	3.72 ± 0.41b
60 Mg/ha	0.40 ± 0.25b	300 ± 60.1bc	4.89 ± 0.51bc	71.2 ± 1.63a	4.21 ± 1.22b	4.12 ± 0.32b	239 ± 47.4b	3.63 ± 0.36b

treatment decreased by almost half compared to the control, the losses of soluble P in surface/subsurface runoff. The inhibition of soluble P by FGDG is achieved by decreasing the soluble P content in the filtrate (He et al. 2017). Therefore, a decrease in farmland EP reduces the possibility P loss by surface runoff.

Effect of FGDG on the change in farmland soil IP

The fixation of P in soils is mainly the transformation of water-soluble phosphate or weak acid-soluble phosphate into a poorly soluble phosphate (such as iron phosphate, aluminum phosphate, calcium phosphate, etc.) (Lindsay et al. 1989; Xiang et al. 2004; Jin et al. 2009). Chen et al. (2017) found, using FGDG to restore soil, that calcium ions react with P ions to transform the majority of P in soil to fixed P, which rapidly decreases the AP concentration. The precipitation and dissolution of insoluble P in alkaline soil is indeed one of the main mechanisms to control the concentration of water-soluble P. Moreover, the farmland soil IP concentration significantly increased after application of FGDG. The increase in the insoluble Ca-P concentration fractions among the IP components was particularly pronounced. The concentrations of Al-P, Fe-P, and O-P were also higher than the control.

The impact of FGDG was greater for the subsurface soil layer than for the topsoil. The reason is that increases in the soil porosity and permeability increase the soil moisture at the bottom, decrease the evaporation intensity, and thus inhibit the movement of the soil IP salts in the middle and bottom layers to the top layer.

In this study, the concentrations of Ca₂-P and Ca₁₀-P in the soil Ca-P gradually increased as the applied FGDG increased. The Ca₈-P concentration was higher for each treatment than for the control. The exchangeable calcium ions react with the phosphate ions, resulting in a general increase in the concentration of each calcium phosphate. The increased calcium phosphates are mainly Ca₈-P and Ca₁₀-P, which are relatively stable; therefore, the majority of P can be fixed using FGDG, which decreases the possibility of runoff erosion.

Effect of FGDG on the growth and output of crops

The results reported by Stout et al. (2003) showed that when FGDG was used to improve soils for crops, the decrease in AP within a certain range did not affect the growth and maturation of crops. The result in this study shows that the biomass and output of crops were higher for each FGDG treatment than for the control. The application of FGDG did not affect plant uptake of P from the soil, although EP decreased. Determination of AP is often determined by extraction with sodium bicarbonate P. However, the sodium bicarbonate extractable P did not accurately represent the availability of soil P because the uptake of P into rice plants increased even though its concentration decreased. Soil AP is thought to include partially and slightly soluble inorganic P and mineralizable organic P. However, the latter two types of P cannot be absorbed directly by plants but must first undergo transformation processes.

Al-P and Ca₂-P are considered to be available P sources for crops. Ca₈-P is a potential slow-release P source, while Ca₁₀-P is mostly unavailable for absorption by crops (Wang et al. 2010). Although sodium bicarbonate EP decreased as the FGDG treatment concentration increased, the growth of crops was sustained by P released from the increased available P sources of Al-P/Ca₂-P and the potential slow-release Ca₈-P. Moreover, the large amount of calcium ions and sulfur ions, in addition to P contained in FGDG, can promote the growth and maturation of crops.

The results reported by Clark et al. (2001) and Mao et al. (2016) showed that excessive application of FGDG can result in excessive accumulation of soil salts, thus affecting the growth of crops. Our results also showed that the biomass and output of crops reached a maximum for the 30- and 45-Mg/ha FGDG treatments but decreased for the 60 -Mg/ha treatment. This finding indicates that excessive FGDG inhibits the growth of crops. Therefore, the key to achieve both good crop growth and inhibition of P in the soil is to apply the appropriate amount of FGDG. The optimum amount of FGDG for the conditions in this study was 30–45 Mg/ha.

Both sodic and acid soils can benefit from gypsum (Watts and Dick 2014). DeSutter et al. (2014) and Kost et al. (2014) applied up to 22-Mg/ha FGDG in North Dakota (acid soil) and

Ohio (near-neutral pH), respectively. Crop grain yields were generally unaffected by the gypsum application. Zhang et al. (2013) and Xu et al. (2015) applied 45-Mg/ha and 30-Mg/ha FGDG in northern China, where soils contain high concentrations of exchangeable sodium ion. Both crop yields and soil physical properties were significantly improved during the experimental periods. The soil in the demonstration field exhibited weak alkalinity. Moreover, the Na–Ca exchange reaction will increase the application of FGDG to a certain extent. Thus, if FGDG is applied in other normal farmland to control soil P loss, the application should be reduced accordingly.

