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Review

Fertilizer management practices and greenhouse gas emissions from rice systems: A quantitative review and analysis

Bruce A. Linquist[a,*], Maria Arlene Adviento-Borbe[a], Cameron M. Pittelkow[a], Chris van Kessel[a], Kees Jan van Groenigen[b,c]

[a] *Department of Plant Sciences, University of California, Davis, CA 95616, USA*
[b] *Department of Biological Sciences and Merriam-Powell Center for Environmental Research, Northern Arizona University, Flagstaff, AZ 86011, USA*
[c] *Department of Botany, School of Natural Sciences, Trinity College Dublin, Dublin 2, Ireland*

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ABSTRACT

Flooded rice systems emit both methane (CH_4) and nitrous oxide (N_2O). Elevated CH_4 emissions in rice systems can lead to a high global warming potential (GWP) relative to other crops, thus strategies to reduce greenhouse (GHG) emissions, particularly CH_4, are needed. Altering water, residue (carbon) and fertilizer management practices are commonly suggested as options for mitigating GHG emissions in rice systems. While the effects of water and residue management have been reported on elsewhere, the impact of fertilizer management on GHG emissions has not been reviewed quantitatively. We conducted an exhaustive search of peer-reviewed field studies that compared various side-by-side fertilizer management options. Where sufficient studies were available a meta-analysis was conducted to determine average treatment effects of management practices on both CH_4 and N_2O emissions. Results show that low inorganic fertilizer N rates (averaging 79 kg N ha^{-1}) increased CH_4 emissions by 18% relative to when no N fertilizer was applied, while high N rates (average of 249 kg N ha^{-1}) decreased CH_4 emissions by 15%. Replacing urea with ammonium sulfate at the same N rate significantly reduced CH_4 emissions by 40%, but may increase N_2O emissions. Overall, the fertilizer-induced emission factor for all inorganic N sources was 0.22%. Dicyandiamide (DCD), a nitrification inhibitor, led to lower emissions of both CH_4 (−18%) and N_2O (−29%). Limited field data suggest that deep placement of N fertilizer reduces CH_4 emissions but increases N_2O emissions. When compared to inorganic N fertilizers, farmyard manure (FYM) increased CH_4 emissions by 26% and the green manure (GrM) *Sesbania* by 192%. Neither FYM nor GrM had a significant impact on N_2O emissions when compared to an inorganic N treatment at the same N rate. Sulfate fertilizers reduced CH_4 emissions by 28% and 53% at average rates of 208 and 992 kg S ha^{-1}, respectively. These findings demonstrate that a variety of fertilizer management practices affect GHG emissions from rice systems. To develop effective GHG mitigation strategies future work is needed to (i) quantify the effects on GWP (accounting for both CH_4 and N_2O emissions), (ii) investigate options for combining mitigation practices (e.g. deep placement of ammonium sulfate), and (iii) determine the economic viability of these practices.

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* Corresponding author. Tel.: +1 530 752 3125; fax: +1 530 752 4361.
E-mail address: balinquist@ucdavis.edu (B.A. Linquist).

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1. Introduction

Agriculture accounts for approximately 10–12% of total global anthropogenic emissions of greenhouse gases (GHG), which amounts to 60% and 50% of global nitrous oxide (N_2O) and methane (CH_4) emissions, respectively (Smith et al., 2007). Climate change concerns have led to efforts to reduce GHG emissions from agricultural systems. Carbon dioxide is another GHG; however, on a global scale, soil CO_2 fluxes are largely offset by net primary productivity and atmospheric CO_2 fixation by crop plants, and thus contribute less than 1% to the global warming potential (GWP) of agriculture (Smith et al., 2007). Nitrous oxide is a more potent GHG with a radiative forcing potential approximately 12 times larger than CH_4 (IPCC, 2001). Upland agricultural systems primarily emit N_2O; however flooded rice (*Oryza sativa*) systems emit both CH_4 and N_2O. Linquist et al. (2012) reported that the GWP of GHG emissions from rice systems is roughly four times higher than either wheat (*Triticum aestivum*) or maize (*Zea mays*). On average, rice systems emit 100 kg CH_4-C ha^{-1} season^{-1}, which accounts for 89% of the GWP (Linquist et al., 2012). Therefore, efforts to reduce the overall GWP of rice systems should focus on reducing CH_4 emissions; however both CH_4 and N_2O need to be considered as many strategies that reduce CH_4 emissions tend to increase N_2O emissions (Hou et al., 2000).

