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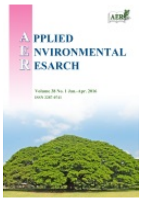

Reduction of GHG Emissions using Zeolite 4A under Different Fertilizer Usages in Rice Cultivation

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Abstract

This investigation examined the potential of zeolite 4A to reduce emission of greenhouse gases (GHGs) in rice cultivation under different fertilizer regimes. A completely randomized design was used with four treatments (different fertilizer application method) and 2 blocks (zeolite 4A application, using rice variety RD-41 sown at a seed rate of 15.625 g m^{-2}, and harvested in 105 d in Lam Ta Khong Research Station, Nakhon Ratchasima. The experimental results demonstrated that significant reduction in GHG emissions in zeolite 4A treated plots, either alone or in combination with chemical fertilizers, with GHG reduction of 43.27 % and 34.69 %, respectively. It was concluded that zeolite 4A has potential to reduce GHG emissions in rice cultivation, and that effect may be dose-dependent.

Keywords: Greenhouse gases; Rice cultivation; Reduction emission; Zeolite 4A; Adsorption

Introduction

Emission of greenhouse gases (GHGs) from various activities has been intensively inventoried using methodologies specified in the GHG calculation manual of the Intergovernmental Panel on Climate Change (IPCC). In Thailand, the energy sector was responsible for the highest GHGs emissions, at 256.44 million tons of carbon dioxide equivalent (CO_{2eq}) or 73.13 % of total emissions. Emissions from agriculture, forestry and land use amounted to 55.71 million tons of CO_{2eq}, or 15.89 % of the country's total emissions. In addition, industrial process and product use emitted 33.50 million tons of CO_{2eq} or 9.55 % of the country's total emissions, while the waste management sector emitted 5.03 million tons of CO_{2eq} or 1.43 % of total emissions. However, the agriculture, forestry and land use sector also sequesters CO_2 through accumulation of biomass. It was calculated that in 2012, forest areas and perennial plantations such as oil palm, rubber and fruit orchards sequestered 122.95 million tons of CO_{2eq}. Deducting emissions, this sector is therefore responsible for net GHG sequestration of 67.25 million tons of CO_{2eq} [1]. Carbon dioxide (CO_2) was the highest GHG emitted in the energy sector, while methane (CH_4) dominated in the agriculture and livestock sector, as well as nitrous oxide (N_2O) in soil management [2].

Rice cultivation is responsible for the majority of agriculture sector emissions, mainly methane from anaerobic degradation in flooded soils, as well as from organic and synthetic nitrogen fertilizers that emit nitrous oxide. Emissions from rice are this highly dependent on water management and the use of nitrogen fertilizers. Flooding, leading to anaerobic decomposition of soil organic matter, stubble and straw, as well as application of organic fertilizers, generate methane gas. In addition, nitrous oxide is emitted during nitrification and denitrification reactions of nitrogen fertilizer usage. Nitrification reduces urea fertilizer in the soil to nitrate and nitrite, and then to ammonia, nitrogen or nitrous oxide. The emission of nitrous oxide occurs in the outgrowing and drainage around 1.6 g N_2O m^{-2} crop as well as the methane gas emission conducted in the plantation and transplantation as 48 g CH_4 m^{-2} crop. So that, the GHGs emission was equal to 8.3 kg CO_{2eq} kg^{-1} paddy [3]. The emission of nitrous oxide occurs in the outgrowing and drainage around 476.8 g CO_{2eq} m^{-2} crop as well as the methane gas emission conducted in the plantation and transplantation as 1,200 g CO_{2eq} m^{-2} crop. So that, the GHGs emission was equal to 1,676.8 g CO_{2eq} m^{-2} crop [3].

Generally, CH_4 emissions occur in soils containing decomposing organic matter such as rice straw or organic fertilizers, where methanogenic bacteria produce CH_4 gas under anaerobic condition in the soil [4-5]. CH_4 gas bubbles in the soil diffuse into the rice roots and are released into the atmosphere via the stomata. This mechanism releases 90-95 % of total CH_4 emissions in rice fields, while 2-8 % of the total CH_4 emissions are released directly from the water surface to the atmosphere [6]. CH_4 is emitted throughout the duration of cultivation, with the highest amounts emitted during the reproductive phase and when the field is flooded [7]. Peak CH_4 emissions during the reproductive phase can reach 48 g CH_4 m^{-2} crop, or 8.3 kg CO_2eq kg^{-1} rice [3].

Methane emissions from rice fields in Thailand have been investigated in relation to geography, water management, fertilization and seasonal influences. For in-season paddy fields, methane emissions in the country's north and northeastern region amounted to 21.11 g CH_4 m^{-2}, while those in the central and southern regions equaled 18.86 g CH_4 m^{-2}. On the other hand, second-season paddy fields in the northern, northeastern, central and southern regions emitted 6.78 g CH_4 m^{-2}. CH_4 emissions are strongly affected by water and fertilizer management. In continuously flooded rice fields with no organic fertilizer, emissions were calculated at 18.72 g CH_4 m^{-2}. However, where continuously flooded paddy fields were fertilized using organic fertilizers, emissions increased to 44.04 g CH_4 m^{-2} [8]. This highlights the role of organic fertilizers as a cause of increased CH_4 emissions in rice cultivation. The water level in the paddy field was also found to affect methane emissions. For example, at 20 cm water depth, methane emissions were measured at 20.53 g CH_4 m^{-2} crop. For a water depth of 10 cm, emissions were reduced to 17.42 g CH_4 m^{-2} crop, and for a water depth of 5 cm, emissions were reduced further to 15.75 g CH_4 m^{-2} crop.

