

## Suppression of Methane Emission from Rice Paddy Soils with Fly ash Amendment

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**ABSTRACT:** Fly ash, a by-product of the coal-burning industry, and a potential source of ferro-alumino-silicate minerals, which contains high amount of ferric oxide and manganese oxide (electron acceptors), was selected as soil amendment for reducing methane (CH<sub>4</sub>) emission during rice cultivation. The fly ash was applied into potted soils at the rate of 0, 2, 10, and 20 Mg ha<sup>-1</sup> before rice transplanting. CH<sub>4</sub> flux from the potted soil with rice plants was measured along with soil Eh and floodwater pH during the cropping season. CH<sub>4</sub> emission rates measured by closed chamber method decreased gradually with the increasing levels of fly ash applied, but rice yield significantly increased up to 10 Mg ha<sup>-1</sup> application level of the amendment. At this amendment level, total seasonal CH<sub>4</sub> emission was decreased by 20% along with 17% rice grain yield increment over the control. The decrease in total CH<sub>4</sub> emission may be attributed due to suppression of CH<sub>4</sub> production by the high content of active and free iron, and manganese oxides, which acted as oxidizing agents as well as electron acceptors. In conclusion, fly ash could be considered as a feasible soil amendment for reducing total seasonal CH<sub>4</sub> emissions as well as maintaining higher grain yield potential under optimum soil nutrients balance condition.

**Key Words:** Fly ash, CH<sub>4</sub> emission, electron acceptor, rice

### INTRODUCTION

Methane (CH<sub>4</sub>) is an active trace greenhouse gas, which may affect the photochemical reactions in the atmosphere due to its radiative effects<sup>1)</sup>. The present atmospheric concentration of CH<sub>4</sub> remains around 1.8 ppmV<sup>2)</sup>, which may lead to an increase in global mean surface temperature<sup>3)</sup>. Wetland rice agriculture is an important source of CH<sub>4</sub> that accounts for 20-26 % of the global anthropogenic methane emissions to the atmosphere<sup>4)</sup>. To sustain rice productivity as well as reducing CH<sub>4</sub> emissions from floodwater rice paddy soils fundamental countermeasures proposed so far are to maintain the plow layer in an oxidative condition<sup>5)</sup>, which is dependent on the amount of oxidizing a-

gents exists in the soil. Methane production results from the anaerobic decomposition of organic compounds where CO<sub>2</sub> acts as inorganic electron acceptor. Microorganisms which are capable of reducing the energetically more favourable electron acceptors such as NO<sub>3</sub><sup>-</sup>, Mn<sup>4+</sup>, Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> may outcompete those (methanogens) using the less favourable electron acceptor such as CO<sub>2</sub><sup>6)</sup>. Therefore, methane production could be reduced by supplying alternative electron acceptors like NO<sub>3</sub><sup>-</sup>, Mn<sup>4+</sup>, Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup><sup>7,8)</sup>.

Fly-ash, a by-product of the coal-burning industry, produced ca. 3.7 million tons in 1997 and projected to increase about 6 million tons by 2010<sup>9)</sup>, as coal is the primary energy source in Korea. Fly-ash has already recognized as a potential soil amendment to neutralize soil acidity and beneficial for plant growth<sup>10,11)</sup>, because it contains high amount of mineral nutrients such as Si, Ca, K, Mg, Mn, etc.<sup>10)</sup>. Since Korean paddy soils

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generally contain low level of available silicate<sup>12)</sup>, and rice plant requires large amounts of silicon for healthy growth and desirable yield, therefore, fly ash could be a feasible soil amendment to improve rice productivity. In addition, fly ash, being an amorphous mixture of ferro-alumino-silicate minerals, contains high amount of silica, iron and manganese oxides, therefore, alkaline fly ash might be a good soil amendment to suppress methane emission along with improving soil nutrient status in acidic paddy soil.

In this study, we investigated the effects of different levels of fly ash applications on CH<sub>4</sub> emissions, rice plant growth and soil properties during rice cultivation.