Methane is an end product of organic matter decomposition under anaerobic soil conditions (Conrad, 2002). Therefore, the two strategies often proposed to reduce CH_4 emissions are to limit the period of soil submergence (e.g. draining the field) and reduce carbon inputs (e.g. residue management). Management of these two factors has been the focus of many studies, which have been reviewed by Yan et al. (2005). Emissions of CH_4 and N_2O are also affected by fertilizer management and have been qualitatively reviewed (e.g. Cai et al., 2007; Majumdar, 2003; Yagi et al., 1997); however research findings appear inconsistent, with fertilizer management affecting CH_4 and N_2O fluxes at some locations but not at others. A quantitative synthesis and analysis of research data is therefore needed to identify the response of GHG emissions to fertilizer management practices. Thus, our objective was to analyze the peer reviewed literature to determine and quantify the effects of fertilizer management options on GHG emissions from rice systems in order to determine potential mitigation strategies for rice systems. We focused on the following areas: N management (rate, source, placement), the use of enhanced-efficiency N fertilizers (EENF), sulfate inputs, farmyard manure (FYM) and green manure (GrM).

2. Materials and methods

2.1. Data

We extracted data on soil N_2O and CH_4 fluxes for studies on flooded rice systems in which the effect of various fertilizer management practices were assessed in side-by-side field experiments. An exhaustive literature survey of peer-reviewed publications was carried out using ISI-Web of Science and Google Scholar (Google Inc., Mountain View, CA, USA) for articles published before August 2011. Studies needed to meet several criteria to be included in our analysis. First, N_2O and/or CH_4 fluxes must have been measured under field conditions for the entire growing season (i.e. planting to harvest). Second, seasonal fluxes and the number of field replications had to be reported for both control and treatment plots. Third, growing conditions in the control and treatment plots had to be identical (except for the management practice being studied). Studies were incorporated into seven separate datasets (Table 1). Each dataset includes studies on the response of both N_2O and CH_4 fluxes, unless indicated otherwise:

(1) *Inorganic N addition*. Studies in which a treatment without fertilizer N addition (control) was compared to treatments with fertilizer N addition (treatment). We did not include treatments that used nitrate-N, as nitrate N sources are not recommended for flooded rice systems due to the high potential of denitrification losses. To be included, studies needed to report exact fertilizer N rates. We omitted five N_2O observations (Aulakh et al., 2001; Ahmad et al., 2009; Yao et al., 2010-Suzhou site only) from the database as these appeared to be outliers as all N_2O fluxes were between 2.3 and 4.5 standard deviations higher than the mean. For the meta-analysis on the effect of N rate there were 24 studies (72 observations) and 18 studies (60 observations) for CH_4 and N_2O, respectively. We distinguished three N rate classes (low, moderate and high) that had equal number of observations. For CH_4 the average N rate of the three N classes were 79, 147 and 249 kg N ha^{-1} and for N_2O they were 96, 177, and 276 kg N ha^{-1}. Fertilizer-induced N_2O emission factors were determined by taking the difference in seasonal N_2O emissions between the control and the treatment with added N fertilizer and dividing by the amount of fertilizer N added.

(2) *Urea vs. ammonium sulfate*. Studies in which a treatment with fertilizer N added in the form of urea (control) was compared to a treatment in which the same rate of fertilizer N was added in the form of ammonium sulfate (treatment). For the meta-analysis there were 8 studies (17 observations) and 4 studies (8 observations) for CH_4 and N_2O, respectively.

(3) *Enhanced-efficiency N fertilizers (EENF).* We included studies in which a treatment without EENF (control) was compared to a treatment with EENF (treatment) using the same N rate and N source. To be included, studies needed to report the type of EENF used. Due to limited observations for a number of EENF products, a meta-analysis was only conducted on (a) all EENF and (b) DCD alone. Results reported by Li et al. (2009) were included in the meta-analysis of "All EENF" but not in the DCD meta-analysis, because all treatments in this study combined DCD with hydroquinone.

Table 1
Overview of data used for the different analyses. An "X" indicates that the study was included in that particular database while a Y (yes) or N (no) indicate if CH_4 or N_2O were reported in the study.