For 0 cm water depth, emissions fell further to only 12.11 g CH_4 m^{-2} crop. It can thus be concluded that water depth in the field affects methane emission, since deeper water favors the reducing conditions in the soil that allows methane gas generation [9].

Thailand has a policy to reduce GHGs emission in all economic sectors. In the agricultural sector, the potential to reduce GHGs emissions by 2020 is estimated at 8.57 million tons of CO_{2eq} [10]. In rice, there are several ways to reduce emissions, including microbial selection to accelerate decomposition of stubble, rice straw and soil organic matter, under both aerobic and anaerobic conditions [11-12]. The use of adsorbents such as zeolite NaA, NaX, and NaY has also been proposed as an innovative approach to further reduce emissions [13-14].

Zeolite is commonly used as a soil amendment or nutrient supporter for rice and other cereals, vegetables and fruit crops due to its ability to slow down nutrient leaching and release of minerals [15]. Its high porosity and high cation exchange capacity boosts the soil's ability to absorb water, cations, and nutrients for plant growth [16]. Zeolite is already widely applied in agriculture as a carrier for N and K fertilizers [17], and its high buffering capacity can help stabilize soil pH [15].

Zeolite is also used for adsorption of organic and inorganic substances, especially gas separation and purification due to its ability to absorb or separate different gases such as methane, ethane, and propane according to their different molecular sizes [13]. In industry, zeolite 4A is valued for its efficiency in methane adsorption [14].

Natural zeolite and dolomite were studied for their utility for GHG reduction in peatland used in rice production in Jakeman, Indonesia. It was found that the two soil amendments could reduce emissions by approximately 27.3 % and 21.4 %, respectively [18]. In another study, natural and synthesized zeolite as well as reed straw was shown to adsorb GHG emissions from stored duck manure [19].

The use of zeolite 4A to reduce GHG emission from rice cultivation has been studied in Pathum Thani Province, Thailand. Zeolite 4A and synthesized zeolite from rice stubble were used as absorbents to reduce GHG emissions. The study found that synthesized zeolite could reduce CH_4 and CO_2 emissions by 27.87 % and 33.14 %, respectively while the zeolite 4A could reduce these two GHGs; CH_4 and CO_2 emisisons 49.47 %, and 62.70 % [20].

Therefore, this research focused on the reduction emission efficiency of zeolite 4A as an adsorbent for rice variety RD-41 grown in northeast Thailand under different fertilizer regimes. The study also investigated fertilizer application methods to optimize production parameters as well as achieve reduction in GHG emissions.

Materials and methods

1) Paddy cultivation

The rice field was located at the Lamtakong Research Station, Mitrapap Road, Kaenghom Sub-district, Pakchong District, Nakhon Ratchasima Province (latitude 14.770389 °N and longitude 101.518518 °E). Using a completely randomized design (CRD) with 4 treatments (different fertilizer application methods) and 2 blocks (zeolite 4A applications). The experimental plots were divided into 8 plots as shown in Table 1. The ratio of zeolite 4A to fertilizer was 3:1. The chemical fertilizers and slow-release organic fertilizer used were 16-20-0, 46-0-0 and 6-6-6 at a rate of 31.25 g m^{-2}, respectively. Rice (variety RD-41) was cultivated using a seed rate of 15.625 g m^{-2} and was harvested after 105 days. The harvested grain was then sun-dried for 3 d.

Table 1 Experimental plots

Treatments	Block I with zeolite	Block II without zeolite
Control (no fertilizer)	CI	CII
Single fertilizer (16-20-0 and 46-0-0 after sowing 20 d)	SFI	SFII
Two fertilizer applications (16-20-0 20 d after sowing, and 46-0-0 60 d after sowing)	TTFI	TTFII
Slow-release organic fertilizer (6-6-6 applied 20 d after sowing)	SROFI	SROFII

2) Properties of zeolite 4A

Zeolite 4A is an alkaline aluminosilicate, and is the sodium form of the zeolite type A crystal structure. It has an effective pore diameter of approximately 4 Å and possesses a high cation exchange capacity. It can effectively adsorb chemical substances such as oxygen, nitrogen, carbon dioxide, cations such as NH_4^+, K^+, Ca^{2+}, as well as straight-chain hydrocarbons such as methane. The properties and characteristics of the commercial grade of zeolite 4A are shown in Table 2 [21].

3) Chamber collector

A chamber collector constructed in the form or an acrylic box with dimensions 70x50x50 cm was pushed into the soil to a depth of 20 cm, leaving 50 cm above the soil surface as shown in Figure 1. A gas storage box cover was placed in the gutter, with an air circulation fan and gas collecting tube located on the top of the cover.

4) Gas collection

Ten days after sowing, a gas sample was collected at 10.30-12.00 h once per week throughout the growing season, according to the following steps [22-24]:

1) Close the gas storage tank and open the fan throughout the collection period.

2) Take the sample in triplicate every 15 min for 5 cycles.

3) Collect the gas sample in the box with a syringe (Figure 2b).

4) Inject the gas sample into a vacuum tube and wrap with paraffin.

