# Reducing Phosphorus Release from Paddy Soil by Coal Ash and Phospho-Gypsum Mixture

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ABSTRACT: As a silicate source to rice, a coal ash was selected and mixed with phosphor-gypsum (50:50, wt wt<sup>-1</sup>) to reduce the potential of boron toxicity and to supply calcium element. We expected that high content of calcium in this mixture might convert water-soluble phosphorus to less soluble forms and then reduce the release of soil phosphorus to surface runoff. The mixture was applied with the rate of 0, 20, 40, and 60 Mg ha<sup>-1</sup> in paddy soil (Nagdong series, a somewhat excessively drained loamy fine sand) in Daegok, Jinju, Korea The mixture reduced significantly water-soluble phosphorus (W-P) in the surface soils by shifting from W-P and Fe-P to Ca-P and Al-P during whole rice cultivation. In contrast with W-P, plant available phosphorus increased significantly with the mixture application due to high content of phosphorus and silicate in the mixture. The mixture of coal ash and phosphor-gypsum (50:50, wt wt<sup>-1</sup>) would be a good alternative to reduce a phosphorus export in rice paddy soil together with increasing rice yields.

Key Words: paddy soil, phosphorus, phosphogypsum, coal ash

## INTRODUCTION

1)

With increasing the fertilizer consumption salts including phosphate have accumulated in arable soils with time higher than the optimum ranges and so make new problems in agricultural and environmental sides in Korea. In particular, phosphorus enrichment of streams, lakes and freshwater portions of estuaries is often the cause of algae blooms in these water bodies. A major source of such phosphorus enrichment can be surface runoff from croplands that have high levels of soil phosphorus. A national soil survey revealed that the phosphorus content in arable soils had increased continuously with time. In rice paddy soil, the content of available phosphate (P<sub>2</sub>O<sub>5</sub>) analyzed using the Lancaster method<sup>1)</sup> was just 60 mg kg<sup>-1</sup> in the 1960s and then increased continuously with time to about

130 mg kg<sup>-1</sup> in the 1990s, which largely exceeded the limitation 100 mg kg<sup>-1</sup> for rice<sup>2</sup>. These high phosphorus levels increase the amount of water-soluble phosphorus in the soil, thereby increasing the potential for phosphorus export in surface runoff to streams<sup>3),4</sup>. On the standard fertilizing condition in Korea, about 11 kg ha<sup>-1</sup> yr<sup>-1</sup> of phosphate (P<sub>2</sub>O<sub>5</sub>) was estimated to be lost out of the surface layer in a long term fertilized rice paddy soil<sup>5),6</sup>. In spite of phosphate accumulation, phosphate fertilizer has applied in farming fields every cropping time, due to low availability of phosphate. For example, minimum 30 kg ha<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> is recommended for rice irrespective with phosphate content in soil<sup>2</sup>, and average 20 kg ha<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub> was over-fertilized higher than the recommendation (45 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup>) in Korean rice paddy soil, recently<sup>7</sup>.

One way of controlling the release of soil phosphorus to surface runoff is to reduce its solubility by precipitation with other elements such as calcium, iron and aluminum<sup>8)</sup>. coal ash and phosphor-gypsum are sources of elements and compounds that can precipitate phosphorus in soil. In

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Korea, approximately 3.7 Tg of coal ash was produced in 1997, and it will rise to 6 Tg by the year 2010 in Korea<sup>9</sup>, and phospho-gypsum resulting from the production of phosphate fertilizer has accumulated for over 35 years. To satisfy the silicon and calcium requirements of rice and to decrease the potential for boron toxicity of coal ash in paddy soils, we made the mixture of coal ash and phospho-gypsum (50:50, wt wt<sup>-1</sup>) and achieved the positive effects on stimulating rice growth and improving soil quality<sup>10</sup>. In this study, our research purpose was to determine if this coal ash and phospho-gypsum mixture would reduce the amount of water-soluble phosphorus in the soil, thereby reducing the potential for phosphorus export into streams and lakes.

#### MATERIALS AND METHODS

#### Experimental site and treatment

The same coal ash and phospho-gypsum used in our previous research <sup>10),11)</sup>, which collected from the thermal power plant located at Hadong and from the phosphate fertilizer producing plant (Namhae Chemical Co. Ltd.) in Yeosu in southern Korea, respectively, were used for the field test. The same experimental plots used on evaluating the effect of coal ash and phospho-gypsum mixture (50:50, wt wt<sup>-1</sup>) on rice productivity in the previous study <sup>10)</sup> were used to investigate the effects of mixture on reducing phosphorus export in paddy soils, Daegok (Nagdong series, a somewhat excessively drained loamy fine sand with high phosphorus content) in Jinju (35°26′ N and 128°20′ E) in southern Korea.

