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Effect of Phospho-gypsum on reduction of methane emission from rice paddy soil

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ABSTRACT: Phospho-gypsum, a primary waste by-product in phosphate fertilizer manufacturing industry and a potential source of electron acceptors, such as mainly of sulfate and a trace amount of iron and manganese oxides, was selected as soil amendment for reducing methane (CH_4) emissions during rice cultivation. The selected amendment was added into potted soils at the rate of 0, 2, 10, and 20 Mg ha^{-1} before rice transplanting. CH_4 flux from the potted soil with rice plant was measured along with soil Eh and floodwater pH during the rice cultivation period. CH_4 emission rates measured by closed chamber method decreased with increasing levels of phospho-gypsum application, but rice yield markedly increased up to 10 Mg ha^{-1} of the amendment. At this amendment level, total CH_4 emissions were reduced by 24% along with 15% rice grain yield increment over the control. The decrease in total CH_4 emission may be attributed due to shifting of electron flow from methanogenesis to sulfate reduction under anaerobic soil conditions.

Key Words: CH_4 emission, electron acceptor, phospho-gypsum, rice

INTRODUCTION

Wetland rice agriculture is a major source of biogenic methane (CH_4) that accounts for approximately 25% (on an average 60 Tg CH_4 y^{-1}) of the global anthropogenic CH_4 emissions to the atmosphere (Neue and Roger, 1993). The contribution of this CH_4 emissions from rice fields is expected to increase by about 1.1% yr^{-1} (Anastasi et al., 1992) due to extension of flood water rice cultivation area at a rate of 1% yr^{-1} to fulfil the rice demand of the expanding human populations (Minami 1994, Dubey, 2001). Therefore, feasible soil amendment should be applied in floodwater paddy soils to sustain rice productivity as well as reducing CH_4 emissions during rice cultivation.

The biogenic CH_4 is mostly produced from the anaerobic decomposition of organic compounds by methanogenic archaea under highly reduced conditions in floodwater rice field, where CO_2 acts as inorganic electron acceptor (Garica et al., 2000, Hattori et al., 2001). After flooding of rice field soils, common electron donors such as acetate and hydrogen are present in excess for anaerobic respiration and methanogenesis occurs in parallel to iron and sulfate reduction (Achtnich et al., 1995; Patrick et al., 1978; Roy et al., 1997). When electron donors for microbial respiratory processes become limiting, methanogenesis could be suppressed by supplementing alternative electron acceptors such as ferric or sulfate (Achtnich et al., 1995, Lovely et al., 2004), which may result a combination of inhibition effects and competitive effects with different microorganisms for the common electron donors (Achtnich et al., 1995; Jakobsen et al., 1981). It has been recognized that sulfate reduction provides 1.5 times more energy for sulfate reducers than methanogens (Capone et al., 1988), and, therefore, CH_4 emission

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could be decreased by increasing sulfate concentration in rice paddy soils (Bartlett et al., 1985, 1987). The mechanism behind this could be the competition between CH_4 producing bacteria (methanogens) and sulfate reducing bacteria for the same substrate (Kristjansson et al., 1982; Schonheit et al., 1982).

Phosphogypsum is a primary waste by-product, which is generated from the phosphoric acid and phosphate fertilizer industry (US Environmental Protection Agency, 1993). It consists mainly of calcium sulfate di-hydrate (pH around 3.0) and a trace amount of radionuclides, which limits its use in agriculture. However, phosphogypsum may be used in wetland as well as upland agricultural crop farming as soil amendment and fertilizer source within the range 1 to 10 Mg ha^{-1} depending on specific plant nutrients requirements, soil properties and crop production goals (Abrol et al., 1985, Beaton et al., 1985; Fox and Blair, 1986, Brady et al., 1990, Arman et al., 1990). Phosphogypsum may increase the availability of Ca, Mg, K, P, Fe and Mn (Singh et al., 1990, Khalil et al., 1990). In addition, phosphogypsum may reduce aluminum toxicity in the rooting zone of crop plants due to its self-liming effect (Alba et al., 1990, Carbonell et al., 1999).