5) Gas analysis

The quality and quantity of CO_2, CH_4 and N_2O were analyzed by gas chromatography (GC) using a Shimadzu 2014 model. Helium gas was used as the carrier gas, passing through an Unibeads C GC column. Injector, column and thermal conductivity detector (TCD) temperatures were set to 150 °C, 230 °C and 130 °C, respectively. The sample chromatogram (Figure 2c) shows the chromatogram of CH_4 and CO_2 at 3.370 and 5.843 min, respectively. Reduction in GHG emissions was determined in the form of the reduction emission efficiency and rate per gram of zeolite.

Table 2 Properties and characteristics of commercial zeolite 4A

Properties	Unit	Specificatior
Diameter	mm	1.7
Bulk density	g/cm^3	$\geq$ 0.72
Pore diameter	A	4
Pore volume	cm^3 / g	0.45
Porosity	%	0.55
Crushing strength	N	$\geq$35
Attrition	wt %	7.35
Moisture	wt %	$\leq$ 1
Adsorption capacity	g H_2O 100 g^{-1} zeolite	$\geq$ 22
	g methanol 100 g^{-1} zeolite	$\geq$ 15
Cation exchange capacity (CEC)	meq 100 g^{-1} zeolite	738-797

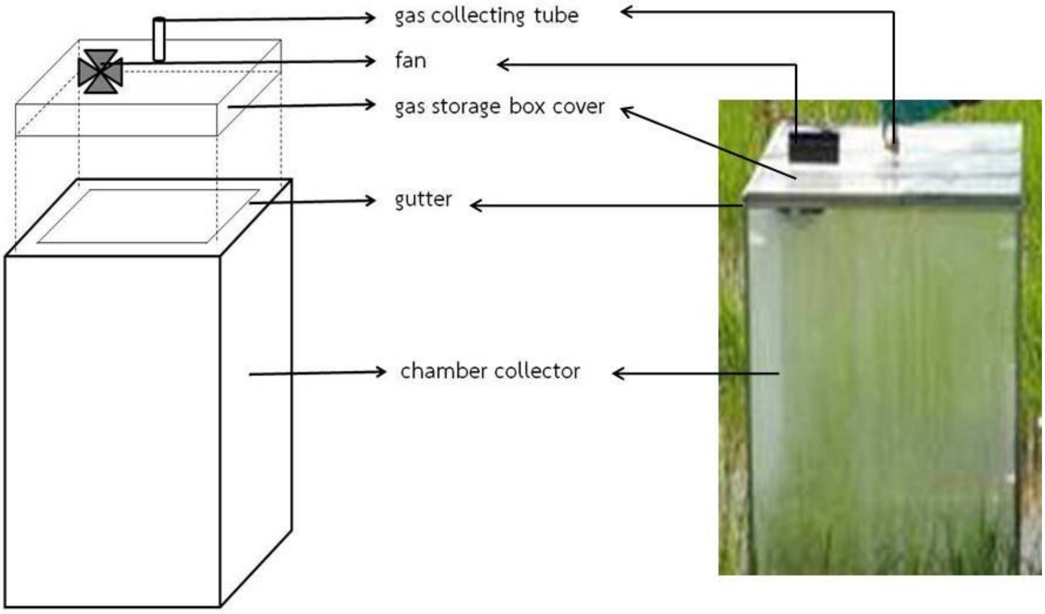


Figure 1 Chamber collector.