Four different rate of the mixture (0, 20, 40 and 60 Mg ha<sup>-1</sup>) were selected as treatments. Chemical fertilizers N (120 kg ha<sup>-1</sup>), P<sub>2</sub>O<sub>5</sub> (48 kg ha<sup>-1</sup>) and K<sub>2</sub>O (80 kg ha<sup>-1</sup>) were applied in all the treatments. The experimental plots (10 m×10 m in size) were arranged in a completely randomized design with triplicate replication. Hwayongbyeo as rice cultivars were transplanted in Daegok (LS) on June 5, 1998 and harvested on October 16. Nitrogen and potassium were applied separately with three and two times during rice cultivation, respectively, but total phosphate was treated as a basal fertilizer on June 3. The mixture was applied on May 8-9 and mixed with soil by rotating into a depth of 15 cm.

#### Chemical Properties and Phosphorus Fraction

Soils sampled during rice cultivation were air-dried and crushed to pass through a 0.5 mm sieve. Sequential extra-

ctable P fractionation from the soil samples was performed as follows: extraction with H<sub>2</sub>O (water-soluble-P, W-P), 25 g L<sup>-1</sup> acetic acid and 1 M NH<sub>4</sub>Cl (calcium bound-P, Ca-P), 1 M NH<sub>4</sub>F (aluminum bound-P, Al-P), and 1 M NaOH (iron bound-P, Fe-P)<sup>12),13)</sup>. Available P content was analyzed by Melhich-3 <sup>14)</sup>, and Lancaster methods (RDA, 1988, 5g soil were extracted with 20 ml of 0.33 M CH<sub>3</sub>CHOOH, 0.15 M lactic acid, 0.03 M NH<sub>4</sub>F, 0.05 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 0.2 M NaOH at pH 4.25).

### RESULTS AND DISCUSSION

The coal ash-phosphogypsum mixture reduced significantly water-soluble phosphorus (W-P) concentrations in the surface soils during rice cultivation (Fig. 1). This reducing effect was increased with increasing the mixture application, irrespective with soils. On July 20, the 45th day after rice transplanting, about 1.5% (6.7 mg kg<sup>-1</sup>) of extractable P was W-P in CP-0 in Daegok (LS), which phosphorus was accumulated highly and the mixture was not applied, and then dramatically decreased to 5.0, 2.7 and 1.4 mg kg<sup>-1</sup> by applying 20, 40 and 60 Mg ha<sup>-1</sup> the mixture. The effect of the mixture application on reducing water solubility of soil phosphorus was continued during the whole rice cultivation. The transfer of P in water draining from agricultural land to surface waters can contribute to euthrophication, toxic algal blooms, and a general deterioration of water quality 14). Concern over agricultural P pollution has been heightened recently, because of the risks from aquatic organisms to human health, notably the potential for neurological damage from outbreaks of the dinoflagelatte P fieteria piscidia in the Chesapeake Bay area of eastern USA<sup>15)</sup>. Although the amounts of P transferred from the land are small in agronomic terms, typically <1 kg ha<sup>-1</sup> yr<sup>-1</sup> in general, low concentrations of P in excess of 35 µg L<sup>1</sup> can contribute to euthrophication 16). In these field testes, the maximum rice yields were achieved at the rate of 36 Mg ha<sup>-1</sup> of the mixture in the sites<sup>10)</sup>. Water soluble phosphorus was reduced by 75-80% in this level of mixture application on July 20 in the site. This tendency was kept during the whole rice cultivation, even though there was the variation on the reducing efficiency of water soluble phosphorus content depending on rice growing stage. In contrast with decreasing W-P content, Ca-P content was increased significantly with the mixture application (Table 1). The CaSO4 in the mixture displaces H<sup>+</sup> from weakly acidic organic groups and clay surfaces, or generates H<sup>†</sup> by displacing  $A^{3+}$  and  $Fe^{3+}$  oxides from the soil exchange complex  $^{17}$ . The

added H<sup>+</sup> reacted with soluble phosphorus to form phosphorus compounds not readily extracted with water. This is evidenced by the effect of the mixture on soil extractable phosphorus fractions (Table 1). The difference in the distribution of the P fractions depends on the kinds of phosphate fertilizer applied, the soil mineralogical characteristics, the soil pH and other soil factors. Ca-P is the predominant form of P in alkaline soils while Fe-P and Al-P predominate in acidic soils. In acid soils, the original superficial, loosely bound phosphates [Fe and Al oxides, available to plant] are converted gradually via a reprecipitation process into highly crystalline Fe-P and Al-P [not available to plant]. Different with upland soil, rice paddy is flooded for more than 100 days and therefore the soil is changed aerobic state into anaerobic condition. Iron is of a ferric type in aerobic conditions, with low solubility, and is reduced to ferrous iron in anaerobic conditions with high mobility<sup>19)</sup>. As a result, the high solubility of P and iron in this paddy condition might affect the decrease in the Fe-P concentration during rice cultivation. Amendment with the mixture resulted in a shift from W-P and Fe-P fractions to Ca-P and Al-P under flooded condition. The amended soil showed a little increase in pH following the increase of the mixture<sup>10)</sup>: pH 5.7 in CP-0 increased to 6.2 by 60 Mg ha<sup>-1</sup> of the mixture (CP-60) at the harvesting in Daegok (LS).

