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Experimental quantification of greenhouse gas (CH$_4$) emissions from fertilizer amended rice field soils of Kashmir Himalayan Valley

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Abstract

Background: Methane, considered second major greenhouse gas after CO$_2$, with significant fluxes from agro-ecosystems is held responsible for global warming and climate change. In order to address this environmental challenge, world-wide attention continues to focus on this important topic. Field data are provided on much-needed information on this greenhouse gas from little–explored hilly and temperate region of Kashmir Himalaya, India.

Methods: Methane determination was done by collecting the gas samples using closed chambers, and analyzed by Gas Chromatograph (Shimadzu 14BPSTF) fitted with flame ionization detector (FID).

Conclusions: Rice in some circles is condemned as the major culprit for the global warming, climate change and environmental degradation. The application of biodigested manures over the fresh organic manures like farmyard manure, green manure etc constitutes one of the amelioration mechanisms to retard methane emission in rice cultivation. As such rice (and livestock) deserves adequate attention to target CH$_4$ emission reduction. Livestock are well implicated in highest methane emissions as compared to other subsectors of agriculture. However, there is a need to strike a balance between food security through rice protection and sustainability of resource-base and global climate.

Keywords: Greenhouse gas, Kashmir Himalaya, CH$_4$ estimation, rice field soils

Introduction

Natural wetlands of Kashmir Himalayan valley, India, researched over the years continue to remain the focus of recent attention of workers [1,2]. However, rice fields considered an integral part of wetland ecological research and source of potential green house gas (methane) have been almost ignored.

Methane ranks second major greenhouse gas (GHG) after CO$_2$ with significant fluxes from agro-ecosystems. Rice fields, in particular, are considered [3,4,5] to be one of the important sources (20%) of CH$_4$ emission on a global scale. During the last 200 years, its concentration in the atmosphere has more than doubled; the preceding 40 years witnessed about 50% increase. Some recent estimates have been provided [6] of methane from global rice fields; 25.6 Tg CH$_4$ year^{-1}, with 95% certainty range of 14.8-41.7 Tg CH$_4$ year^{-1}. Sporadic country-wise methane emissions are also available. Very recent study [7] quantified methane emissions from rice paddies in northeast China by integrating remote sensing mapping with a biogeochemical model, and the results showed that total 1.44 Mha (million ha) of rice paddies in the plain emitted 0.43-0.58 Tg CH$_4$ year^{-1} methane. Similarly, studies conducted state-wise for 1994 in India [8] indicated national methane budget estimate of 4.09 Tg CH$_4$ year $^{-1}$ and the trend from 1979 to 2006 was in the range of 3.62 to 4.09

Tg CH$_4$ year^{-1}. Four higher emitting or "hotspot" states (West Bengal, Bihar, Madhya Pradesh and Utter Pradesh) in India account for 53.9% of total methane emission.

Data reported [9] show that Indian methane emissions have grown from 18.85 Tg CH$_4$ in 1985 to 20.56 Tg CH$_4$ in 2008. The important sources of atmospheric methane documented [10] are microbial mineralization of organic matter under strict anaerobic conditions such as landfills, paddy fields, biomass burning etc. In view of this scenario, methane is rightly implicated in global climate change. Reports [11] indicate that 70% increase in green house gases (GHGs) occurred during 1970-2004, and the global increases in CO$_2$ are attributed mainly to fossil fuel use while those of methane (and nitrous oxide) are primarily due to agriculture activities. Further, agriculture sector in India contributes 28% of the total GHG emissions. According to Intergovernmental Panel on Climate Change [12] the global average from agriculture is 13.5%. Irrigated rice production, a major food source for a large portion of the world's population is recognized to be a major anthropogenic source of methane. Global emission estimates [13] for this source range from 20 to 100 Tg CH$_4$ year^{-1}, which may be 4–30% of the total anthropogenic contribution to the atmosphere. Average estimate of methane 110 Tg CH$_4$ within a range of 25-170 Tg CH$_4$ released annually from rice-paddies are reported in Asia [14]. Moreover, Asia

Table 1. Details of treatments and agronomic practices.