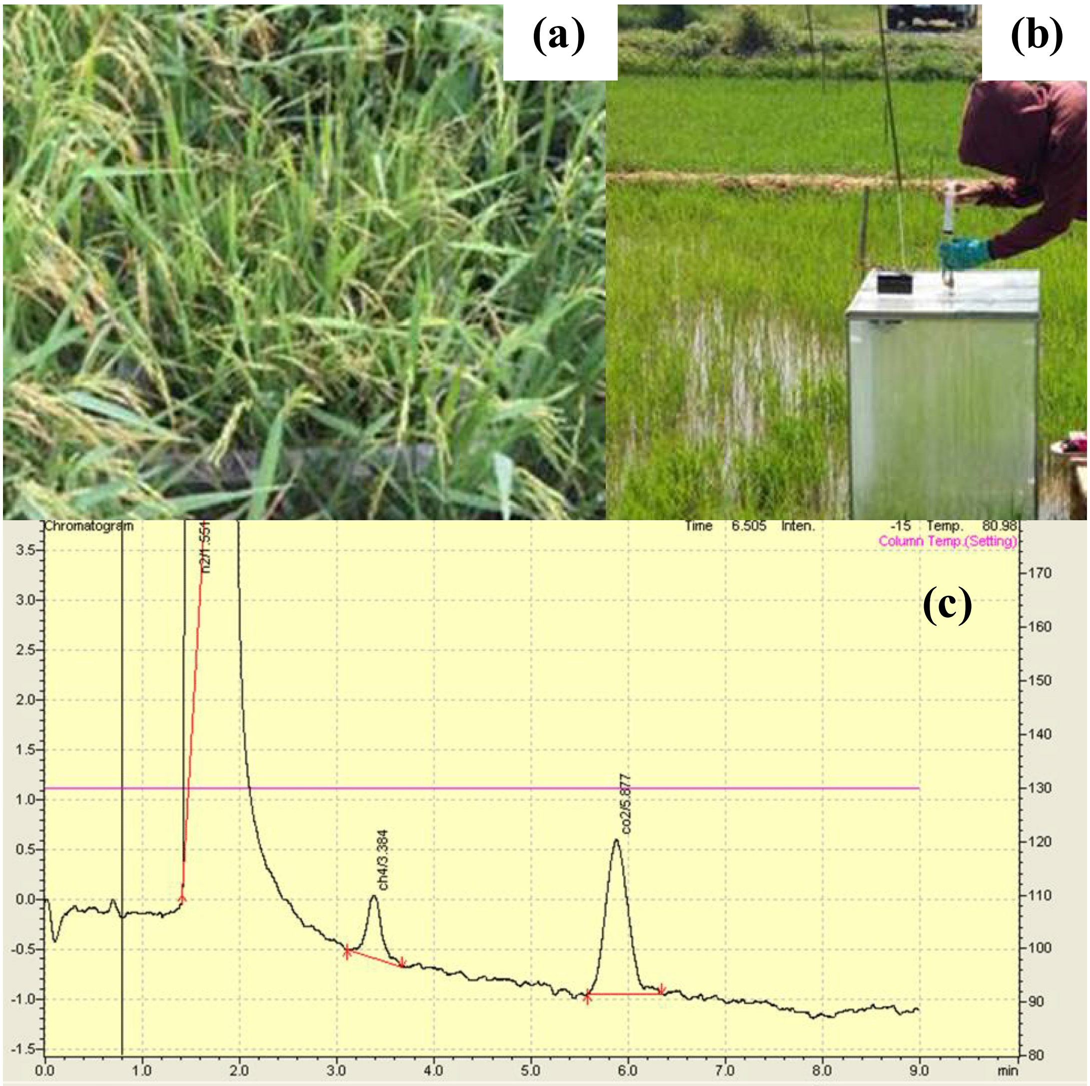


Figure 2 Pictures showing (a) rice plantation, (b) gas collection, and (c) sample chromatogram.

Results and discussion

1) Type of soil series and soil properties in the field

Soils in the northeast of Thailand typically have low integrity as shown in Table 3 [25-26]. The soil type is classified in the Korat soil series as dark brown or brown sandy loam. The clay particles do not exceed 35 % and are brown or yellowish brown. Topsoils are acidic to slightly acidic (pH 5.5-6.5) with lower horizons very acidic (pH 4.5-5.0). The experimental site was located in a rice field at the Lamtakong Research Station in the northeast of Thailand. Soil properties on the station were superior to those typically found in the Korat soil series, as shown in Table 4. The soil in the experimental site had higher available P, K and CEC than typical Korat soils, making it suitable for rice cultivation.

2) Growth result and paddy yield

As shown in Table 5 and Figure 3, addition of zeolite 4A resulted in no statistical improvement at $p \leq 0.05$ in crop growth; however, fertilizer application methods produced statistically significant differences. In addition, application of a single chemical fertilizer (SFI, SFII) produced no significant difference compared with the untreated controls (CI, CII). However, significant differences were found with two applications of chemical fertilizer (TTFI, TTFII) and the slow-release organic fertilizer (SROFI, SROFII). Meanwhile, TTFI, TTFII, SROFI and SROFII showed increased crop growth at 63.53, 62.59, 62.61 and 60.35 cm, respectively. This demonstrated that nutrients from the TTF and SROF were retained in the topsoil for a long time during crop growth, allowing increased uptake by the crop [27].

The combination of zeolite 4A + fertilizer resulted in significant increase in % good grain at $p \leq 0.05$. Treatments CI and TTFI in particular resulted in higher % good grain than CII and TTFCII. This showed that zeolite 4A is acting as a nutrient adsorbent to regulate nutrient mobility and release [28]. For the fertilizer treatments, TTF and SF resulted in higher % good grain compared with SROF, achieving percentages of good grain of 86.55 %, 83.93 % and 76.61 %, respectively. This reflects the higher solubility of the chemical fertilizer compared with the organic fertilizer. The zeolite 4A adsorbs the nutrients and releases them slowly over, mimimizing loss by leaching and mazimizing crop uptake [15].

Table 3 Characterization and properties of Korat series soils

Characteristic	Depth (cm)		
	0-25	25-50	50-100
Organic matter (%)	1.0-1.5	1.0-1.5	1.0-1.5
CEC (Cmol kg^{-1})	3-5	3-5	3-5
Basic saturation (%)	< 35	< 35	< 35
Phosphorus* (mg kg^{-1})	6-10	6-10	6-10
Potassium** (mg kg^{-1})	< 30	< 30	< 30
Integrity (score)	< 7	< 7	< 7

Note: * available P
** available K

Table 4 Properties of soil in the experimental rice field

Parameter	Unit	Value
pH	-	6.39
EC	dS m^{-1}	0.06
OM	%	0.54
Total N	mg kg^{-1}	0.03
Available P	mg kg^{-1}	12.12*
Available K	mg kg^{-1}	96.76*
CEC	Cmole kg^{-1}	13.52*

Note: * means better than the Korat soil series

Nevertheless, treatments combining zeolite 4A and fertilizer were not statistically significant for total yield, except TTF and a control. CII had the lowest total grain yield at 298 g m^{-2}, while TTFI had the highest total grain yield at 493 g m^{-2}, consistent with higher crop growth and % good grain recorded in these treatments, and supports the hypothesis that zeolite 4A adsorbs nutrients, making them available for crop uptake throughout crop duration [15]. In addition, SROF of both with (I) and without (II) zeolite 4A had the total paddy field 430 and 375 g m^{-2}, successively while the total yield from the treatments of SFI and SFII were 363 and 350 g m^{-2}, respectively. These results reveal that the four ttreatments; SROF (I,II) and SF(I,II) had no significant difference statistical at $p \leq 0.05$. This again is consistent with the evidence for the role of zeolite 4A in adsorbing nutrients for slow release to the crop over the growing season [29].