As Korean arable soil is generally characterized by low levels of calcium and sulfur (RDA 1999; Kim et al. 1997), therefore, phospho-gypsum, which contains over 90% of $CaSO_4 \cdot 2H_2O$, could be a good soil amendment to supplement mainly calcium and sulfur for rice cultivation. The high content of sulfate in phosphogypsum will act as electron acceptor and might suppress methanogenesis by accelerating the activity of sulfate-reducing bacteria for the common substrates (Hori et al, 1990, 1993, Lindau et al., 1994; Denier vander Gon and Neue, 1994 ; Corton et al., 2000).

In this study, we investigated the effects of phosphogypsum on suppression of CH_4 emissions from anaerobic paddy soil conditions considering rice growth and soil properties.

Materials and Methods

Pot preparation and rice cultivation

The experiment was conducted in pot culture under the greenhouse condition. Soil was collected from a rice paddy field, air-dried, sieved (< 10 mm) and filled into Wagner pots (1/2000 a size) with 1.1 g cm^{-3} of bulk density. The physico-chemical characteristics of the collected soils were mentioned in Table 1. The dried ground rice straw was added at the rate of 30 Mg ha^{-1} and mixed mechanically within 10 cm depth of the potted surface soil prior to flooding. The pots were arranged in a completely randomized design and each treatment was carried out in triplicate. Dongjinbyeo was selected as rice cultivar and fertilized with the rate of $N\text{-}P_2O_5\text{-}K_2O$ = 110-45-58 kg ha^{-1} following as Korean standard rice cultivation guideline (RDA 1999). The powder form phospho-gypsum was selected as soil amendment (Table 2) and applied with 0, 2, 10, and 20 Mg ha^{-1} one day before rice transplanting. Simultaneously, the basal chemical fertilizers were applied into potted soils before rice transplanting according to: 55 kg N ha^{-1} as urea, 45 kg P_2O_5 ha^{-1} as super phosphate and 40.6 kg K_2O ha^{-1} as potassium chloride. Tillering fertilizer (22 kg N ha^{-1}) was added on 15th day after transplanting and panicle fertilizer (33 kg N ha^{-1}, 17.4 kg K_2O ha^{-1}) on 45th day after transplanting. Water level was controlled around 5-7 cm depth during the cropping season and rice was harvested after passing 120 days. At the harvesting stage, plant growth and yield characteristics were investigated by Korean standard (RDA, 1995).

Measuring CH_4 flux, soil redox potential and floodwater pH

CH_4 flux from the rice planted pot was measured by closed chamber method (Rolston, 1986). The air gas samples from the transparent poly acrylic plastic chamber (Diameter 23.88 cm, and height 100 cm) were collected by 50 ml gastight syringes at 0, and 30 minutes intervals after chamber placement over the rice planted pots. Gas sampling was carried out du-

Table 1. Chemical properties of soil used in the experiment

Parameters	Mean	SD
pH (1:5, H_2O)	5.1	0.07
Organic matter (g kg^{-1})	28.3	0.37
Available P_2O_5 (mg kg^{-1})	70	13.6
Available SiO_2 (mg kg^{-1})	85.6	2.15
Ex. Cations ($cmol^+$ kg^{-1})		
K	0.45	0.10
Ca	4.8	1.30
Mg	1.6	0.44
Soil texture	Silt loam	

ring 2.00-3.00 pm with recording air temperature inside the chamber. CH_4 concentrations in the collected air samples were measured by Gas Chromatography (Shimadzu, GC-2010, Tokyo) packed with Porapak NQ column (Q 80-100 mesh) and a flame ionization detector (FID). The temperatures of column, injector and detector were adjusted at 100°C, 200°C, and 200°C respectively. Helium and H_2 gases were used as carrier and burning gases, respectively. A closed-chamber method was used to estimate methane fluxes from each treatment (Rolston, 1986). Total CH_4 flux for the entire crop period were computed by the formula (Singh et al., 1999), total CH_4 flux = Σ_i^n (Ri x Di), where Ri is the rate of methane flux (g m^{-2} d^{-1}) in the ith sampling interval, Di is the number of days in the i th sampling interval, and n the number of sampling intervals.