## 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<sup>-3</sup> of bulk density. The physico-chemical characteristics of the collected soils were mentioned in Table 1. The powder form fly ash was selected as soil amendment (Table 2) and applied with 0, 2, 10, and 20 Mg ha<sup>-1</sup> one week prior to flooding. Simultaneously, dried ground rice straw was added at the rate of 30 Mg ha<sup>-1</sup> and mixed mechanically within 10 cm depth of the potted surface soil. The pots were arranged in a completely randomized design and each treatment was carried out in triplicate. Dongjinbyeon was selected as rice cultivar and fertilized with the rate of N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O = 110-45-58 kg ha<sup>-1</sup> following as Korean standard rice cultivation guideline<sup>12)</sup>. The basal chemical fertilizers applied into potted soils 2 days before rice transplanting were as follows: 55 kg N ha<sup>-1</sup> as urea,

**Table 1. Chemical properties of soil used in the experiment**

Parameters	Mean	SD
pH (1:5, H <sub>2</sub> O)	5.1	0.07
Organic matter (g kg <sup>-1</sup> )	28.3	0.37
Available P <sub>2</sub> O <sub>5</sub> (mg kg <sup>-1</sup> )	70	13.6
Available SiO <sub>2</sub> (mg kg <sup>-1</sup> )	85.6	2.15
Ex. Cations (cmol <sup>+</sup> kg <sup>-1</sup> )		
K	0.45	0.10
Ca	4.8	1.30
Mg	1.6	0.44
Soil texture	Silt loam	

45 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup> as super phosphate and 40.6 kg K<sub>2</sub>O ha<sup>-1</sup> as potassium chloride. Tillering fertilizer (22 kg N ha<sup>-1</sup>) was added on 15<sup>th</sup> day after transplanting and panicle fertilizer (33 kg N ha<sup>-1</sup>, 17.4 kg K<sub>2</sub>O ha<sup>-1</sup>) on 45<sup>th</sup> 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<sup>13)</sup>.

### Measuring CH<sub>4</sub> flux, soil redox potential and floodwater pH

CH<sub>4</sub> flux from the rice planted pot was measured by closed chamber method<sup>14)</sup>. The air gas samples from the transparent poly acrylic plastic chamber (Diameter 23.88 cm, and height 100 cm) were collected by 50 ml

**Table 2. Chemical properties of fly ash used in the experiment**

Parameters	Mean
pH (1:5 with H <sub>2</sub> O)	8.5
Chemical composition (% wt/wt)	
Al <sub>2</sub> O <sub>3</sub>	24.7
CaO	6.2
Fe <sub>2</sub> O <sub>3</sub>	7.7
MnO	0.09
MgO	0.70
K <sub>2</sub> O	1.07
P <sub>2</sub> O <sub>5</sub>	0.88
SiO <sub>2</sub>	55
SO <sub>3</sub>	1.06
1M NH <sub>4</sub> OAc extractable (cmol <sup>+</sup> kg <sup>-1</sup> )	
Ca	18.6
K	0.19
Mg	0.6
Iron concentration (mg Fe kg <sup>-1</sup> )	
Active	1330
Free	1307
Water soluble	16.2
Manganese concentration (mg Mn kg <sup>-1</sup> )	
Active	19.4
Free	9.9
Water soluble	0.2
Water soluble NO <sub>3</sub> <sup>-</sup> (mg kg <sup>-1</sup> )	1.9
Water soluble SO <sub>4</sub> <sup>2-</sup> (mg kg <sup>-1</sup> )	35

gastight syringes at 0, and 30 minutes intervals after chamber placement over the rice planted pots. Gas sampling was carried out during 2.00-3.00 pm with recording air temperature inside the chamber. CH<sub>4</sub> 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<sub>2</sub> gases were used as carrier and burning gases, respectively. A closed-chamber method was used to estimate methane fluxes from each treatment<sup>(14)</sup>. Total CH<sub>4</sub> flux for the entire crop period were computed by the formula<sup>(15)</sup>, total CH<sub>4</sub> flux =  $\sum_{i=1}^n (R_i \times D_i)$ , where R<sub>i</sub> is the rate of methane flux (g m<sup>-2</sup> d<sup>-1</sup>) in the *i*th sampling interval, D<sub>i</sub> 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.