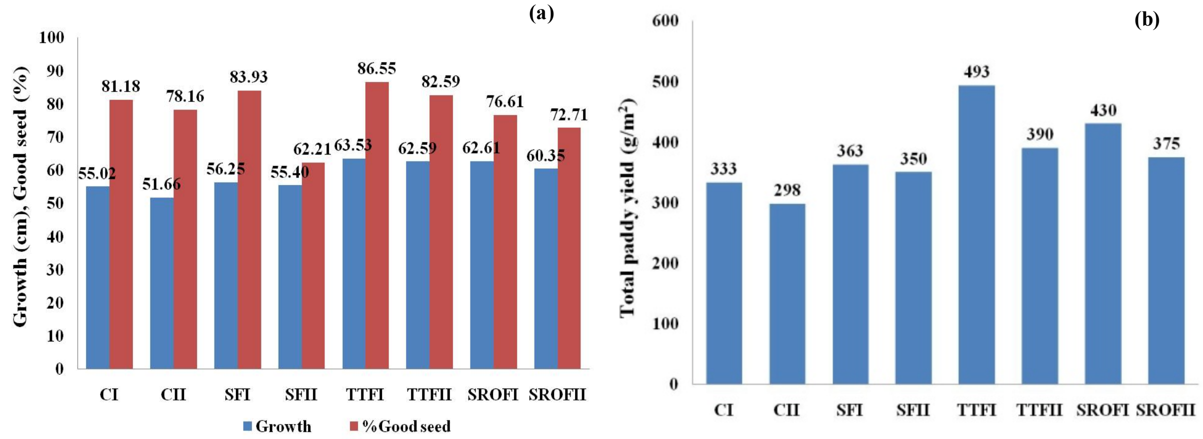


Figure 3 Graphs of (a) growth and % good grain and (b) total paddy yield.

Table 5 Paddy production, rice growth, good grain % and grain yield

		Growth (cm)		**Good grain (%)**		**Total paddy weight (g m^{-2})**	
		X	**SD**	**X**	**SD**	**X**	**SD**
C	**I**	55.02^{a}	8.26	81.18^{a}	7.05	333^{ab}	35.36
	II	51.66^{a}	9.53	78.16^{b}	11.24	298^{a}	60.10
SF	**I**	56.25^{a}	7.49	83.93^{a}	8.32	363^{ab}	67.18
	II	55.40^{a}	10.00	62.21^{c}	17.41	350^{ab}	91.92
TTF	**I**	63.53^{b}	7.51	86.55^{a}	6.04	493^{b}	21.21
	II	62.59^{b}	6.26	82.59^{a}	9.17	390^{ab}	17.68
SROF	**I**	62.61^{b}	7.66	76.61^{b}	13.50	375^{ab}	35.35
	II	60.35^{b}	6.63	72.71^{b}	13.38	430^{ab}	80.21
F-test		7.259		11.760		2.216	
Sig.		0.000		0.000		0.144	

Note: C = Control (no fertilizer), SF = One fertilizer application, TTF = Two fertilizer aplications, SROF = Slow-release organic fertilizer, I = with zeolite 4A, II = without zeolite 4A
^{a,b,c} = group no. was not statistically significant ($p \leq 0.05$)

3) GHG emissions from each plot

From Table 6-7 and Figure 4, zeolite 4A addition and fertilizer application were statistically significant at $p \leq 0.05$ for the cumulative emissions of both CH_4 and CO_2. The results demonstrated that zeolite 4A addition affected the net cumulative emissions of CH_4, and CO_2 over the season less than the other treatments, particularly CH_4. However, cumulative emissions for CH_4, CO_2 and total GHG were similar to a control, SF and TTF. For the controls (CI and CII) cumulative emissions of CH_4, CO_2 and total GHG were 1,682, 1,508, and 3,190 gCO_{2eq} m^{-2} crop, respectively for CI and 4,350, 1,721, and 6,071 g CO_{2eq} m^{-2} crop, respectively for CII. Meanwhile, the reduction in GHG emission efficiency was 47.46 % with the rate of 32.01 g CO_{2eq} m^{-2} g^{-1} zeolite. For the SF, the cumulative emission of CH_4, CO_2 and total GHG was 1,490, 1,389, 2,877 gCO_{2eq} m^{-2} crop, respectively for the SFI, and 3,351, 1,720, and 5,071 gCO_{2eq} m^{-2} crop, respectively for the SFII. Likewise, the reduction of GHGs emission efficiency of the SF was 43.27 % with the rate of 24.38 gCO_{2eq} m^{-2} g^{-1} zeolite.

On the other hand, CH_4, CO_2 and GHG emissions from the TTFI were found 2,138, 1,526, and 3,664 gCO_{2eq} m^{-2} crop. For those without zeolite 4A; TTFII the gas emissions were 4,355, 1,255, and 5,610 gCO_{2eq} m^{-2} crop. Therefore, the reduction of GHGs emission efficiency of the TTF was 34.69% with the rate of 21.62 g CO_{2eq} m^{-2} g^{-1} zeolite. For the SROFI, the cumulative emission of CH_4, CO_2 and GHG were 4,121, 1,577, and 5,699 gCO_{2eq} m^{-2} crop, respectively. Meanwhile, the emissions of those gases from the SROFII were 4764, 1,022, and 5,786 gCO_{2eq} m^{-2} crop, respectively. With this result, the reduction of GHGs emission efficiency for the SROF was 1.50 % with the rate of 0.97 gCO_{2eq} m^{-2} g^{-1} zeolite.