Conclusion

- 4.1 The application of FGDG improves the physical structure of the soil, decreases the soil density, and improves the soil permeability. After the 2-year experiment, the permeability of the soil applied with FGDG significantly increased. For the 60-Mg/ha treatment, the soil permeability increased 4.8 times compared to the control, which suggests that the application of FGDG can decrease farmland runoff and thus decrease the possibility of P loss in the soil by surface runoff.
- 4.2 The application of FGDG has no significant effect on the farmland soil TP. However, the EP at different depths all decreased as the amount of FGDG increased. For the soils between 0 and 10 cm, 10 and 20 cm, and 20 and 30 cm, the mean EP concentration decreased by 22.0–46.1%, 26.9–40.5%, and 22.8–34.8%, respectively.
- 4.3 The IP concentration in the soil increased as the amount of FGDG increased. The increased IP was mainly as water-insoluble calcium phosphate. For the FGDG-treated soil, Ca₂-P, Ca₈-P, and Ca₁₀-P were all higher than the control.
- 4.4 Although the increased Ca-P cannot be easily absorbed by crops, the available P source (Ca₂-P) and potential slow-release P (Ca₈-P) can be released and absorbed by crops for their growth requirements. The decrease in AP and increase in IP did not affect the growth or output of the studied crops.

Funding information This study was supported by the National Public Project of Environmental Protection (No. 201109023) and the Shanghai Science and Technology Commission (15dz1207904).

References

- American Coal Ash Association (2013) Coal combustion products production and use statistics [EB/OL]. 2013-6-15[2013-07-05].<http://acaaffiniscape.com/displaycommon.cfm?an=1&subarticlenbr=3>
- Bao SD (2000) Analysis of soil and agrochemistry. China Agriculture Press, Beijing (in Chinese)
- Brauer D, Aiken GE, Pote DH, Livingston SJ, Norton LD, Way TR, Edwards JH (2005) Amendment effects on soil test phosphorus. *J Environ Qual* 34:1682–1686
- Bu YS, Magdoff FR (2003) A comparison of ten methods for determination of available phosphorus. *Acta Pedol Sin* 40(1):140–146
- Buckley ME, Wolkowski RP (2011) Wisconsin research with FGDG. Midwest soil improvement symposium: research and practical insights into using gypsum. University of Wisconsin Arlington Ag Research Station, Arlington
- Buckley ME, Wolkowski RP (2014) In-season effect of flue gas desulfurization gypsum on soil physical properties. *J Environ Qual* 43:322–327
- Chen LM, Dick WA (2011) Gypsum as an agricultural amendment: general use guidelines. The Ohio State University, Columbus, pp 1–5
- Chen L, Dick WA (2012) Gypsum as an agricultural amendment: general use guidelines [EB/OL]. 2012-12-24 [2013-01-04]. <http://ohioline.osu.edu/b945/index.html>
- Chen LM, Kost D, Dick WA (2008) Flue gas desulfurization products as sulfur sources for corn. *Soil Sci Soc Am J* 72:1464–1470
- Chen XH, Qian XY, Li XP, Zhang H, He K, Li J (2017) Inhibiting effects and mechanism experiment of flue-gas desulfurization gypsum on soil phosphorus loss. *Trans Chin Soc Agric Eng* 33:148–154 (in Chinese)
- Clark RB, Ritchey KD, Baligar VC (2001) Benefits and constraints for use of FGD products on agricultural land. *J Fuel* 80:821–828
- Damodhara RM, Anita MT (2011) Polyacrylamide coated Milorganite TM and gypsum for controlling sediment and phosphorus loads. *Agric Water Manage* 101:27–34
- DeSutter TM, Cihacek LJ, Rahman S (2014) Application of flue gas desulfurization gypsum and its impact on wheat grain and soil chemistry. *J Environ Qual* 43:303–311
- Favaretto N, Norton LD, Johnston CT (2012) Nitrogen and phosphorus leaching as affected by gypsum amendment and exchangeable calcium and magnesium. *Soil Sci Soc Am J* 76:575–585
- He K, Li XP, Zhou CL, Zhou J, Dong LL, Mao YM (2017) Influence of flue gas desulfurization gypsum on speciation of phosphorus in coastal cultivated soils. *Acta Ecol Sin* 37:2935–2942 (in Chinese)
- Jiang B, Gu YA (1989) Suggested fractionation scheme of inorganic phosphorus in calcareous soils. *Nutr Cycl Agroecosyst* 20:159–165 (in Chinese)
- Jin L, Zhou JM, Wang HY (2009) Transformation and translocation of fertilizer-P with monocalcium phosphate monohydrate application in fertilosphere of calcareous soil. *Soils* 41:72–78 (in Chinese)
- Kost D, Chen L, Guo X, Tian Y, Ladwig K, Dick WA (2014) Effects of flue gas desulfurization and mined gypsums on soil properties and on hay and corn growth in eastern Ohio. *J Environ Qual* 43:312–321
- Li Y, Yi HF, Zhao B (2010) Study on improving Xinjiang sodic soils amelioration with desulfurized gypsum. *Ecol Environ* 19:1682–1685
- Li XP, Mao YM, Liu XC (2015) Flue gas desulfurization gypsum application for enhancing the desalination of reclaimed tidal lands. *Ecol Eng* 82:566–570
- Lindsay WL, Vlek PLG, Chien SH (1989) Phosphate minerals. In: Dixon JB, Weed SB (eds) Minerals in soil environment, 2nd edn. Soil Sci Soc Am J, Madison, pp 1089–1130
- Mao YM, Li XP, Dick WA, Chen LM (2016) Remediation of saline-sodic soil with flue gas desulfurization gypsum in a reclaimed tidal flat of southeast China. *J Environ Sci* 45:224–232
- Olsen SR, Cole CV, Watanable FS, Dean LA (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate. Government Printing Office, Washington, DC
- Ou HP, Zhou LQ, Huang MF (2016) Phosphorus balance in paddy soils and its environmental effect under different phosphorus application rates. *Plant Nutrition and Fertilizer Science* 22:40–47 (in Chinese)