Variety	Paddy (SKAU-23)
Number of treatments	3
Statistical design	Randomized block
Details of treatments	(a) Control (b) Urea (100% N)
	(c) Amm. Nitrate (100%) (d) BMSA
	(e) Methyl chloride (f) FYM (100% N)
	(g) Wheat straw+Urea (h) Wheat straw+Cellulolytes
	(i) Vermicompost (100% N)
	(j) Aquatic weeds
	(k) Aquatic weeds+FYM

Table 2. Physico-chemical characteristics of SKUAST-K Shalimar soil.

Properties	Value
Textural class	Silty clay loam
Sand (%)	
Coarse	0.91
Fine	14.20
Silt (%)	50
Clay (%)	34
Bulk density (g cm^{-3})	1.25
pH (1:2 Soil: water)	6.8
Electrical conductivity (ds m^{-1})	0.26
Organic carbon (%)	0.9
CEC (c molc kg^{-1})	12
Available N (kg ha^{-1})	280
Available P (kg ha^{-1})	14
Available K (kg ha^{-1})	220

claims almost 90% of world's harvested rice-area; 60% production of it in China and India from where sufficient scientific data on this GHG (CH_4) are not available. In order to meet the growing demands of surging trend of population increased rice production is inevitable by adopting modern technologies in all rice ecologies. Therefore, global CH_4 emission from wetland rice agriculture is likely to increase. However, an effective land and water resource management can reduce the emissions substantially.

Throughout the world, attention on various amendments in CH_4 emission is making the research field subject of high importance. Kashmir valley, located in the Western Indian Himalaya is aptly referred to as 'rice bowl' with 2385 thousand quintal production of rice [15], having 12th rank. The rice being staple food, is the principal *Kharif* (rainy season) crop cultivated on an area of more than 1.4 lac hectare, and grown between March-April and harvested in autumn. Except for preliminary report [16] on methanogenesis, no work has been carried out from temperate region of Kashmir valley. The impact on CH_4 emission is influenced by combination of nature, rate and application method of minerals as well as organic fertilizers. The research findings [17] show that the influence of organic amendments with inorganic fertilizers cause enhanced CH_4

gas emission as compared to the use of inorganic fertilizer alone. The paucity of information from temperate regions is a constraint in analyzing global scenario of CH_4 flux from wetlands. Adequate experimental data from various agro-climatic regions of the valley are sorely desired to aid in assessing overall role to national/global methane scenario. However, using IPCC coefficients, it is estimated to be 50 Gg (Gg=10^9).

The present research paper provides the results of field experimentations on CH_4 emission from Kashmir Himalayan valley rice field soils amended with various inorganic and organic fertilizers to augment research base-data from little-explored temperate regions.

Materials and methods
Field set-up and agronomic practices
Field experiments were conducted during *Kharif* season in the year 2004 at the Research Farm of S-K University of Agricultural Sciences and Technology of Kashmir (SKUAST-K), Shalimar, to study the impact of different nitrogen (N) sources (organic and inorganic) on CH_4 emissions by rice (*Oryza sativa*) cultivation. In Kashmir, paddy is grown under submerged conditions with water depth of 5-10 cm. The recommended amount of organic fertilizer FYM being 10 tonnes ha^{-1}; inorganic fertilizer (ha^{-1}) with respect to different sources being N (80 kg), P_2O_5 (60 kg), K_2O (30 kg), $ZnSO_4$ (10-15 kg). Seedlings of paddy (SKAU-23) were transplanted on June 17, 2004. Treatments were applied through different sources viz-a-viz control, urea (100% N), Ammonium nitrate (100% N) [100% N refers to application of total recommended N in the form of respective material i.e., Urea or Ammonium nitrate (eg., 100% N from Urea means application of 174 kg urea, Urea has 46% N], Bromethane sulphonic acid (BMSA), Methyl chloride, FYM (100%), wheat straw + cellulolytes, vermicompost (100% N), aquatic weeds, and aquatic weed+FYM. Each treatment was replicated in randomized block design (RBD). The FYM, wheat straw, aquatic weeds, vermicompost and different blends (referring to mixtures of inputs used in the study), as per treatments, were incorporated one week prior to transplantation. Ammonium nitrate, BMSA and Methyl chloride were applied one day after transplanting. A basal dose of Nitrogen (50% of urea) was applied along with 60 kg P ha^{-1} and 40 kg K ha^{-1} the rest of the Nitrogen was applied in two–split doses i.e., 3 weeks and 6 weeks post transplantation. Basal dose of fertilizers refers to recommended P_2O_5, K_2O and 50% of recommended N (i.e., 40 kg N); tillering stage (15-18 days after transplanting)=25%N; panicle initiation stage (38-42 days after transplanting)=25%N. The details of treatments and agronomic practices are given in **Table 1**.