Authors	Location	CH_4	N_2O	N rate	Urea vs. AS[a]	EENF[a]	N placement	Sulfate (non-N)	FYM[a]	GrM[a]
Abao et al. (2000)	Philippines	Y	Y			X				
Adhya et al. (2000)	India	Y	N	X		X				X
Ahmad et al. (2009)	China	Y	N	X						
Aulakh et al. (2001)	India	N	Y							X
Bharati et al. (2000)	India	Y	N	X						
Bhatia et al. (2005)	India	Y	Y	X					X	X
Bronson et al. (1997)	Philippines	Y	Y		X					X
Cai et al. (1997)	China	Y	Y	X	X					
Chen et al. (2011)	China	Y	N	X					X	
Corton et al. (2000)	Philippines	Y	N		X			X		
Debnath et al. (1996)	India	Y	N	X					X	
Denier van der Gon and Neue (1994)	Philippines	Y	N					X		
Denier van der Gon and Neue (1995)	Philippines	Y	N							X
Dong et al. (2011)	China	Y	N	X						
Ghosh et al. (2003)	India	Y	Y	X	X	X				
Jain et al. (2000)	India	Y	N						X	
Jermsawatdipong et al. (1994)	Thailand	Y	N							X
Kumar et al. (2000)	India	N	Y	X	X	X				
Lauren et al. (1994)	USA	Y	N	X						
Lee et al. (2010)	Korea	Y	N	X						
Li et al. (2009)	China	Y	Y			X				
Lindau (1994)	USA	Y	N	X	X					
Lindau and Bollich (1993)	USA	Y	N	X						
Lindau et al. (1991)	USA	Y	N	X						
Lindau et al. (1993)	USA	Y	N		X	X		X		
Lindau et al. (1994)	USA	Y	N					X		
Lindau et al. (1998)	USA	Y	N					X		
Liu et al. (2010)	China	N	Y	X						
Lu et al. (2000)	China	Y	N						X	
Ma et al. (2007)	China	Y	Y	X						
Majumdar et al. (2000)	India	N	Y	X		X				
Malla et al. (2005)	India	Y	Y			X				
Pathak et al. (2002)	India	N	Y	X		X			X	
Pathak et al. (2003)	India	Y	N	X		X			X	
Qin et al. (2010)	China	Y	Y						X	
Rath et al. (1999)	India	Y	N	X		X	X			X
Schutz et al. (1989)	Italy	Y	N	X	X		X			
Setyanto et al. (2000)	Indonesia	Y	N				X		X	
Shang et al. (2011)	China	Y	Y	X						
Singh et al. (1999)	India	Y	N	X						
Smith et al. (1982)	USA	N	Y	X						
Suranto et al. (1998)	Indonesia	N	Y	X			X			
Wang et al. (2011)	China	N	Y	X						
Wassman et al. (1993)	China	Y	N					X		
Wassman et al. (2000)	Philippines	Y	N		X					X
Xie et al. (2010)	China	Y	N	X						
Xiong et al. (2002)	China	N	Y	X						
Yao et al. (2010)	China	N	Y	X						
Zhang et al. (2010)	China	Y	Y	X						
Zheng et al. (2000)	China	N	Y	X						

[a] Ammonium sulfate (AS), enhanced-efficiency N fertilizer (EENF), farmyard manure (FYM), and green manure (GrM).

(4) *N placement*. We included studies in which a treatment with a surface application of fertilizer N (control) was compared to a treatment with deep fertilizer N application (treatment) with similar N source and rate in both treatments.

(5) *Sulfate additions.* We included studies in which a treatment without sulfate addition (control) was compared to treatments with added sulfate (treatment). To be included, studies needed to report sulfate source and addition rates. Because N addition affects plant growth and GHG emissions, we only included studies using non-N sulfate sources. Since we found only one study that reported the effect of sulfate additions on N_2O emissions (Kumar et al., 2000), we restricted our analysis to studies reporting the effect of sulfate additions on CH_4 emissions. Studies were divided into two classes based on the rate of S applied; the average S addition rates for the two classes were 208 and 992 kg S ha^{-1}. For this analysis there were 6 studies (21 observations).

(6) *Farmyard manure*. We included studies in which treatments with an inorganic fertilizer N (control) were compared to treatments in which all or part of the fertilizer N was added as FYM (treatment). To be included, exact fertilizer N rates needed to be reported. In all studies for this analysis urea-N was used as the inorganic N source. The FYM treatment received the same total N rate as the control treatment. The N amount contributed from FYM ranged from 11 to 180 kg N ha^{-1} and represented 9–100% of the total N rate. No attempt was made to distinguish between FYM types as many studies did not report the type of FYM used or how it was handled before application. For the meta-analysis there were 8 studies (14 observations) and 3 studies (6 observations) for CH_4 and N_2O, respectively.

