Methane Fluxes and Rice Yields as a Function of Sulfate Fertilizer with Incorporated Rice Stubble

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Abstract

A trial was conducted by applying different sulfate (SO_4) rates on methane (CH_4) emissions and grain yields (GY) in a field with recently incorporated rice stubble (IRS), 7.5 t ha^{-1}. Ammonium phosphate SO_4 fertilizer (42% SO_4) was applied at the rates of 0, 50, 100, and 210 kg SO_4 ha^{-1}. The whole field was kept flooded with irrigation water. The results showed that the impact of SO_4 on CH_4 emissions weakened through the stages of rice growth. High daily CH_4 fluxes at the reproductive stage governed the quantities of seasonal CH_4 emission (SME), and led to a high ratio of SME/IRS. Only the highest rate of 210 kg SO_4 ha^{-1} could reduce SME by 66.9%. The highest GY was 4.08 t ha^{-1} at 100 kg SO_4 ha^{-1}. The whole experiment gave high values of SME/GY and SME/IRS. To reduce CH_4 emission without adverse effects on GY, split application of SO_4 at 100-155 kg SO_4 ha^{-1} with the last application preferably during the late tillering stage should be tested, along with incorporating rice stubble into the soil immediately after harvest.
Keywords: *ammonium phosphate sulfate, global warming potential, methane emission, paddy*

1. Introduction

One of the greatest sources of atmospheric methane (CH_4) is cultivation of irrigated rice (*Oryza sativa* L.). In the year 2009, global CH_4 emission from rice growing areas accounts for 25.6 Tg annual^{-1} (1). Since almost half of the world's population depends on rice as its staple food, irrigated rice cultivation can be expected to continue to generate CH_4 emissions into the atmosphere.

Sulfate (SO_4) is one of the most promising inputs for the reduction of CH_4 emission from paddy soil (2). Our previous rice-planting pot experiment showed that CH_4 emissions were suppressed through the growing period in soils with increasing sulfate contents, illustrating that sulfate has the potential to mitigate CH_4 production and emission from paddy soil (3). From the farmer perspective, obtaining high yields is the major concern in rice production

systems. Sulfate is a necessary nutrient for rice productivity but the potential negative effect of high SO_4 rates on rice yields needs further study in the paddy field (3)(4)(5) also reported that a very high dose of SO_4 is most likely to limit the rice yields.

In Northeast Thailand, rice stubble remaining in the paddy field from the previous cropping season is the main source of organic matter inputs into the soil. Inputs of organic matter are necessary for nutrient cycling and maintaining soil productivity. Local rice farmers commonly incorporate rice stubble into paddy soils during soil preparation immediately before seed sowing. Therefore, this case study, we are focusing on the positive effects of SO_4 on reducing CH_4 emissions with its potential negative effects on rice yield in soils with incorporated rice stubble at the time of sowing.

2. Materials and Methods

2.1 Field experiment

The field experiment was conducted in an irrigated paddy field in Na-Ngam village, Khon Kaen province (102° 51.27'E, 16° 32.83'N) at an elevation of 157 m above mean sea level. The soil is Paleaquults (6) and Roi-et in the Thai soil series. The soil chemical properties were: organic C 8.1 g kg^{-1}, total N 0.64 g kg^{-1}, available P 5 mg kg^{-1}, exchangeable-K 21 mg kg^{-1}, exchangeable-Ca 75 mg kg^{-1}, exchangeable-Mg 825 mg kg^{-1}, CEC 11 $cmol_+$ kg^{-1}, SO_4-S 6.4 mg kg^{-1}, NH_4-N 9.7 mg kg_{-1}, total Fe 6.33 g kg^{-1} and potentially reducible Fe^{2+} 2.92 g kg^{-1}, pH 5.1, EC 0.12 dS m^{-1}, while soil texture was loamy.

The experiment was in the second rice crop during the dry season of year 2011. Climatic data during the growing period in January, February, March, and April, for monthly average temperature were 24.8, 27.0, 28.1 and 31.8 °C (CV 2-2.5%); mean monthly rainfall 58.7, 19.5, 0 and 27.3 mm (CV 0-3.6%); monthly solar radiation 17.5, 16.6, 18.6 and 20.4 MJ d^{-1} (CV 2.3-4.2%).