Soil analysis
The soil samples of the experimental sites were analyzed by standard methods of Analysis [18]. The main physical and chemical characteristics of the soil are given in **Table 2**.
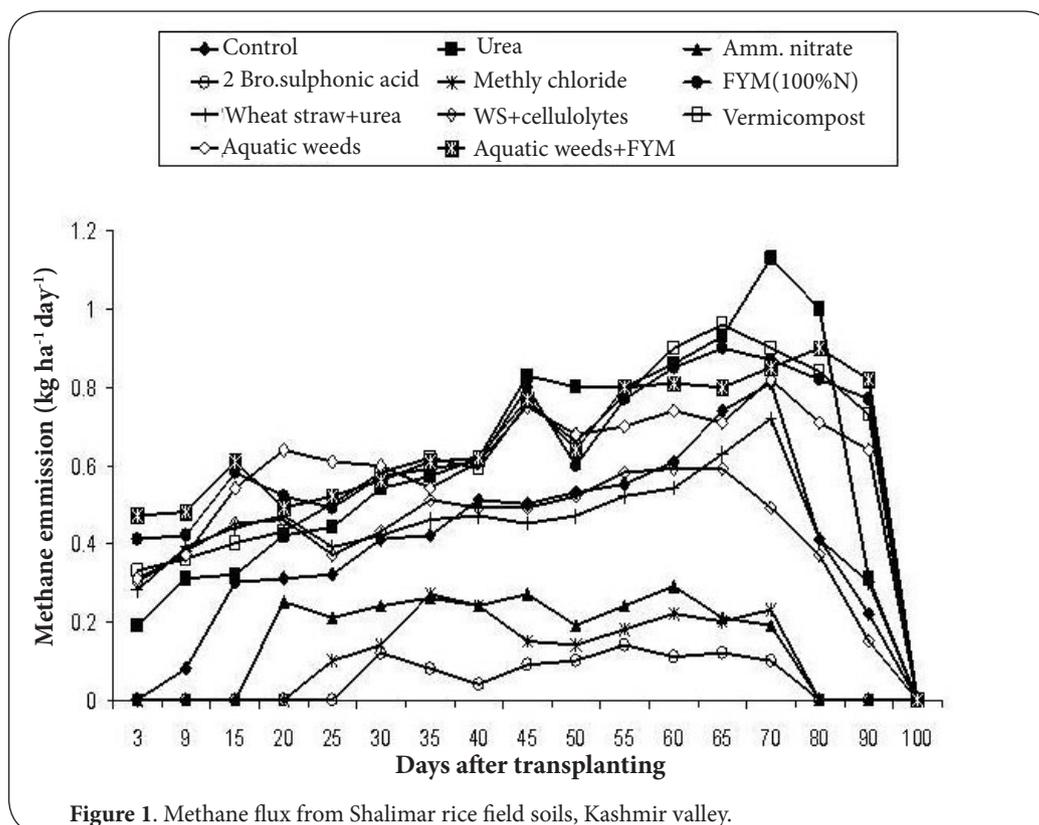
Figure 1. Methane flux from Shalimar rice field soils, Kashmir valley.