(7) *Green manure*. We included studies in which treatments with inorganic fertilizer N applications (control) were compared to treatments in which all or part of the fertilizer N was added as GrM (treatment). In all studies urea-N was used as the inorganic N source. To be included, exact fertilizer N rates needed to be

reported and the GrM treatment received the same total N rate as the control treatment. The N amount contributed from GrM ranged from 20 to 60 kg N ha^{-1} and represented 25–100% of the total N rate. *Sesbania rostrata* was the primary GrM used in the studies. Since CH_4 emissions have been shown to differ among GrM crops (Adhya et al., 2000), our meta-analysis only included data for *Sesbania*. For the meta-analysis there were 7 studies (9 observations) and 3 studies (5 observations) for CH_4 and N_2O, respectively.

For datasets 1 and 5, we categorized studies according to fertilizer rate. To do so, we first ranked studies according to N (dataset 1) or sulfate (dataset 5) input rates, and then split up the datasets into three groups (dataset 1) or two groups (dataset 5) of equal size. Whenever observations with identical input rates were spread over two adjacent groups, they were randomly distributed between the groups in question.

2.2. Data analysis

For the meta-analysis, for each study in each dataset, all comparisons between control and treatment for net seasonal N_2O and CH_4 emissions were included as separate data points ("observations"). As such, multifactorial studies (i.e. studies in which management practices were combined with other treatments in a factorial design) could contribute more than one data point to the dataset. Results were averaged over years when experiments were repeated over time.

Due to the high variability of GHG emissions between studies, our analyses focused on the percentage change (not total) in GHG emissions resulting from a given management practice. We used the natural log (ln *R*) of the response ratio as our effect size (Hedges et al., 1999):

$$\ln R = \ln\left(\frac{GHG_T}{GHG_C}\right) \qquad (1)$$

where GHG is the mean value of the N_2O/CH_4 flux in the treatment plot (T) or the control plot (C). Studies were weighted by replication:

$$w_i = n \qquad (2)$$

where w_i is the weight for the *i*th observation and n is the number of field replicates (i.e., plots per treatment combination). By favoring field experiments that were well replicated, our weighting approach assigns more weight to more precise effect size estimates. Mean effect sizes were estimated as:

$$\overline{\ln R} = \frac{\Sigma(\ln R_i \times w_i)}{\Sigma(w_i)} \qquad (3)$$

with $\ln R_i$ as the effect size for GHG emissions from the *i*th observation, and w_i as before. We used METAWIN 2.1 to generate mean effect sizes and 95% bootstrapped CIs (4999 iterations) (Rosenberg et al., 2000). To ease interpretation, the results for the analyses on ln *R* were back-transformed and reported as percentage change under management treatment in question relative to the control situation ($[R-1]\times 100$). Treatment effects were considered significant if the 95% CI did not overlap with zero, and marginally significant if the 90% CI did not overlap with zero. *P*-values for differences between categories of studies were calculated using resampling techniques incorporated in MetaWin 2.1.

The datasets for assessing the effect of individual EENF products other than DCD (part of dataset 3) and fertilizer placement (dataset 4) were too small for a meta-analysis. In these cases the average effect of a treatment on CH_4 and N_2O emissions and standard errors across observations are reported.

3. Results and discussion

While results for both N_2O and CH_4 emissions are needed to fully assess the effect of a management practice on GWP, most studies measured only one of these gases. The number of studies with both CH_4 and N_2O measurements was low and did not warrant a meta-analysis. In rice systems, it has been shown that CH_4 emissions are high relative to N_2O emissions and therefore the focus should be on reducing CH_4 emissions (Linquist et al., 2012). Accordingly, when evaluating the relative effect of a management practice on either CH_4 or N_2O emissions, the relative change in CH_4 is more important than for N_2O in reducing GWP. For example, Linquist et al. (2012) reported that on average 89% of GWP from rice was from CH_4. Based on this value the relative treatment effect of management on N_2O (in %) needs to be roughly 9 times as large as the effect on CH_4 to have a similar effect on GWP. Similarly, in the studies used for this analysis, when all data were combined, CH_4 contributed 93% to total GWP. In studies where both N_2O and CH_4 were measured, CH_4 contributed 92% to total GWP.