Table 6 Cumulative GHGs emissions

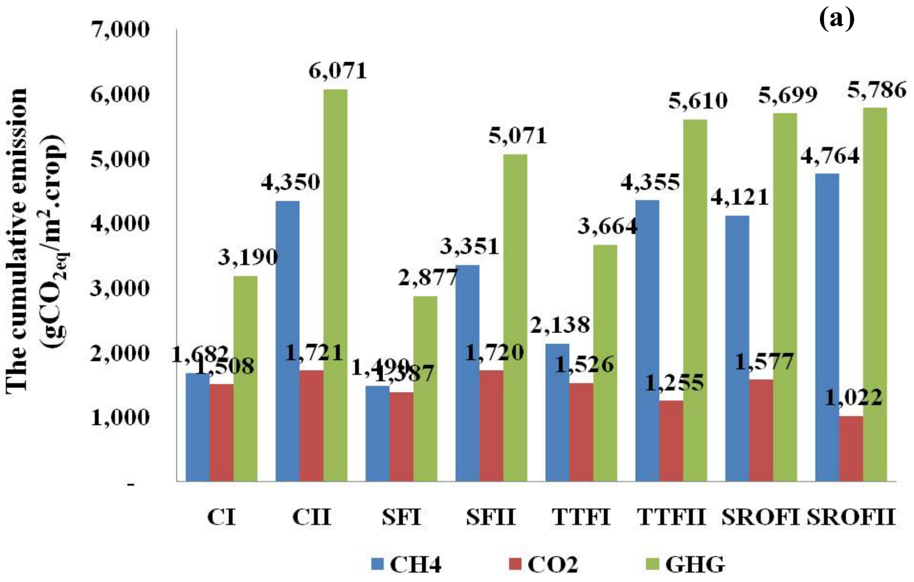
		Cumulative emissions (gCO^{2}_{eq} m^{-2}.crop)					
		CH_4		**CO_2**		**Total GHG**	
		X	**SD**	**X**	**SD**	**X**	**SD**
C	**I**	$1,682^{a}$	56	$1,508^{a}$	49	$3,190^{a}$	70
	II	$4,350^{b}$	64	$1,721^{b}$	48	$6,071^{b}$	16
SF	**I**	$1,490^{c}$	98	$1,387^{c}$	34	$2,877^{c}$	64
	II	$3,351^{d}$	52	$1,720^{b}$	74	$5,071^{d}$	22
TTF	**I**	$2,138^{e}$	41	$1,526^{ae}$	59	$3,664^{e}$	18
	II	$4,355^{b}$	34	$1,255^{d}$	22	$5,610^{f}$	56
SROF	**I**	$4,121^{f}$	18	$1,577^{e}$	78	$5,699^{g}$	60
	II	$4,764^{g}$	55	$1,022^{f}$	39	$5,786^{h}$	16
F-test		1793.991		118.274		3393.840	
Sig.		0.000		0.000		0.000	

Note: C = Control (no fertilizer), SF = 1 x chemical fertilizer, TTF = 2x chemical fertilizer, SROF = Slow-release organic fertilizer, I = with zeolite 4A, II = without zeolite 4A
^{a,b,c,d,e,f,g,h} = letters in same group are not statistically different at $p \leq 0.05$.

Table 7 Emission reduction efficiency and rate per gram zeolite

	Emission reduction			
	Efficiency (%)		**Rate (gCO_{2eq}/m^2.g zeolite)**	
	X	**SD**	**X**	**SD**
C	47.46^a	1.55	32.01^a	1.12
SF	43.27^b	0.83	24.38^b	0.38
TTF	34.69^c	0.79	21.62^c	0.67
SROF	1.50^d	0.62	0.97^d	0.40
F-test	1686.153		1404.587	
Sig.	0.000		0.000	

Note: C = Control (no fertilizer), SF = 1 x chemical fertilizer, TTF = 2x chemical fertilizer, SROF = Slow-release organic fertilizer, ^{a,b,c,d} = letters in same group are not statistically different at $p < 0.05$.