#### 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<sup>(16)</sup>, levels of exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> (1 M NH<sub>4</sub>-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<sup>(17)</sup>. 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<sup>(18)</sup>. Finally, the dissolved iron and manganese concentrations were quantified by atomic absorption spectroscopy (AA, Shimadzu 660, Kyoto). Water soluble NO<sub>3</sub> and SO<sub>4</sub> 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<sup>(19)</sup>. 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<sub>4</sub> emission rates measured at the initial rice growing stage were low, which increased gradually with the development of soil reductive condition and rice plant growth (Fig. 1). After 70 days of rice transplanting (DAT), the peak CH<sub>4</sub> emission rates 172, 160, 138 and 120 mg m<sup>-2</sup> hr<sup>-1</sup> were recorded from 0, 2, 10 and 20 Mg ha<sup>-1</sup> fly ash applications, respectively (Fig. 1). Thereafter, the CH<sub>4</sub> emission rates showed a decreasing trend in all treatments and finally dropped to 15.8, 14.6, 12.6 and 11.0 mg m<sup>-2</sup> hr with 0, 2, 10 and 20 Mg ha<sup>-1</sup> fly ash applications, respectively, one week before harvesting (Fig. 1). It was observed that fly ash slightly suppressed CH<sub>4</sub> emission rates during the rice cultivation. This could be due to increased concentration of iron compounds released

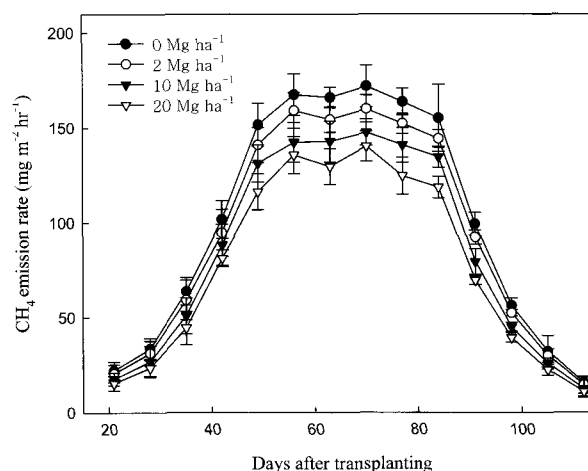


Fig. 1. Changes of CH<sub>4</sub> emission patterns in floodwater paddy soils amended with fly ash during rice cultivation.

from the applied fly ash, which might have resulted a shift of electron flow methanogenesis to iron reduction<sup>20</sup>. The maximum CH<sub>4</sub> emission rate at 70 DAT could be related to the higher availability of organic carbon<sup>21,22</sup> from the rapid decomposition of the applied organic matter and the development of intense reducing conditions (Eh value -234 to -243 mV) in the rice rhizosphere<sup>23</sup> and enhanced conductivity of CH<sub>4</sub> via rice plant<sup>24</sup>. The decrease in CH<sub>4</sub> emissions at the crop maturity stage could be due to aging of rice plants and decreased photosynthetic assimilates supply for methane production, which was supported by other studies<sup>25,26</sup>.

The total seasonal CH<sub>4</sub> flux was estimated 236 g m<sup>-2</sup> from the control treatment, which decreased to 220 (7% reduction), 189 (20% reduction), and 168 (29% reduction) g CH<sub>4</sub> m<sup>-2</sup> under 2, 10 and 20 Mg ha<sup>-1</sup> fly ash applications, respectively (Fig. 3). This decrease in total methane emissions could be due to the electron accepting effects of active iron oxide contained in the applied fly ash. Furukawa et al.,<sup>27</sup> also reported 5-30% reduction in total CH<sub>4</sub> emission during rice cultivation with 20 Mg ha<sup>-1</sup> revolving furnace slag application.