3.1. Inorganic N rate and GHG emissions (dataset 1)

3.1.1. CH_4 emissions

The amount of CH_4 emitted from a rice field is primarily determined by three processes: CH_4 production, oxidation, and transport from the soil to the atmosphere. Although all of these processes are directly or indirectly affected by N fertilizer addition, it is not our intent here to review this topic as this has been adequately done by others (see Schimel, 2000; Cai et al., 2007; Bodelier and Laanbroek, 2004); however, it is necessary to provide some background information for further discussion. In flooded rice systems the interactions between N fertilizer and the CH_4 cycle are complex with different processes occurring at different levels, making it difficult to determine the underlying mechanisms contributing to net effects on CH_4 emissions (Schimel, 2000). At the ecosystem level, N fertilizer generally increases plant growth which both increases carbon supply for methanogens and provides a larger aerenchyma cell pathway for transport of CH_4 from the soil to the atmosphere. At the biochemical level, NH_4^+ inhibits CH_4 consumption which is thought to occur because CH_4 and NH_4^+ are similar in size and structure and as a result, CH_4 monooxygenase (the enzyme that oxidizes CH_4) binds and reacts with NH_4^+ instead of CH_4 (Dunfield and Knowles, 1995; Gulledge and Schimel, 1998). However, at the microbial community level, N fertilization stimulates the growth and activity of CH_4 oxidizing bacteria (methanotrophs) leading to a reduction in emissions (reviewed by Bodelier and Laanbroek, 2004). Our objective was to determine at the field level the net effect of N fertilization on CH_4 emissions. Linquist et al. (2012), based on a meta-analysis, reported no effect of N rate on CH_4 emissions. In that study they evaluated total CH_4 emissions (which were highly variable) across studies. Here a more rigorous evaluation was conducted to determine the relative effect of N additions from studies with side-by-side comparisons.

At low N rates (averaging 79 kg N ha^{-1}) CH_4 emissions increased significantly by 18% (95% CI: 0.01–39%) (Fig. 1). At moderate N rates, there was no significant effect of N additions on CH_4 emissions but at high N rates (averaging 249 kg N ha^{-1}) CH_4 emissions were significantly reduced by 15% (95% CI: −28% to −1%). We hypothesize that these results can be explained by the various effects of N fertilization on CH_4 production, oxidation and transport. Nitrogen generally limits rice growth in flooded soils; therefore, at low N rates plant growth increases more per unit of N applied than at high N rates. Compared to unfertilized smaller plants, fertilized larger plants also provide more carbon substrate for methanogenesis as roots and root exudates serve as a major carbon source for CH_4 production (Lu et al., 2000). Moreover, since most CH_4 is

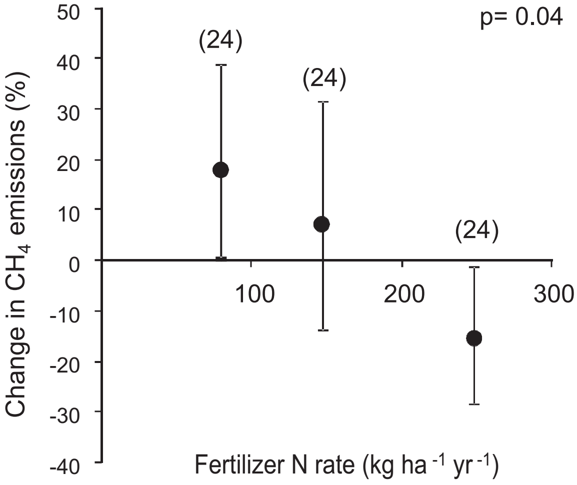

Fig. 1. The effect of inorganic N additions on CH_4 emissions relative to when no N fertilizer was applied. The number in parentheses indicates the number of observations used in the meta-analysis. Error bars represent 95% confidence intervals.