The 8 m x 9 m experimental plots were laid out in randomized complete block design (RCBD) with 4 treatments of different rates of SO_4 with 3 replications. A combined ammonium-phosphate-SO_4 fertilizer, graded N: P_2O_5: K_2O as 16%: 20%: 0%, containing 42% SO_4 in form of SO_4 was used. The SO_4 rates were 210, 100, 50 and 0 kg SO_4 ha^{-1} (3). Meanwhile, the amounts of major nutrient in form of N, P_2O_5, K_2O were kept constant for each treatment at 80, 100 and 80 kg ha^{-1} respectively, as shown in Table 1.

Table 1. Sulfate rates applied for each treatment.

SO_4 (kg/ha)	Fertilizers used (kg/ha)			
	APS	Urea	Rock phosphate	KCl
0	0	173.91	3333.33	133.33
50	119.04	132.52	2540.00	133.33
100	238.10	91.10	1746.00	133.33
210	500.00	-	-	133.33

N, P_2O_5 and K_2O in each treatment were 80, 100 and 80 kg ha^{-1}, respectively. APS: ammonium phosphate sulfate (42% SO_4), urea (46% N), rock phosphate (3% P_2O_5), KCl (60% K_2O)

Rice stubble residue was measured 7.5 t ha^{-1} prior to the experiment. In this paddy field, the rice stubble was not burned. On January 9, 2011, the soil was flooded, then rice stubble was thoroughly incorporated into the top soil 0-20 cm deep by using a 2-wheeled hand tiller for 3 rounds. Soil ridges were constructed to separate 12 adjacent plots. After harrowing, fertilizers (shown in Table 1) were surface applied prior to puddling and leveling. Bases of gas chambers were installed in the plotted soil. Rice seeds cv. Chainat1 were directly sown at 62.5 kg ha^{-1}. Water on the soil surface was drained. For 17 days the plots had no standing water, thereafter they were kept flooded until 10 days before harvest. The length of rice growing season was 107 days.

2.2 Gas sampling

CH_4 gas samplings were done weekly up to harvesting, using the chamber method (7). The gas sampling, CH_4 concentration analysis and calculation of emission flux were modified (8).

$$E = \frac{DC}{Dt} \times Vh \times \frac{mW}{mV} \times \frac{273.2}{(273.2+T)} \times 60 \times 24 \quad (1)$$

Where, E is CH_4 emission flux in mg m^{-2} d^{-1}. is an increase of CH_4 concentration with time in ppm min^{-1}. Vh is the height of head space from water level in m. mW is molecular weight of CH_4 is 16.04 g mole^{-1}. mV is molecular volume of CH_4 is 22.4 L at standard pressure and temperature. T is temperature in the gas sampling chamber in °C.

2.3 Seasonal methane emission (SME), ratio to unit of grain yield (SME/GY), ratio to unit of incorporated rice stubble (SME/IRS) and GWP

The calculation of SME (in mg m^{-2} season^{-1}) was based on cumulative total amount of CH_4 emissions in each sampling interval as follows (7) (8):

$$SME = \left(\frac{1}{2} \times R_1 \times D_1\right) + \left[\frac{1}{2} \times (R_1 + R_2) \times D_2\right] + \cdots \left[\frac{1}{2} \times (R_{n-1} + R_n) \times D_n\right] (2)$$

Where, R_1 is the rate of CH_4 flux (mg m^{-2} d^{-1}) in 1st sampling, D_1 is the number of days in the 1st sampling interval, and R_n is the CH_4 flux in the last sampling, D_n is the number of days in the last sampling interval (between sampling n-1 and n).

In order to perceive strength of the produced grain yield (GY) and of the incorporated rice stubble (IRS) at the time of sowing on seasonal CH_4 emission into the atmosphere, the ratio of SME/GY and SME/IRS were calculated and expressed in terms of percentages. Global warming potential (GWP) of CH_4 was calculated by using the value 23 for GWP of CH_4 (9).

$$GWP\ of\ CH_4 = SME \times 23 \qquad (3)$$

Where, GWP is in CO_2 equivalent (CO_2-e), g m^{-2} season^{-1}. SME is seasonal CH_4 emission in g m^{-2} season^{-1}.

Percentage of GWP reduction based on the control was also computed.

2.4 Yield component

After harvest, number of panicles per plant, grain number per panicle, filled grains, grain weight, 1000 grain weight, percent of filled grain, straw and harvest index (HI), were determined.