Methane emissions and flux measurements

After transplanting 25-days old seedlings in the rice field the determination of methane emissions was done 100 DAT (days after transplanting). Methane was determined after 100 days after transplanting because before this it was not produced in detectable quantities. Gas samples were collected following closed chamber technique [19]. Gas samples were collected once a day between 11:00 and 11:30 hr at regular intervals of 3-4 days using closed chambers. The chambers were installed at the sampling sites and gas samples were collected at 10 minute interval from chambers involving bottomless plexi chambers (100 x 50 x 30 cm) fitted on a permanently installed base unit (open bottom) and removable top. During gas collection, flood water was used to seal the top of the base unit. A rubber septum was fitted in to chamber through which gas was collected. Water level was never allowed to recede below the base unit. Each chamber was fitted with a thermometer to record the ambient temperature. Soil temperature and redox measurements were done at the time of each gas collection. Gas collection was made through rubber septum with a gas-tight syringe containing stainless steel hypodermic needles. Collected gas samples were immediately transferred to pre-evacuated vacutainers by hypodermic needles upon gas collection. The samples were analyzed for CH_4 by Gas Chromatograph(Shimadzu 14 BPSTF) fitted with flame ionization detector (FID). The unknown gas samples (0.1 ml) were injected in to stainless steel column Porpaq Q.

The injector and detector temperatures were maintained at 100 and 120^0C respectively. Standard CH_4 gas was used for comparison. CH_4 gas appeared after retention time of 1.1 minute. The chromatograms were processed by Omega software. The methane flux (F) was calculated using the equation: $F=(V/A)(\Delta C/\Delta t)$ whereas F=CH_4 gas flux, V=volume of head space chamber, A=Soil surface under chamber and $\Delta C/\Delta t$ is change in concentration per unit of time.

Results and discussion
Physico-chemical characteristics of soil
The soil properties of the experimental sites indicate silty clay loam texture having bulk density of 1.25 g cm^{-3} and non-acidic (pH=6.8) character. The fertility status of the soil is medium in relation to available nitrogen, phosphorus and potassium. The physical properties of soil are good enough to support the growth of rice crop (**Table 2**).
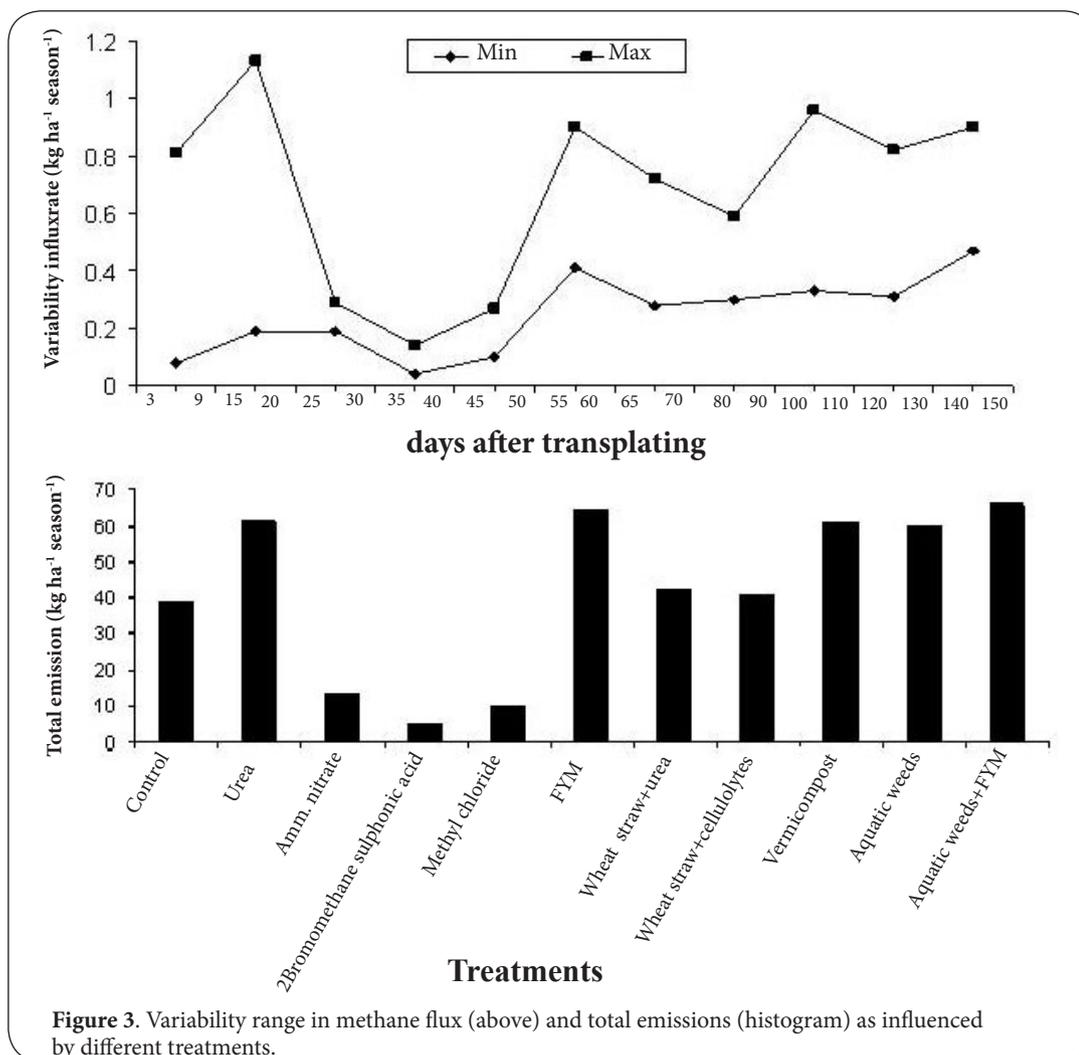
Seasonal methane flux
The methane fluxes from the experimental sites were highly variable. The seasonal changes in daily CH_4 emissions as influenced by urea, Ammonium nitrate, BMSA, Methyl chloride, FYM, wheat straw+urea, wheat straw+cellulolytes, vermicompost, aquatic weeds and aquatic weeds+FYM related to growth stages of rice crop are graphically given in **Figure 1**. The observations revealed that in most of the treatments, CH_4 emissions were at their lowest and beyond detectable levels within first three days after transplantation.