- Sheng HJ, Xia XY, Yang LQ (2004) Effects of phosphorus application on soil available P and different P form in runoff. *Acta Ecol Sin* 24: 2837–2840 (in Chinese)
- Stout WL, Sharpley AN, Weaver SR (2003) Effect of amending high phosphorus soils with flue-gas desulfurization gypsum on plant uptake and soil fractions of phosphorus. *Nutr Cycl Agroecosyst* 67:21–29
- Torbert HA, Watts DB (2014) Impact of flue gas desulfurization gypsum application on water quality in a coastal plain soil. *J Environ Qual* 43:273–280
- Wang JM, Yang PL, Zhang JG, Shi Y (2005) Salinity effect on sunflower at seedling stage during improving sodic soils reclaimed with by-product from flue gas desulphurization (BFGD). *Trans Chin Soc Agric Eng* 21:33–37 (in Chinese)
- Wang J, Liu WZ, Mu HF, Dang TH (2010) Inorganic phosphorus fractions and phosphorus availability in a calcareous soil receiving 21-year superphosphate application. *Pedosphere* 20:304–310
- Warren D, Dan P, Joe N (2013) Reducing phosphorus contributions to Lake Erie by land application of gypsum. 2013 National Nonpoint Source Monitoring and Workshops, Cleveland
- Watts DB, Dick WA (2014) Sustainable uses of FG DG in agricultural systems: introduction. *J Environ Qual* 43:246–252
- Watts DB, Torbert HA (2009) Impact of gypsum applied to grass buffer strips on reducing soluble P in surface water runoff. *J Environ Qual* 38:1511–1517
- Xiang WS, Huang M, Li XY (2004) Progress on fractioning of soil phosphorous and availability of various phosphorous fractions to crops in soil. *Soil Sci Plant Nutr* 10:663–670 (in Chinese)
- Xu XG, Li YY, Meng C, Jiao JX, Shi H, Zhang MY, Wu JS (2013) The characteristics of nitrogen and phosphorus leaching in a paddy soil in subtropics. *J Agro-Environ Sci* 32:991–999
- Xu Y, Xu YH, Lin QM, Li GT, Zhao XR (2015) Effects of *Aneurotepidimu chinense* and desulfurization gypsum on the amelioration of Na₂SO₄ saline soil in Hetao Inner Mongolia. *Agric Res Arid Areas* 33(4):112–116 (in Chinese)
- Yang LZ, Feng YF, Shi WM, Xue LH, Wang SQ, Song XF, Chang ZZ (2013) Review of the advances and development trends in agricultural non-point source pollution control in China. *Chin J Eco-Agric* 21:96–101 (in Chinese)
- Zhang FJ, Xu X, Xiao GJ (2013) Influence of flue gas desulfurization gypsum on the availability of phosphorus in sodic soil. *Acta Agriculturae Boreali-Occidentalis Sinica* 22:151–156 (in Chinese)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.