The changes in soil redox potential (Eh) and floodwater pH were measured as a routine work by Eh meter (PRN-41, DKK-TOA Corporation, Tokyo) and pH meter (Orion 3 star, Thermo electron corporation, Tokyo), respectively, during rice cultivation. Wet soil samples were collected at different rice growth stages to determine the concentration of iron compounds.

Table 2. Chemical properties of phospho-gypsum used in the experiment

Parameters	Mean
pH (1:5 with H_2O)	3.1
Chemical composition (%, wt/wt^{-1})	
Al_2O_3	0.21
CaO	30.6
$FeSO_3$	0.15
MnO	0.05
P_2O_5	0.80
SiO_2	10.0
SO_3	46.7
1M NH_4 OAc extractable ($cmol^+$ kg^{-1})	
Ca	74.0
K	0.15
Mg	0.03
Iron concentration (mg Fe kg^{-1})	
Active	62.1
Free	83.8
Water soluble	10.3
Manganese concentration (mg Mn kg^{-1})	
Active	5.8
Free	9.5
Water soluble	2.7
Water soluble SO_4^{2-} (mg kg^{-1})	3261

Chemical Analysis

Soil samples were collected from the surface layer (0-15 cm depth) after rice harvesting, air-dried and sieved (< 2 mm) and analysed for pH (1:5 water extraction), organic matter content (Wakley and Black method; Allison 1965), levels of exchangeable Ca^{2+}, Mg^{2+}, and K^+ (1 M NH_4-acetate pH 7.0, AA, Shimadzu 660, Kyoto), and available silicate content (1 M Na-acetate pH 4.0, UV spectrometer). The available phosphate content was determined using the Lancaster method (RDA 1988). The total soil iron, active iron and free iron concentrations were determined by modified acid (12 M HCl) digestion, acid ammonium oxalate in darkness and citrate dithionite bicarbonate dissolution procedures, respectively, (Loeppert and Inskeep, 1996). Finally, the dissolved iron and manganese concentrations were quantified by atomic absorption spectroscopy (AA, Shimadzu 660, Kyoto). Water soluble NO_3 and SO_4 concentrations were analyzed by Ion Chromatography System (ICS-3000, Dionex). Chemical composition of the selected fly ash was analyzed by X-ray diffraction method (XRD-6000, Shimadzu, Kyoto). Other chemical properties were analyzed with the same methods used in soil.

Statistical analysis

Statistical analyses were conducted using SAS software (SAS Institute, Anonymous 1990). Rice growth and yield, soil properties and methane emission data were subjected to the analysis of variance and regression. Fisher's protected least significant difference (LSD) was calculated at the 0.05 probability level for making treatment mean comparisons.

Results and discussion

CH_4 emission rates during 21-35 days after rice transplanting were within the range 14-34 mg m^{-2} hr^{-1}, which increased gradually with the development of soil reductive condition and rice plant growth (Fig. 1). The peak CH_4 emission rate 172 mg m^{-2} hr^{-1} was recorded from the control treatment on 63 days after rice transplanting (DAT), whereas phospho-gypsum amended soils with rice plant showed methane peaks 163, 141 and 129 mg m^{-2} hr^{-1} on 70 DAT with 2, 10 and 20 Mg ha^{-1} amendments, respectively (Fig. 1). On an average, significant CH_4 emission rates were observed in all treatments during 56-84 DAT, which could be due to higher availability of organic carbon (Denier van der Gon et al., 1993, Yagi et al., 1994) from the decomposition of the applied organic matter and the development of intense reducing conditions (Eh value -229 to -243 mV) in the rice rhizosphere (Adhya et al., 1994) and enhanced conductivity of CH_4 via rice plant (Mariko et al., 1991). The CH_4 emission rates showed a decreasing trend in all treatments from day 91 onwards and finally dropped to 15.8, 14.2, 11.3 and 10.2 mg m^{-2} hr^{-1} with 0, 2, 10 and 20 Mg ha^{-1}, phospho-gypsum applications respectively, one week before harvesting (Fig. 1). The decrease in