Figure 2. Diel variations in methane flux (kg ha^{-1}) during growing season of rice.
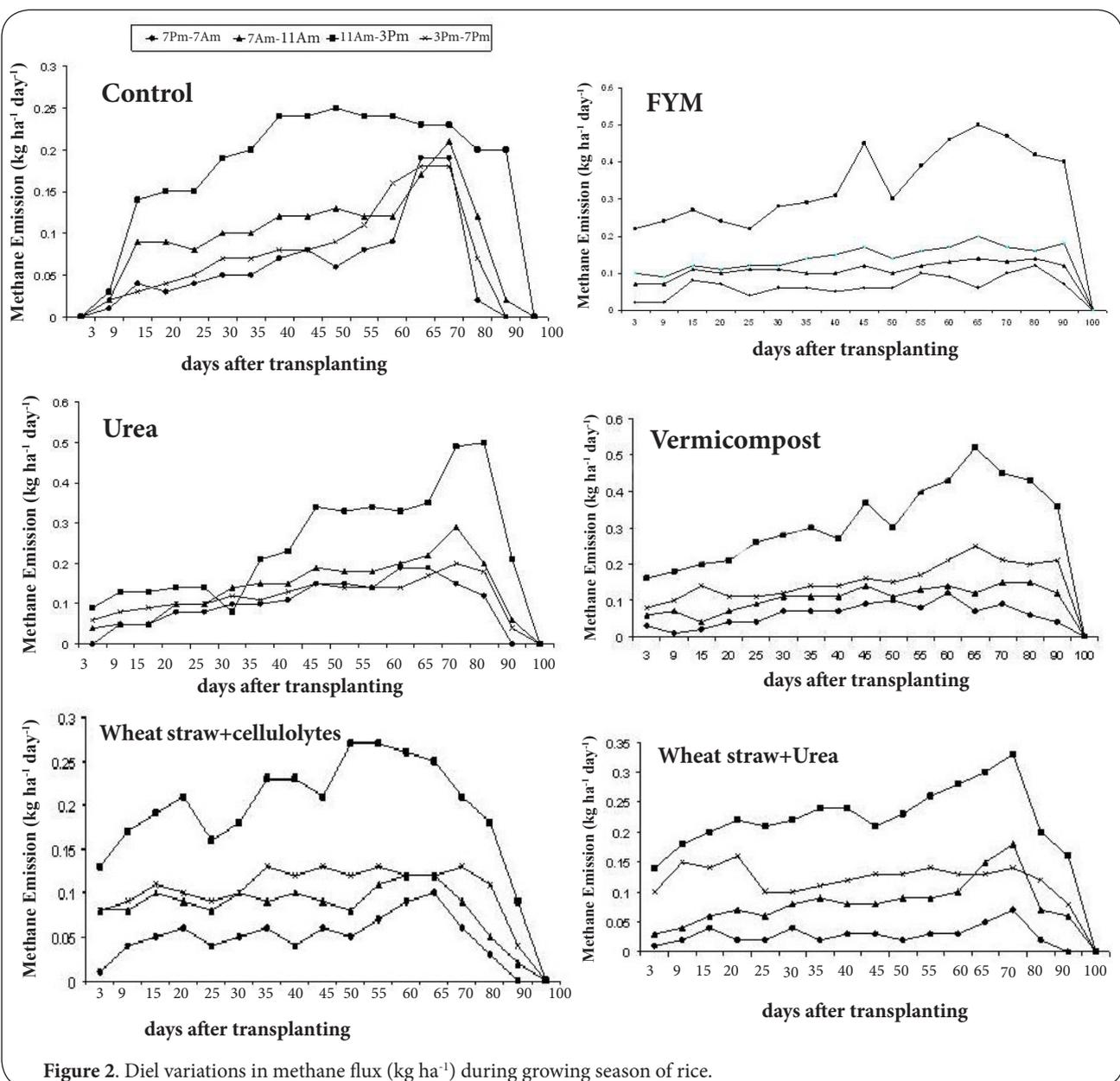
However, treatments of urea, FYM, wheat straw+urea, wheat straw+cellulolytes, vermicompost, aquatic weeds, and aquatic weeds+FYM caused CH$_4$ emission from 0.19 to 0.47 kg ha^{-1} d^{-1}. On 9th day, CH$_4$ flux fluctuated between 0.08-0.48 kg ha^{-1} d^{-1} with peak recorded in relation to aquatic weed+FYM. Thereafter, steady decline in emissions were observed over next 20 days. The second maximum peak (SM) was recorded on 45 DAT touching 0.83 kg ha^{-1} d^{-1} for FYM and 0.77 kg ha^{-1} d^{-1} for aquatic weed+FYM. However, in relation to urea, first maximum 0.83 kg ha^{-1} d^{-1} occurred on 45 DAT while that of vermicompost (0.62 kg ha^{-1} d^{-1}) was on 35 DAT. Methane fluxes registered declining trend over the next 3 weeks. Methane emissions increased substantially during following weeks and reached third maxima on 65 DAT for FYM treatment (0.90 kg ha^{-1} d^{-1}) and