2.5 Statistical analysis

The significant difference between treatments was assessed by performing analysis of variance (ANOVA) based on least significant difference (LSD) using Statistix 8 program (version 8).

3. Results and Discussion

3.1 SO$_4$ fertilizer alleviates CH_4 fluxes

Low CH_4 fluxes (12.3-136.7 mg m^{-2}

d^{-1}) at the seedling stage (2-16 days after sowing, DAS) (Table 2) were not subject to SO_4 application, except at 16 DAS. Irrigation water was supplied from 17 DAS onwards accompanied by marked increases in CH_4 fluxes throughout the whole rice cycle in all plots. During tillering stage (23-44 DAS), CH_4 emissions were negatively affected by increasing SO_4 levels. The presence of SO_4 delayed the decrease in soil Eh; as a consequence, methanogenesis was delayed (Ro et al., 2011) (3). The SO_4-reducing microorganisms may compete with methanogens for H_2 (10) and electrons in reduction of SO_4 to S^{2-} (sulfide). This may be toxic to methanogens (11) and becomes stronger with higher rates of SO_4. At booting stage (51-58 DAS), all levels of SO_4 suppressed CH_4 fluxes in a similar manner compared to the control soil.

During the later stage of rice growth (65-86 DAS) the effects of SO_4 were not clearly seen except at the highest rate of SO_4 210 kg SO_4 ha^{-1} (Table 2). This was possibly because of the gradual decrease in soil SO_4 content under these anoxic soil conditions due to loss of SO_4 through H_2S, percolation (12) and plant uptake, because in this experiment, there was no replenishment of SO_4 after the single basal application prior to seed sowing. At this point, it can be stated that a single application of SO_4 could suppress CH_4 fluxes at tillering stage more effectively than at the later stage of rice growth. Split application of a higher dose of SO_4 with the first half at sowing and the second half at the late tillering stage (between 44 and 51 DAS) might have greater efficacy in reducing CH_4 fluxes.

The peak CH_4 fluxes, which ranged from 1767.7 to 3215.6 mg m^{-2} d^{-1}, occurred during the heading through the ripening stage (65-86 DAS) under the control, 50 and 100 kg SO_4 ha^{-1} (Table 2) were due to high root exudates, autolysed root tissues (13), decomposed roots and crop residues (14). Rice root excretions during the reproductive stage are comprised of various organic substrates, mainly glucose and acetic acid. These mechanisms were pronounced for the Chainat1, categorized as a high CH_4 emitter compared to other Thai rice varieties (15). Moreover, these factors supporting CH_4 production in soil had resulted from the high planting density of 82-107 plants m^{-2} (estimated data) of sowing rice could have resulted in expansion of anaerobic volume in the soil matrix due to declining ability of oxygen transport in older roots of reproductive stage (16). These mechanisms created especially favorable conditions suitable for methanogens at these periods. Moreover, these factors coupled with warm air temperature (31.8°C) and high levels of solar radiation (20.4 MJ m^{-2} d^{-1}) in April of a tropical country accelerated microbial methanogenesis during the reproductive stage (65 to 86 DAS) (Table 2). After the ripening stage, CH_4 flux drastically dropped due to the draining of water prior to harvesting and the remaining CH_4 in soil was oxidized to carbon dioxide.

Table 2. Methane fluxes through various growth stages as influenced by sulfate content in rice stubble incorporated field.

SO$_4$	CH$_4$ (mg m^{-2} d^{-1})													
	2d	9d	16d	23d	30d	37d	44d	51d	58d	65d	72d	79d	86d	106d
(kg ha^{-1})	S		T					B and H			F		R	
0	83.7	22.1	136.7[a]	664.3[a]	428.3[a]	302.2[a]	463.6[a]	1101.4[a]	859.8[a]	1790.2[a]	2780.4[a]	1903.8	2614.7[a]	8.7
50	104.3	12.3	41.8[b]	204.0[b]	246.0[b]	169.5[b]	276.9[b]	362.0[b]	296.6[b]	1767.7[a]	3215.6[a]	2660.7	3083.1[a]	32.7
100	88.3	20.7	56.0[b]	126.9[bc]	85.1[c]	216.9[b]	288.2[b]	323.5[b]	474.0[b]	1851.7[a]	3094.0[a]	2096.2	2523.8[a]	32.6
210	65.3	21.3	34.8[b]	54.8[c]	58.7[c]	68.0[c]	69.3[c]	412.8[b]	246.8[b]	43.3[b]	968.7[b]	1923.3	488.7[b]	27.5

In each column, mean (n = 3) followed by a common letter is not significantly different (P ≤ 0.05). d: days after sowing,
S: seedling stage, T: tillering stage, B: booting stage, H: heading stage, F: flowering stage, R: ripening stage.