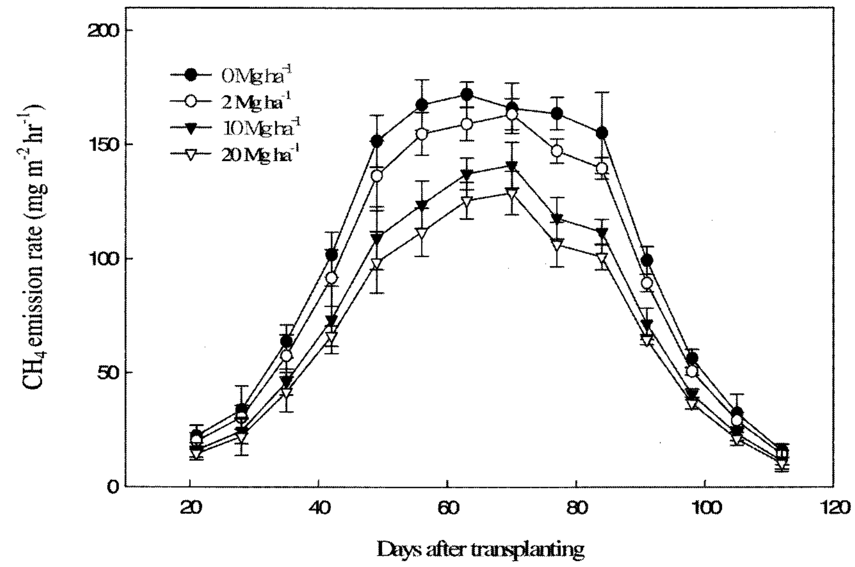

Fig. 1. Changes of CH_4 emission patterns in floodwater paddy soils amended with phospho-gypsum during rice cultivation.

Table 3. Growth and yield characteristics of rice with different levels of phospho-gypsum application at harvesting stage

Parameters	Application levels (Mg ha^{-1})				LSD$_{0.05}$[1]
	0	2	10	20	
Plant height	79.9	83.8	85.5	76.1	3.5
Tiller no. per plant	13.6	14.3	15	9.67	1.2
Leaf area index	1.8	1.8	1.9	1.6	0.08
Shoot biomass (g plant^{-1})	33.2	33.9	35.3	31.6	1.5
Root biomass (g plant^{-1})	8.6	8.7	8.9	8.1	0.19
Root volume (cm^3 hill^{-1})	38.4	40.1	45.8	40.8	1.7
Root porosity (%)	18.7	21.5	26.2	22.5	1.5
Total dry matter production (g plant^{-1})[2]	74.3	76.9	81.8	69.0	2.0
Harvest index (%)[3]	43.7	44.7	46.0	42.4	0.75
Panicle number per plant	15.0	16.3	18.3	13.7	1.3
Number of grains per panicle	80.1	83.5	89.6	79.3	3.9
Ripened grains (%)	82.4	84.5	88.1	79.7	3.1
1000 grains weight (g)	23.8	24.7	25.9	23.4	0.55

1) LSD$_{0.05}$: Least significant difference at 5% level, 2) Total dry matter production is the summation of grain dry weight + shoot dry weight + root dry weight, 3) Harvest index (%) is the grain yield / total dry matter yield X 100.

CH_4 emissions at the crop maturity stage could be due to aging of rice plants and decreased photosynthetic assimilates supply for CH_4 production as supported by Nouchi (1994) and Aulakh et al. (2000).