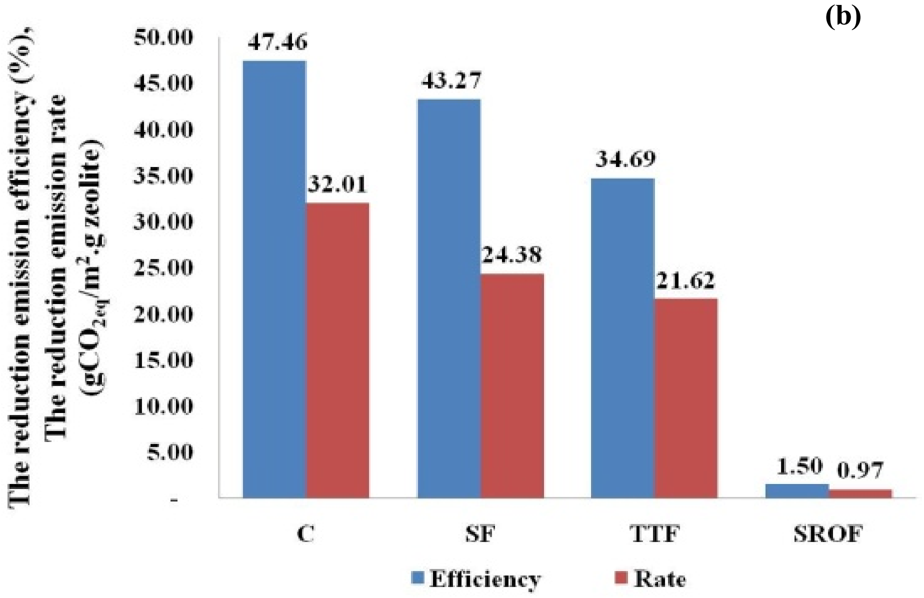


Figure 4 Cumulative emissions and reduction emission rates of CH_4, CO_2 and total GHG.

The results demonstrate the effectiveness of zeolite 4A in adsorbing CH_4 and CO_2; it is likely that efficiency can be further improved because the mineral structure can be adjusted to specifically adsorb different gases [17]. Adsorption occurs through a physico-chemical mechanism, with both CO_2 and CH_4 adsorbed via a physical mechanism by the porous matrix of the zeolite, while CO_2 gas also reacts with adsorbed cations in the zeolite as a chemical mechanism [28, 30].

From statistical analysis, treatments by fertilizer application show significant different results on the GHGs emission both for the emission reduction and rate of emission. The control was found having higher both for the reduction of GHGs emission efficiency and the emission rate than all the treatments; SF, TTF and SROF. It indicates that for the control, zeolite 4A performed as a gas absorber for CH_4 and CO_2. Meanwhile in the treatments of SF and TTF both once and twice chemical fertilizer applications, the zeolite 4A also performed as a nutrient absorbent, especially for ammonium and potassium, etc. Therefore, zeolite 4A can adsorb mineral ions as a chemical adsorption, in conjunction with adsorbs CH_4 and CO_2 gas in its porous [28, 30]. Consequently, the zeolite 4A in the treatment of SF and TTF had not sufficient active porous for a better performance on the reduction of GHGs emission as compared to those of the control, especially, for the twice fertilizer application (TTF). Therefore, the reduction of GHG emission was found decreased [17].

It can be concluded that zeolite 4A not only adsorbed CH_4 and CO_2 gas, but also adsorbed nutrients from fertilizer, especially NH_4^+ , NO_3^- and K^+. [12-13]. When zeolite has adsorbed cations within the pore matrix, less CH_4 and CO_2 can be adsorbed as the pore volume is not sufficient to adsorb both the cations and gases together. For this reason, the cumulative GHG emissions were higher than with SF and the control, hence the reduction of GHG emission efficiency of TTF was reduced compared with other treatments.

For the SROF treatment, the results indicated that zeolite 4A addition had no significant effect on cumulative GHG emissions. The reason was that the organic fertilizer is decomposed to CH_4 gas under anaerobic condition in the soil by methanogenic bacteria [3]. However, it was supported that the CH_4 emission of the paddy cultivation with the organic fertilizer was higher than without [8]. Furthermore, the organic fertilizer application increases CH_4 gas higher than the others, so that the amount of zeolite 4A was not adequate to reduce the additional emissions. It is likely therefore that the effect of zeolite is dose-dependent [20].

Conclusion

Zeolite 4A addition affected cumulative GHG emissions from rice; zeolite 4A was found to adsorb CH_4 and CO_2, reducing total emissions. The combination of zeolite and chemical fertilizer application in one or two applications led to antisynegetic effect. While the higher fertilizer application stimulated crop and resulted in higher yields and percentage of good grain, the efficiency of GHG reduction decreased. The ratio of zeolite 4A to fertilizer should be higher than 3:1 to reduce the elevated GHG emissions resulting from fertilizer use. The treatment resulted in an emission reduction efficiency of 34.69 %, with a rate of 21.62 $gCO_{2eq}\ m^{-2}\ g^{-1}$ zeolite. In the current study, two applications of chemical fertilizer plus zeolite 4A showed the best performance in reducing emissions; however, it is recommended that the ratio of zeolite to fertilizer should be increased. Similarly, the slow-release organic fertilizer resulted in increased CH_4 emissions due to the action of methanogenic bacteria on the organic matter; nevertheless, crop growth, percentage good grain and total grain yield were all increased. It is recommended that further studies examine the optimal ratio of zeolite 4A to organic and synthetic fertilizers for rice cultivation.

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References

[1] Greenhouse gas emission in Thailand. [Online] Available from: http://www.environnet.in.th/archives/3779

[2] Applied Economics Research Center, Faculty of Economics, Kasetsart University. National Report No. 2 for UNFCCC, Office of Natural Resources and Environmental Policy and Planning, Ministry of Natural Resources and Environment, September 2010.

[3] Mungkung, R., Gheewala, S., Poovaroodom, N., Towprayoon, S. Carbon footprint and Carbon label of Rice. The Thailand Research Fund, 2010, 1-83.

[4] Dubey, S.K. Methane Emission and Rice Agriculture. Current Science, 2001, 81, 345-346.

[5] Kumaraswamy, S., Kumar, R.A., Ramakrishnan, B., Sethunathan, N. Wetland rice soils as sources and sinks of methane: a review and prospects for research. Biology and Fertility of Soils, 2000, 31, 449-461.