vermicompost (0.96 kg ha^{-1} d^{-1}). A mean of 1.13 kg ha^{-1} d^{-1} was recorded for urea treated site on 70 DAT. Marked decline in CH$_4$ emission occurred after 70 days, and practically no methane could be recorded on 100 DAT. Studies conducted [20] on IARI rice fields during *kharif* (rainy season) reported CH$_4$ emissions at their lowest value during early submerged and before harvesting period. The authors observed first maximum peak (FM) at 15 DAT, second (SM) at 46 DAT, and third one (TM) at 69 DAT. Higher CH$_4$ emission levels in FYM-treatment site observed during the present study seem consistent with results [20] which is attributable to more readily decomposable organic matter as compared to other treatments. The production of increased CH$_4$ from organic matter treatment in comparison to the plots containing no exogenic organic matter is well documented [21]. The

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Figure 3. Variability range in methane flux (above) and total emissions (histogram) as influenced by different treatments.

noticeable increase in emissions recorded after 3-4 days continued over the next 15 days reaching a first maximum peak (FM) at 15 DAT in relation to FYM (0.58 kg ha^{-1} d^{-1}) and aquatic weed+FYM (0.61 kg ha^{-1} d^{-1}). In relation to Ammonium nitrate, BMSA and Methyl chloride treatments, depressed CH$_4$ fluxes were recorded in the range of 0.19-0.29, 0.04-0.14, and 0.10-0.27 kg ha^{-1} d^{-1} respectively. CH$_4$ emission from treated site was higher than the control. The results obtained during the present study indicate that the findings are in agreement with observations [22] that the fertilized plots emit the higher levels of methane. Recent report [5] indicate that methane emissions in rice fields can be as much as 90% higher in continuously flooded rice fields compared to other water management practices, independent from straw addition.