The total seasonal CH_4 flux was estimated 236 g m^{-2} from the control treatment, which decreased to 215 (9% reduction), 179 (24% reduction), and 161 (32 % reduction) g CH_4 m^{-2} under 2, 10 and 20 Mg ha^{-1} phospho-gypsum applications, respectively (Fig.3). This decrease in CH_4 emissions could be due to mainly of increased sulfate concentration along with iron and manganese compounds in soil released from the applied phospho-gypsum (Table 4), which acted as electron acceptors and suppressed methanogenesis (Van Breemen and Feijtel, 1990; Van der Gon and Neue, 1994). Lindau et al. (1998) found that phosphogypsum application levels 2.5, 5.0 and 10 Mg ha^{-1} in Louisiana rice paddy soils decreased total CH_4 emissions 47, 46 and 51%, respectively, over the 84 days cropping season, even though grain yield and total biomass means were significantly lower than the control mean. Lueders and Friedrich (2002) also reported that the total CH_4 emission was reduced by 69% with gypsum amendment (0.15%) in Italian rice paddy soil.

In this study, soil redox potential (soil Eh) values decreased rapidly after flooding and stabilized within the range -224 mV to -243 mV during 56-84 DAT, thereafter soil Eh increased and stabilized around -100 mV one week before rice harvesting (Fig. 2). However, no significant differences were found among the treatments. The high Ca^{2+} content in phosphogypsum and the decomposition rate of the applied rice straw (30 Mg ha^{-1}, about 6 times higher than the normal practice 5 Mg ha^{-1}) might have accelerated to decrease the soil Eh level under flooded conditions, as supported by Nozoe et al. (1999). On the other hand, floodwater pH increased gradually with the increasing application levels of acidic (pH 3.1) phospho-gypsum until 84 days of rice transplanting, then decreased markedly at the late rice maturation stage (Fig. 2). This initial increase in floodwater pH might be due to high dissolution of calcium and reduction of the dissociated sulfate from phospho-gypsum into sulfide under anoxic conditions. However, re-oxidation of this sulfide into sulfate at the late rice maturation

Table 4. Chemical properties of soil after rice harvest under different levels of phospho-gypsum application

Parameters	Application levels (Mg ha^{-1})				$LSD_{0.05}$
	0	2	10	20	
pH (1:5 with H_2O)	6.1	5.9	5.6	5.5	0.07
Organic matter (g kg^{-1})	36.0	38.0	40.0	33.0	2.25
Available P_2O_5 (mg kg^{-1})	79.0	93.0	107.0	122.0	14.9
Available SiO_2 (mg kg^{-1})	67.0	83.0	120.0	162.0	28.7
Ex. Cations ($cmol^+$ kg^{-1})					
Ca	6.0	8.4	10.9	13.0	0.38
Mg	1.1	1.3	1.6	1.8	0.09
K	1.0	1.2	1.4	1.5	0.08
Iron (g kg^{-1})					
Total	21.7	26.5	27.3	30.3	1.25
Active	9.4	10.4	10.7	10.8	0.46
Free	3.8	4.1	4.4	4.8	0.11
Water soluble (mg kg^{-1})	4.5	9.6	12.7	17.3	0.59
Manganese (mg Mn kg^{-1})					
Total	55.0	71.0	78.0	86.0	4.21
Active	28.0	40.0	61.0	65.0	3.33
Free	127.0	140.0	143.0	144.0	4.54
Water soluble SO_4^{2-} (mg kg^{-1})	22.0	373.0	1242	1841	352.5