[6] Aulakh, M.S., Singh, B. Methane Emissions from Rice Fields - Quantification, Mechanisms, Role of Management, and Mitigation Options. Advances in Agronomy, 2000, 70, 193-260.

[7] Minamikawa, K., Sakai, N. The practical use of water management based on soil redox potential for decreasing methane emission from a paddy field in Japan. Agriculture, Ecosystems and Environment, 2006,116, 181-188.

[8] Graduate School of Energy and Environment. Full Report on Greenhouse Gas Inventories in Thailand. King Mongkut's University of Technology Thonburi, Bangkok: Office of Natural Resources and Environmental Policy and Planning, 2010.

[9] Wanichpongpan, P. Emission and factors influencing the methane emission from paddy fields. Master of Science Thesis, King Mongkut's University of Technology Thonburi, 1993.

[10] Trends in greenhouse gas emission and potential Greenhouse gas reduction. [Online] Available from: http://measwatch.org/sites/default/files/bookfile/3.pdf.

[11] Jahmori, M.F., Liang, J.B., Rosfarizan, M., Goh, Y.M., Shokryazdan, P., Ho, Y. W. Efficiency of rice straw lignocelluloses degradability by Aspergillus terreus ATCC 74135 in solid state fermentation. African Journal of Biotechnology, 2011, 10(21), 4428-4435.

[12] Kausar, H., Sariah, M., Razi, I.M., Mohd S.H., Habib, S.H., Berahim, Z. Development of a potential lignocellulolytic resource for rapid bioconversion of rice straw, 2012, 11(38), 9235-9242.

[13] Kamarudin, K.S.N., Hamdan, H., Mat, H. Methane adsorption characteristic dependency on zeolite structures and properties. The 17th Symposium of Malaysian Chemical Engineers, 2003.

[14] Sansupan, Y. Adsorption isotherms of concentrated hydrocarbon gases on zeolites. Thesis Master of Engineering. Chulalongkorn University, 1998.

[15] Torii, K. Utilization of natural zeolite in Japan, in “Natural Zeolites: Occurrence, Properties, Use” Sand, L.B., Mumpton, F.A., Editor. Pergamon Press, Elmsford, New York, 1978, 441-450.

[16] Butorac, A., Filipan, T., Basic, F., Butorac, J., Mesic, M., Kisic, I. Crop response to the application of special natural amendments based on zeolite tuff. Rostlinná Výroba, 2002, 48, 118-124.

[17] Polat, E., Karaca, M., Demir, H., Naci-Onus, A. Use of natural zeolite (Clinoptilolite) in agriculture. Journal of Fruit Ornamental and Plant Research, 2004, 12, 183-189.

[18] Indonesian Center for Agricultural Land Resources Research and Development (ICALRD). Greenhouse gas emission under different crop management practices in Indonesia. 2010. [Online] Available from: http://www.niaes.affrc.go.jp/marco/marco_gra2010/07_marco_gra_setyanto.pdf

[19] Wang, J.Z., Hu, Z.Y., Zhou, X.Q., An, Z.Z., Gao, J.F., Liu, X.N. …, Kardol, P. Effects of reed straw, zeolite, and superphosphate amendments on ammonia and greenhouse gas emissions from stored duck manure. Journal of Environmental Quality, 2014, 4, 1221-1227.

[20] Natpinit, P., Anuwattana, R., Ditkaew, T., Suppinunt, T. Application of Rice Stubble Synthesized Zeolite for Greenhouse Gas Reduction. Applied Environmental Research, 2016, 38(2), 23-31.

[21] Guangzhou Chemxin Environmental Material Co., Ltd. [Online] Available from: http: www.chemxin.com.

[22] Perkin, T.B., Venterea, R. Sampling protocols. Chapter 3. Chamber-based trace gas flux measurements. In R.F. Follett (Ed.), Sampling protocol, 2010, 1-139.

[23] Sander, B.O., Wassmann, R. Common practices for manual greenhouse gas sampling in rice production: a literature study on sampling modalities of the closed chamber method, Greenhouse Gas Measurement and Management, 2014, 4(1), 1-13.

[24] Perkin, T.B. Effect of sampling frequency on estimates of cumulative nitrous oxide emissions. Journal of Environmental Quality, 2006, 37(4), 1390-1395.

[25] Bureau of Land Resources Survey and Research, Land Development Department, Ministry of Agriculture and Cooperatives. Characteristics and properties of Northeastern soil series: Korat soil series. [Online] Available from http://oss.101ldd.go.th/web_thaisoils/pf_ desc/northeast/Kt.html

[26] Yokthaworn, M., Tawornpruek, Chittamart, N. Soil Fertility Capability Classification for Agricultural Uses on Sloping Areas: A Case Study in Chiang Muan District, Phayao Province Songklanakarin Journal of Plant Science, 2016, 3(1), 30-40.

[27] Ganzhara, N.F. Humus, soil properties and yield. Eurasian Soil Science, 1998, 31, 738-745.

[28] Wong, T.W. Handbook of zeolites: Structure, properties and applications. Nova Science Publishers, 2009.

[29] Milosevic, T., Milosevic, N. The effect of zeolite, organic and inorganic fertilizers on soil chemical properties, growth and biomass yield of apple trees. Plant, Soil and Environment, 2009, 55(12), 528-535.

[30] Shashoua, Y. Zeolites. 1996. [Online] Available from: http://cool.conservation-us.org/byorg/abbey/an/an20/an20-7/an20-702.html