In our study, the changes of soil redox potential (Eh) values were contrasting to the changes of soil pH (Fig. 3). Soil Eh values decreased rapidly after flooding and then stabilized within the range -230 mV to -240 mV, whereas soil pH increased gradually and stabilized around neutral point (Fig. 3). Although fly ash was applied to maintain the soil under oxidative condition, soil Eh values decreased markedly both in fly ash and control treated potted soils during rice cultivation, which may be due to high Ca<sup>2+</sup> con-

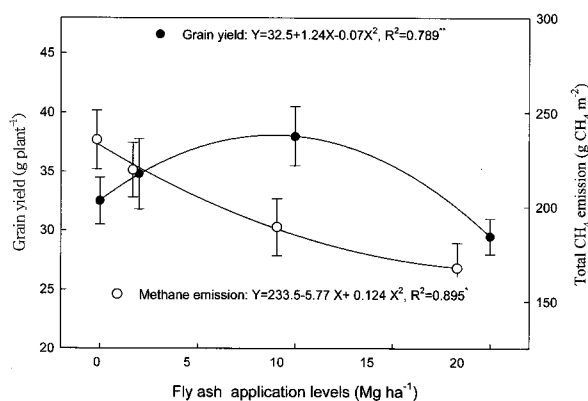


Fig. 2. Rice grain yield and total CH<sub>4</sub> emission in paddy soils amended with fly ash during rice cultivation

centration as well as alkaline pH (8.5) of fly ash as supported by Nozoe et al.<sup>28</sup> and Furukawa et al.<sup>29</sup>. Moreover, the decomposition of the applied rice straw (30 Mg ha<sup>-1</sup>, about 6 times higher than the normal practice 5 Mg ha<sup>-1</sup>) might have accelerated to decrease the soil Eh level under flooded conditions.

Fly ash application significantly increased the concentrations of iron and manganese compounds such as total, active and free Fe and Mn components in soil at rice harvesting stage (Table 3). This increased iron and manganese compounds might have acted as electron acceptors, and thereby, suppressed CH<sub>4</sub> production as well as CH<sub>4</sub> emissions during rice cultivation.

The available silicate and phosphate concentration significantly increased in the amended soils, probably due to high contents of silicate (55%) and phosphate (0.88%) in fly ash (Table 2). The high con-

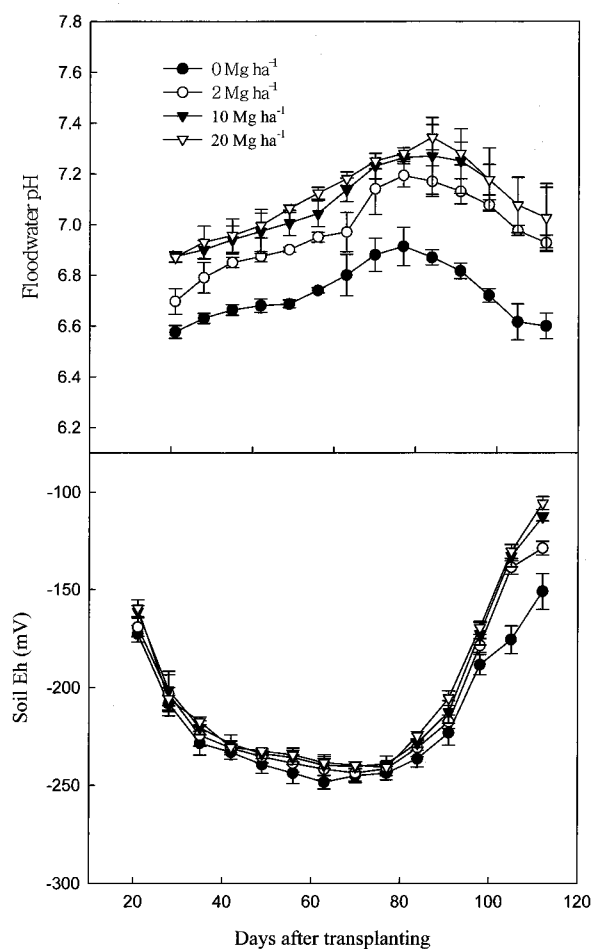


Fig. 3. Changes in soil Eh and pH of floodwater amended with fly ash during rice cultivation.

tent of base nutrients and alkaline pH of fly ash neutralized the soil acidity and increased the available phosphate concentration in soil, which may be due to de-sorption of phosphate by silicate ions from the ligand exchange sites<sup>30</sup>. Bohn et al.<sup>31</sup> also reported the maximum phosphate availability around neutral pH range. The exchangeable cations such as Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> content in the amended soils slightly increased (Table 3). The improved soil nutrients balance due to application of the fly ash stimulated rice plant growth and ultimately increased rice productivity.