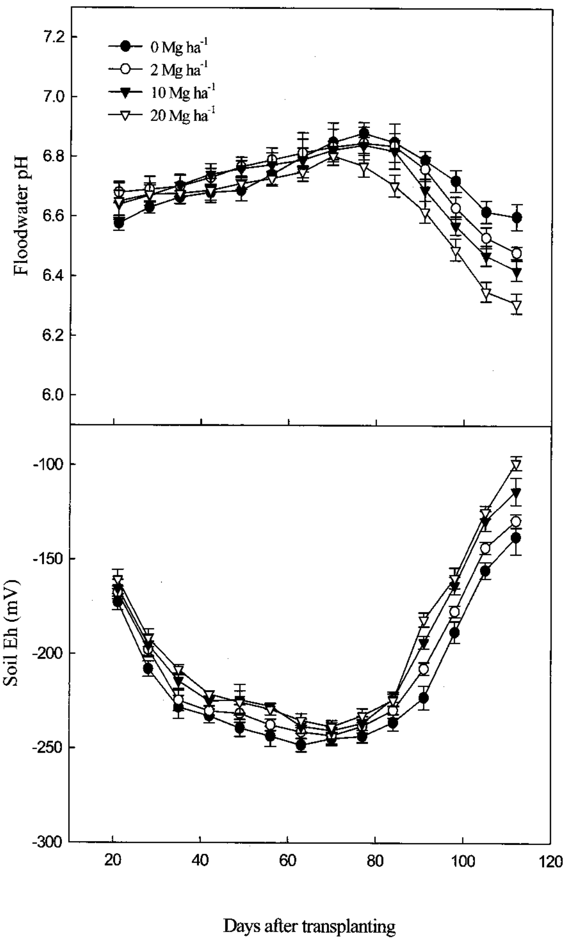

Fig. 2. Rice grain yield and total CH_4 emission in paddy soils amended with phospho-gypsum during rice cultivation

stage might have released free hydrogen ion, which significantly decreased soil pH at rice harvesting stage (Table 4). This inverse relationship between the changes in soil Eh and pH was supported by Nozoe et al. (1999).

The concentrations of sulfate, iron and manganese compounds in soil significantly increased with the application levels of phosphogypsum (Table 4), which might have acted as electron acceptors, and thereby, suppressed CH_4 production as well as CH_4 emissions during rice cultivation. In addition, the high concentrations of sulfate and sulfide in the amended soil might have caused toxic effects on methanogens (Van Breemen and Feijtel, 1990; Van der Gon and Neue, 1994). The available silicate and phosphate concentration significantly increased in the amended soils (Table 4), which may be due to high content of silicate and phosphate in phospho-gypsum (Table 2) as supported by Lee et al. (2002). The organic matter level in soil after rice harvest significantly increased (Table 4) with 2-10 Mg ha^{-1} phospho-gypsum applications, probably due to stimulation of rice growth and dry matter production (Table 3).

Rice grain yield also significantly increased with the increasing levels of phospho-gypsum applications up to 10 Mg ha^{-1}, thereafter, decreased markedly with 20 Mg ha^{-1} (Fig. 3). Using the quadratic yield equation model (rice grain yield ,Y = 32.9 + 1.17 x PG -0.067