Diel cycle of methane flux
Data on diel variations of CH$_4$ flux recorded at different intervals for 24 hr duration are set in **Figure 2**. First observation for overnight emission was done at 07 hr. Collection during the day were made at regular intervals of four hour (11, 15, 19 hrs). The results clearly show that higher emission rates were recorded in the afternoon. Published report [23] shows high methane emissions rates during 12-15 hr. The diel-cycle sequence of CH$_4$ flux was in the order of 15 hr>11hr>19>07hr. The diel emissions in relation to various treatments depicted marked fluctuations. The qualitative trend, though similar displayed significant quantitative variability with FYM, vermicompost, and urea treatments showing higher CH$_4$ emissions as compared to other treatments during afternoon period. The wheat straw+urea, and wheat straw+cellulolytes treatment had almost similar diel pattern of methane flux.

Total methane flux
Total estimated CH$_4$ emission obtained by integrating the seasonal variations is representative of annual values as the rice fields, after crop harvest are not flooded until next spring season. Total emission in the control ranged from a minimum of 0.08 to a maximum of 0.81 kg ha^{-1} and seasonal

emission was estimated to be 39.32 kg ha^{-1}. Higher values of 65.78 kg ha^{-1} season^{-1} was obtained for aquatic weed + FYM followed by 64.24 for FYM-treated soil. Vermicompost treatment gave a value of 60.96 kg ha^{-1} season^{-1} (**Figure 3**). Markedly low values of 4.85, 9.98 and 13.67 kg ha^{-1} season^{-1} were recorded for 2BMSA, Methyl chloride and Ammonium nitrate treated soils respectively. Except for these three, in all other treatments, the seasonal emissions were higher than the control depending on the type of fertilizer amendments. The results reveal that the impact on CH$_4$ emission is influenced by type of fertilizer. The inhibition of methanogenesis due to nitrate-addition may be due to toxic effects or the presence of intermediate nitrites. Inhibition effect of sulphate could be due to high redox conditions as well as competition amongst diverse microorganisms for methanogenic substrate. Field experiment conducted [24] at research farm of the IARI, New Delhi, during wet season (July-October) with various rice cultivars reported maximum seasonal emission (27.2 kg ha^{-1}) for 'PUSA 933' and minimum (15.6 kg ha^{-1}) for 'PUSA 169'.

The present study shows that methane emission was higher in treatments (aquatic weed+FYM), FYM, Urea, and vermicompost indicating readily decomposable organic materials stimulate the emission of methane in rice-fields. In order to meet the demand of an increasing population, global rice production has been estimated to double by the year 2020, which may increase CH$_4$ production by up to 50% [13] . Such a scenario calls for improved rice cultivation techniques and manure management to retard methane emissions as an amelioration strategy.

Conclusion
The present study concludes that methane emissions from natural wetlands including rice fields are deeply implicated in global warming and their experimental quantification is a research topic of high priority today. Rice in some circles is condemned as the major culprit for the global warming, climate change and environmental degradation. The application of biodigested manures over the fresh organic manures like farmyard manure, green manure etc constitute one of the amelioration mechanisms to retard methane emission in rice cultivation. As such rice (and livestock) deserves adequate attention to target CH$_4$ emission reduction. Recent report [25] shows highest (>70%) methane emission contribution from Indian livestock as compared to various other subsectors from agriculture. Deficient data on this greenhouse gas, especially from temperate regions, limits the interpretation of fall-out of climate change. There is a need to strike a balance between food security through rice protection and sustainability of resource-base and global climate.

Competing interests
The authors declare that they have no competing interests.

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