In our study, the application levels of fly ash up to 10 Mg ha<sup>-1</sup> stimulated rice plant growth and yield parameters markedly (Table 3), however, 20 Mg ha<sup>-1</sup> application badly affected rice growth and yield (Fig. 2) The larger root biomass, root volume and root porosity under fly ash applications were expected to diffuse more CH<sub>4</sub> gas from soil to the atmosphere as compared to that of control<sup>24</sup>. However, the reverse trend was observed in this study, which could be due accelerated atmospheric oxygen transport from the plant's top to the roots<sup>32</sup>. As a consequence, CH<sub>4</sub> oxidation was enhanced in the root rhizosphere and suppressed CH<sub>4</sub> emission<sup>33,34</sup>.

Rice grain yield was significantly influenced by the application levels of fly ash (Fig. 2). Grain yield significantly increased with increasing levels of fly

ash applications up to 10 Mg ha<sup>-1</sup>, thereafter, decreased markedly with 20 Mg ha<sup>-1</sup>. Using the quadratic yield equation model (rice grain yield,  $Y = 32.5 + 1.24 \times FA - 0.07 FA^2$ ;  $R^2 = 0.789^{**}$ , where yield is expressed as g plant<sup>-1</sup> and FA is Fly ash application rate as Mg ha<sup>-1</sup>), the maximum grain yield was estimated 38 g plant<sup>-1</sup> (16.9% increase) at 10 Mg ha<sup>-1</sup> application level of fly ash (Fig. 2). This might have attributed due to mainly of inorganic nutrients such as Si, P, Ca, Mg, K, and Fe released from the applied fly ash. Other studies have shown that rice grain yield was increased by 9% with 10 Mg ha<sup>-1</sup> fly ash application<sup>35</sup> and 7-13% with 40-120 Mg ha<sup>-1</sup> fly ash applications<sup>36</sup>.

Tiller number, leaf area index, shoot biomass, and root biomass were positively correlated with seasonal CH<sub>4</sub> flux, whereas root volume, root porosity, grain yield and harvest index were negatively correlated (Table 5), which were supported by other studies<sup>15,37,38</sup>. The soil organic carbon and pH were positively correlated with total seasonal CH<sub>4</sub> flux<sup>37</sup>, at rice harvesting stage, whereas soil Eh, total soil iron, active iron, active manganese, water soluble iron, water soluble nitrate and sulfate, available phosphate and silicate content in soil showed negative correlations with total seasonal CH<sub>4</sub> flux (Table 5). Therefore, the effects of iron and manganese oxides, nitrate and sulfate ions released from the applied fly ash might have acted as

**Table 3. Growth and yield characteristics of rice with different levels of fly ash application at harvesting stage**

Parameters	Application levels (Mg ha <sup>-1</sup> )				LSD <sub>0.05</sub> <sup>1)</sup>
	0	2	10	20	
Plant height	79.9	81.4	82.7	77.6	3.79
Tiller no. per plant	13.6	14	16.3	10.3	1.33
Leaf area index	1.8	1.8	1.9	1.5	0.11
Shoot biomass (g plant <sup>-1</sup> )	33.2	34.3	35.5	26.8	1.46
Root biomass (g plant <sup>-1</sup> )	8.6	8.8	9.0	8.3	0.15
Root volume (cm <sup>3</sup> hill <sup>-1</sup> )	38.4	40.7	44.2	40.9	1.34
Root porosity (%)	18.7	21.2	26.6	21.7	1.13
Total dry matter production (g plant <sup>-1</sup> ) <sup>2)</sup>	74.3	77.2	82.5	71.9	2.0
Harvest index (%) <sup>3)</sup>	43.7	45.0	46.1	44.5	0.70
Panicle number per plant	15.0	16.6	19.0	16.3	1.5
Number of grains per panicle	80.1	85.3	91.5	79.8	4.1
Ripened grains (%)	82.4	84.7	88.4	80.8	3.2
1000 grains weight (g)	23.8	24.9	26.1	23.6	0.64

1) LSD<sub>0.05</sub>: 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.