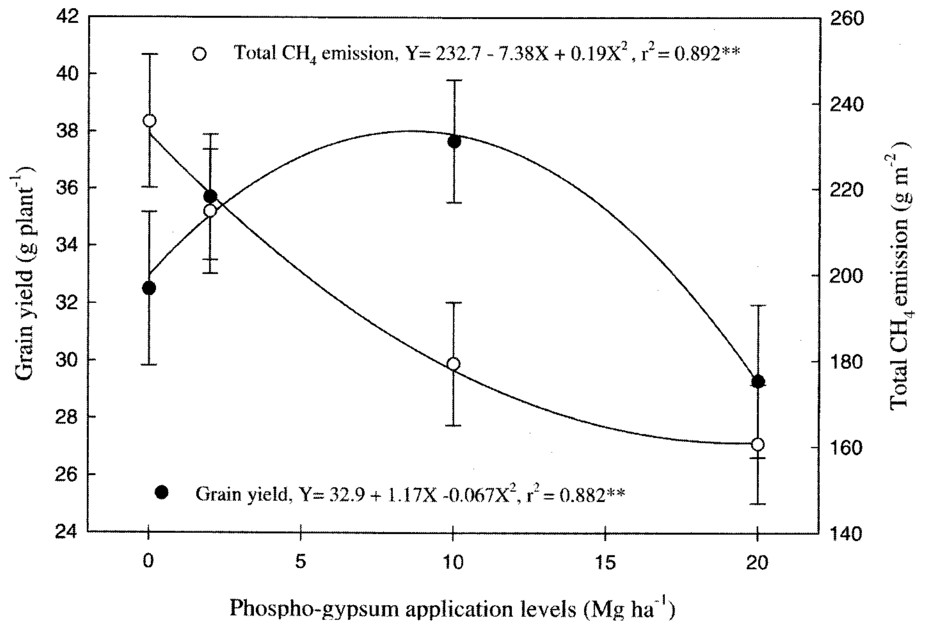

Fig. 3. Rice grain yield and total CH_4 emission in paddy soils amended with phospho-gypsum during rice cultivation

Table 5. Correlations of seasonal CH_4 emissions with rice plant growth, yield and soil properties at harvesting stage (n = 15)

Plant characteristics		Soil characteristics	
Parameters	Correlation coefficient (r)	Parameters	Correlation coefficient (r)
Plant height	0.236	Soil pH	0.364
Tiller number	0.610*	Organic carbon	0.352
Leaf area index	0.589*	Available P_2O_5	-0.549*
Shoot biomass	0.197	Available SiO_2	-0.642**
Root biomass	0.395	Exchangeable Ca	-0.796***
Root volume	-0.560*	Exchangeable Mg	-0.676**
Root porosity	-0.702**	Exchangeable K	-0.697**
Total biomass	0.218	Total Fe	-0.516*
Panicle number	-0.062	Active Fe	-0.543*
Grain number	-0.017	Free Fe	-0.687**
Ripened grains	-0.174	Total Mn	-0.668**
1000 grain wt.	-0.057	Active Mn	-0.684**
Grain yield	-0.174	Free Mn	-0.580
Harvest index	-0.181	Water soluble SO_4	-0.793***

*, ** and *** denotes significant at 5%, 1% and 0.1% levels, respectively.

PG^2; $r^2 = 0.882^*$, where yield is expressed as g $plant^{-1}$ and PG is phospho-gypsum application rate as Mg ha^{-1}), the maximum grain yield 37.9 g $plant^{-1}$ (15.7% increase over the control) was estimated with 10 Mg ha-1 application of phospho-gypsum (Fig. 3). Sohn et al. (2007) reported that brown rice yield was increased 5-12% with 3 Mg ha^{-1} phospho-gypsum application as compared to control in two different sites in Korea. Lee et al. (2002) found that rice grain yield was increased by 15.3% with fly ash-gypsum mixture (3 : 1) at 40 Mg ha^{-1} application level. Van der Gon and Neue (1994) also reported that gypsum application (6.7 tons ha^{-1}) significantly reduced (55-70%) CH_4 emissions from rice field in Philippine, but there was no significant difference for grain yield between the amended and control plots.

In our study, plant height, tiller number, leaf area index, shoot biomass, and root biomass were positively correlated with seasonal CH_4 flux, whereas root volume, root porosity, grain yield and harvest index were negatively correlated (Table 5), which was supported by Gogoi et al. (2005); Singh et al. (1999); (Corton et al 2000). The soil organic carbon and pH were positively correlated with total seasonal CH_4 flux (Gogoi et al., 2005), whereas water soluble sulfate, soil iron and manganese compounds, available phosphate and silicate content in soil showed strong negative correlations with total seasonal CH_4 flux (Table 5). Therefore, the effects of sulfate ion, iron and manganese oxides released from the applied phospho-gypsum might have acted as oxidizing agents as well as electron acceptors and ultimately reduced total CH_4 emissions during rice cultivation.

Conclusion

Phospho-gypsum is an effective soil amendment on reducing CH_4 emissions as well as increasing rice grain productivity. The total seasonal CH_4 emission was reduced by 24% along with 15% yield increment over the control with 10 Mg ha^{-1} application level. The suppression of CH_4 emission may be attributed due to high concentration of sulfate ion along with iron and manganese compounds in the amended soil, which acted as electron acceptors.

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