3.2 Grain yields as a function of SO$_4$

Sulfate is essential for chlorophyll formation and protein production. In this soil, SO$_4$ content is 6.4 mg S kg^{-1}, it's status is considered to be low as critical level of extractable soil S in general ranged from 5-10 mg S kg^{-1} (5). Therefore, additional application of SO$_4$ should be performed. At the stage of grain filling, S is transported to the panicle (17) which explains why there is an increase in grain weight with SO$_4$ addition. The maximum grain weight (4.08 t ha^{-1}) produced with medium rate 100 kg SO$_4$ ha^{-1} was likely due to the high weight of 1000 grains (26.2 g) and the higher number of grains per panicle (Table 3). This medium rate of SO$_4$ also gave the highest amount of straw biomass (5.2 t ha^{-1}) which may have contributed to higher GY. Although the highest grain number per panicle (78 grains) was occurred the highest at rate of SO$_4$ 210 kg ha^{-1}, the lower number of panicles per plant (1.7 panicles plant^{-1}) at this rate may have contributed to the lower GY weight (3.69 t ha^{-1}) with this high rate of SO$_4$. The highest rate 210 kg SO$_4$ ha^{-1} may induce anionic imbalance in soil, antagonistic effect of SO$_4$ on other anion absorption by rice root which may result in phosphorus, boron or molybdenum limitation in rice. The reduced GY under the application of highest rate 210 kg SO$_4$ ha^{-1} was accompanied by reduced straw biomass, suggesting that toxicity of H$_2$S to rice plants may have occurred. In order to achieve a high GY above 4.08 t ha^{-1}, 100-155 kg SO$_4$ ha^{-1} is recommended.

Table 3. Yield components and grain yield of Chainat1 rice variety with different sulfate rates.

SO_4 (kg ha^{-1})	Panicle number plant^{-1}	Grain yield			Straw biomass (t ha^{-1})	Grain filling (%)	HI
		Number panicle^{-1}	1000-grain weight (g)	Total weight (t ha^{-1})			
0	2.4[a]	68[b]	25.2[b]	3.36[c]	3.8[c]	98.0[b]	0.47
50	2.2[a]	70[b]	26.7[a]	3.52[bc]	4.8[b]	99.1[a]	0.42
100	2.2[a]	73[ab]	26.2[a]	4.08[a]	5.2[a]	98.7[ab]	0.44
210	1.7[b]	78[a]	26.1[a]	3.69[b]	4.9[b]	98.2[b]	0.43
CV (%)	7.8	4.1	1.7	6.2	9.1	4.1	9.1

Means (n = 3) followed by same letters in each column are not significantly different at P ≤ 0.05. HI represents harvest index.

3.3 SO_4 fertilizer alleviates SME

In this experiment, ammonium-phosphate-SO_4 fertilizer (42% SO_4) could alleviate SME in rice soil by 66.9% at the application rate of 210 kg SO_4 kg^{-1} (Table 4). Our finding is in keeping with the previously recommended use of SO_4-containing fertilizers for reduction of CH_4 emissions. Experiments by other researchers have shown that ammonium thiosulphate applied at 45.6 and 60 kg N ha^{-1} could reduce CH_4 emissions by approximately 38 and 60% respectively, compared to the control (4). However, results from the present experiment show that SO_4 impact became progressively weaker over time and the amounts of CH_4 produced in the soil became much larger at the reproductive stage. This suggests that another application of SO_4 just before the beginning of the booting stage might further help to control CH_4 fluxes.

Table 4. Seasonal methane emissions (SME), global warming potentials (GWP), their reductions, SME/GY and SME/IRS.