**Table 4. Chemical properties of soil after rice harvest under different levels of fly ash application**

Parameters	Application levels (Mg ha <sup>-1</sup> )				LSD <sub>0.05</sub>
	0	2	10	20	
pH (1:5 with H <sub>2</sub> O)	6.1	6.3	6.4	6.5	0.04
Organic matter (g kg <sup>-1</sup> )	36	38	41	35	2.1
Available P <sub>2</sub> O <sub>5</sub> (mg kg <sup>-1</sup> )	79	99	124	139	8.4
Available SiO <sub>2</sub> (mg kg <sup>-1</sup> )	67	160	239	290	23.5
Ex. Cations (cmol <sup>+</sup> kg <sup>-1</sup> )					
Ca	6.0	6.3	6.5	6.6	0.30
Mg	1.1	1.5	1.7	1.9	0.09
K	1.0	1.3	1.5	1.8	0.16
Iron (g Fe kg <sup>-1</sup> )					
Total	21.7	25.5	25.9	26.1	2.5
Active	9.4	10.6	10.8	11.3	0.50
Free	3.8	4.9	5.0	4.2	0.32
Water soluble (mg kg <sup>-1</sup> )	4.5	17.1	19.0	22.4	2.0
Manganese (mg Mn kg <sup>-1</sup> )					
Total	55	87	96	96	4.9
Active	28	38	56	84	3.4
Free	127	144	161	153	6.5
Water soluble NO <sub>3</sub> <sup>-</sup> (mg kg <sup>-1</sup> )	0.64	1.25	1.38	2.77	1.1
Water soluble SO <sub>4</sub> <sup>2-</sup> (mg kg <sup>-1</sup> )	22	32	41	49	27.8

**Table 5. Correlations of seasonal CH<sub>4</sub> 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	0.332	Soil pH	0.394
Tiller number	0.507*	Organic carbon	0.390
Leaf area index	0.645**	Available P <sub>2</sub> O <sub>5</sub>	-0.585*
Shoot biomass	0.557*	Available SiO <sub>2</sub>	-0.680**
Root biomass	0.596*	Exchangeable Ca	-0.598*
Root volume	-0.547*	Exchangeable Mg	-0.512*
Root porosity	-0.566*	Exchangeable K	-0.543*
Total biomass	0.565*	Total iron	-0.405
Panicle number	-0.470	Active iron	-0.508*
Grain number	0.453	Free iron	-0.531
Ripened grains	0.191	Total Manganese	-0.435*
1000 grain wt.	0.283	Active Manganese	-0.438
Grain yield	-0.337	Free Manganese	-0.640**
Harvest index	0.356	Water soluble SO <sub>4</sub>	-0.516*
		Water soluble NO <sub>3</sub>	-0.539*
		Water soluble SO <sub>4</sub>	-0.688**

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

oxidizing agents as well as electron acceptors and ultimately reduced total CH<sub>4</sub> emissions during rice cultivation.

### Conclusion

Fly ash is an effective soil amendment on reducing CH<sub>4</sub> emissions as well as increasing rice grain productivity. The total seasonal CH<sub>4</sub> emission was reduced by 20%, along with 17% yield increment over the control with 10 Mg ha<sup>-1</sup> application level. The suppression of CH<sub>4</sub> emission may be attributed due to high concentration active iron and manganese compounds, and sulfate ions in soil, which acted as electron acceptors. In addition, fly ash increased the availability of nutrients for rice plant growth through raising the acidic soil pH and improved the soil nutrient balance.

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