Table 1. Changes of extractable phosphorus fraction in surface soil during rice cultivation (Unit: mg kg<sup>-1</sup>)

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Sampling data	Р	Mixture	Application	Level	(Mg ha <sup>-1</sup> )	LSD <sub>0.05</sub>
	fraction	0	20	40	60	
20 July 1998	Ca-P	33	44	76	86	15
	Al-P	314	369	409	438	37
	Fe-P	230	163	121	107	41
	ExtP <sup>1)</sup>	584	584	614	642	45
19 Aug. 1998	Ca-P	30	69	77	82	19
	Al-P	308	364	403	422	33
	Fe-P	123	122	117	112	ns
	ExtP	468	563	606	627	<i>7</i> 9
22 Sep. 1998	Ca-P	32	44	74	93	18
	Al-P	296	349	394	419	35
	Fe-P	138	135	125	115	ns
	ExtP	472	536	601	636	59
15 Oct. 1998	Ca-P	25	48	59	65	18
	Al-P	285	307	372	398	52
	Fe-P	145	120	117	107	27
	ExtP	461	481	556	579	71

Ext.-P means extractable phosphorus content which calculated by the sum of Ca-P, Al-P and Fe-P.

This indicates that Ca<sup>2+</sup> content of the mixture is the first factor and the neutralizing capacity is the secondary factor in shifting a sizable portion of the soil phosphorus to the calcium-bound phosphorus fraction.

The available phosphorus contents in the soil, detected using two different methods, increased with the increase in the quantity of the mixture added during rice cultivation (Table 2), due to the high content of available phosphorus in the coal ash supplied to the soil. The mixture contained about 700 mg kg<sup>-1</sup> of available P<sub>2</sub>O<sub>5</sub>, which calculated from 1323 and 73 mg kg<sup>-1</sup> of available P<sub>2</sub>O<sub>5</sub> in coal ash and phosphogypsum, respectively<sup>11)</sup>, and around 14, 28 and 42 kg ha-1 of available P2O5 were supplied by the application of 20, 40 and 60 Mg ha<sup>-1</sup> of the mixture, respectively. In addition, soil phosphate might be desorbed by the high content of silicate. Silicate enhances the availability of soil phosphate by displacing P from ligand exchange sites 18) and by inhibiting P sorption for the same specific anion exchange site<sup>20),21),22)</sup>. This was evidenced by the increase in the available P2O5 contents, determined by Lancaster method1),

Table 2. Changes of available phosphate contents in surface soil during rice cultivation. (Unit:  $mg P_2O_5 kg^{-1}$ )

Analysis method	Sampling data	Mixture	Application	Level	(Mg ha <sup>-1</sup> )	ICD	
		0	20	40	60	- LSD <sub>0.05</sub>	
Mehlich 3	July 20	182	207	280	342	43	
	Aug. 19	172	185	262	296	35	
	Sep. 22	175	188	216	276	26	
	Oct. 15	164	219	238	293	39	
Lancaster	July 20	151	215	244	302	42	
	Aug. 19	159	202	229	250	33	
	Sep. 22	1 <b>7</b> 1	182	220	250	29	
	Oct. 15	161	202	239	293	34	

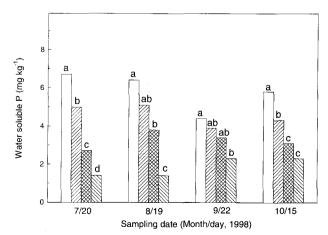


Fig 1. Changes of water soluble phosphorus in surface soil during rice cultivation

<sup>2)</sup> ns means not significant within LSD  $_{0.05}$ 

in the soils treated with the silicate fertilizer (209 mg kg<sup>-1</sup> in Daegok) compared with CP 0 (161 mg kg<sup>-1</sup> in Daegok)<sup>10)</sup>. The mixture contained about 556 mg kg<sup>-1</sup> of available SiO<sub>2</sub>, which estimated from 1100 and 12 mg kg<sup>-1</sup> of available SiO<sub>2</sub> in coal ash and phosphogypsum, respectively<sup>11)</sup>, and around 11, 22 and 33 kg ha<sup>-1</sup> of available SiO<sub>2</sub> was applied by 20, 40 and 60 Mg ha<sup>-1</sup> of the mixture, respectively. The available SiO<sub>2</sub> content increased significantly following the mixture application<sup>10)</sup>: it was 38 mg kg<sup>-1</sup> in CP-0 in Daegok (LS), at the harvesting time and then increased 117 mg kg<sup>-1</sup> by 60 Mg ha<sup>-1</sup> of the mixture (CP-60). This increase might increase plant available phosphate content in soil during the investigation period.

#### CONCLUSION

From an agronomic aspect, the mixture (50:50, wt wt<sup>-1</sup>) would be a desirable form to use on reducing phosphorus export from soils where phosphorus loss in surface runoff is a concern and on increasing rice productivity. The mixture reduced water-soluble phosphorus with increasing plant-available phosphorus. Furthermore, since coal ash may contain generally boron, selenium and other trace element concentrations that may be toxic to plants and animals if applied in large amounts, the mixture of coal ash and phospho-gypsum (50:50, wt wt<sup>-1</sup>) would be a very good alternative to decrease the potential for boron toxicity of fly ash and to supply silica and calcium elements for rice.

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