SO_4	SME	GWP of CH_4 as CO_2-e	Reduction of SME and GWP	SME/GY	SME/IRS
(kg ha^{-1})	(g CH_4 m^{-2} season^{-1})	(g m^{-2} season^{-1})	(%)	(%)	(%)
0	93.92[a]	2160.2[a]	-	28.06	12.52
50	92.37[a]	2124.4[a]	1.66	26.02	12.32
100	81.61[a]	1877.0[a]	13.11	19.94	10.88
210	31.11[b]	715.5[b]	66.88	8.46	4.15
CV (%)	21.3	21.3	-	43.6	43.4

GY: grain rice yield; IRS: incorporated rice stubble, 7.5 t ha^{-1}; CO_2-e: carbon dioxide equivalent. The same letters are not significantly different among the means (n = 3) at P ≤ 0.05.

3.4 SME, SME/IRS, SME/GY and GWP

Daily CH$_4$ fluxes during the reproductive stage (65-86 DAS) (Table 2) made an enormous contribution to SME (Table 4). The high average daily CH$_4$ flux from that period, 2069.09 mg m^{-2} d^{-1} (n = 16, calculated from the 4 treatments) was 2.78 times higher than that for the whole experiment, 744.53 mg CH$_4$.m^{-2} .d^{-1} (n = 56). The ratio of SME/IRS was generally high 12.52, 12.32 and 10.88%, except for the highest rate of SO$_4$ (Table 4). Those high values reflect the influence of incorporation of a large amount of rice stubble (7.5 t ha^{-1}) just before sowing on SME. Xu and Hosen (17) demonstrated that in potted soils at 100% water holding capacity, CH$_4$ emissions per unit weight of rice straw applied were 0.277 and 0.145 g CH$_4$ g^{-1} dry matter for pre-planting rice straw application at the rates of 0.91 and 4.55 g ka^{-1}, respectively. Assuming the weight of 1 ha furrow slice (0.15 m deep, bulk density 1.36 t m^{-3}) was 2040 t soil, the applied rice straw in their experiment were 1.86 and 9.28 t ha^{-1}, which could induce CH$_4$ emissions per unit weight of applied rice straw of 27.7 and 14.5%, respectively. Our findings in the present field experiment are in accord with the high CH$_4$ emissions as a function of rice straw application under saturated soil reported by Xu and Hosen (18).

Additional research should be done to determine if rice stubble incorporation done immediately after harvesting, when the soil moisture content is usually around field capacity to allow enough time for residue decomposition in aerobic soil conditions, results in lower fluxes. In addition, to avoid adverse effect on grain yield as well as to enhance SO$_4$ suppressive effect on SME, split application of SO$_4$ at the rate of 100-150 kg S ha^{-1}, with the last application preferably during the late tillering stage, should be tested. These management measures might reduce the stimulating effect of rice stubble incorporation on SME, GWP, SME/GY and SME/IRS from the rice fields.

4. Conclusion

Application of higher sulfate levels resulted in reduction of methane flux, particularly at the tillering stage of rice growth. However, rice stubble incorporation into the soil just before seeding contributed large amounts of organic substrates and also enlarged the areas of anaerobic soil matrix for methane production resulting in very large methane emissions during the reproductive stage. Moreover, the losses of sulfate through consumption by the rice plants, sulfate reduction to H$_2$S and leaching loss from the soil system had lessened its suppressive effect on methane production at the later stage. Only the highest amount of sulfate (210 kg SO$_4$ ha^{-1}) reduced methane fluxes through the whole season, but it had negative effects on rice yield due to H$_2$S toxicity. The results of this study suggest a way to make a compromise between obtaining acceptable rice yields and reducing methane emissions in rice-stubble incorporated-irrigated paddy fields employing sulfate-containing fertilizer. It may be possible to achieve both higher rice yields and lower methane emissions by changing the way that sulfate fertilizers are applied so as to prolong the effects of sulfate for the whole growing season. This might be done by addition of sulfate at a level of from 100-150 kg ha^{-1} as a split application, preferably with the first dose applied at the sowing or planting and the other dose at the late tillering stage.

Suggested changes in cultivation practices include soil aeration for a few days at the reproductive stage coupled with incorporating the rice stubble into the soil immediately after rice harvesting in order to decrease the amount of organic substrates in soil for the following rice cropping season. If successful, all these management measures will boost rice yields while also reducing TME, TME/IRS, TME/GY and GWP.

5. Acknowledgement

6. References

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