emitted through the plant (Wassman and Aulakh, 2000), larger plants with more tillers also provide a larger pathway for CH_4 to be transported to the atmosphere. Considering these factors and given that the plant removes NH_4^+ from the soil solution at low to moderate N rates (meaning NH_4^+ is not available to stimulate CH_4 oxidation), it is understandable that CH_4 emissions would increase relative to the control at low N rates, most likely as a result of larger plants. In contrast, the relative effect of N rate on plant productivity diminishes at higher N rates, leaving more NH_4^+ in the soil solution to stimulate CH_4 oxidation (Bodelier and Laanbroek, 2004). Our analysis suggests that excess soil NH_4^+, as would be expected at high N rates, has the net effect of promoting CH_4 oxidation rather than inhibiting CH_4 consumption, thereby reducing CH_4 emissions at the field scale compared to low N rates and the control. Several studies evaluating a wide range of fertilizer N rates have also reported that CH_4 emissions declined with increasing fertilizer N rates (Sass et al., 2002; Yao et al., 2012). Therefore, our results suggest that contradictory reports in the literature on the effect of N fertilization on CH_4 emissions may be in part explained by differences in N rate.

Assuming that optimal N rates for most rice production systems are between 100 and 200 kg N ha^{-1}, our data suggest that at these rates there is little to no net effect of fertilizer N on CH_4 emissions. Thus, in order to optimize yield while reducing environment costs, our analysis suggests that optimal N rates which provide maximum yields will likely reduce the amount of CH_4 emitted per unit of grain produced as compared to suboptimal N rates. van Groenigen et al. (2010) termed this metric, where GHG emissions are reported per unit of yield, as "yield-scaled" emissions. In their study they found that yield-scaled N_2O emissions (kg N_2O kg yield^{-1}) were lowest when N rates matched crop demand. Although we did not analyze yields, in theory our analysis for rice systems supports this concept, particularly in the low to optimal N rate range. While we also found that CH_4 emissions (and presumably yield-scaled emissions) were further reduced at high N rates, we do not suggest applying N in excess of demand as a CH_4 mitigation option. Indeed, it has been well documented that N applied in excess of crop demand leads to increased N_2O emissions (van Groenigen et al., 2010; Venterea et al., 2011) in addition to other environmental problems, and would not be economically justifiable.

3.1.2. N_2O emissions

Nitrous oxide emissions increased significantly with increasing N rate. In the low N class, N_2O emissions averaged 0.24 kg N_2O-N ha^{-1} (95% CI = 0.16–0.33) and this increased significantly to 0.63 kg N_2O-N ha^{-1} (95% CI = 0.40–0.91) in the high N class (Fig. 2a). Measured across N rates, the fertilizer-induced emission factor was similar across the N rates – averaging 0.22% (95% CI = 0.17–0.28) (Fig. 2b). Akiyama et al. (2005) analyzed N_2O emissions from rice systems and reported an average fertilizer-induced emission factor of 0.31% ± 0.31%). The difference in value with Akiyama et al. (2005) is most likely due to (1) differences in size of dataset (we had more observations), (2) the fact that we only included observations for inorganic N inputs while they included both organic and inorganic N inputs (below we address organic N inputs separately) and (3) they simply reported the mean and standard deviations of all observations while we conducted a weighted meta-analysis. Thus, specifically with respect to inorganic N inputs, our value is likely more robust than Akiyama et al. (2005). We further examined the fertilizer-induced emission factor by dividing the N database into fields that were continuously flooded versus fields that experienced one or more drain events during a season. In this analysis there was no significant difference in the fertilizer-induced emission factor between these two management practices (data not shown). However, a closer examination of side-by-side comparisons of the fertilizer-induced emission factor for continuously flooded fields and drained fields in the N database (10 and 14 observations for continuous flood and drained treatments, respectively) indicated that continuously flooded fields had a fertilizer-induced emission factor of 0.21% (95% CI = 0.12–0.32) versus 0.40% (95% CI = 0.31–0.49) in fields that were drained (data not shown). In theory, higher N_2O fertilizer emission factors may be expected in fields that experience mid-season drains as this creates soils that are close to saturation which promote N_2O production (Zheng et al., 2000).

3.2. N source and GHG emissions (dataset 2)

Fertilizer N source influences both CH_4 (Cai et al., 2007) and N_2O emissions (Bouwman et al., 2002; Snyder et al., 2009; Burger and Venterea, 2011). In our analysis, urea was the most commonly used fertilizer although ammonium sulfate was also frequently used. Nitrate based N fertilizers have been shown to reduce CH_4 emissions relative to urea (Lindau, 1994) by either preventing a decline in redox potential (Bouwman, 1991) and/or contributing to poor rice growth and root development, as much of the added NO_3^- is denitrified and unavailable for plant growth (Lindau et al., 1991). Wang et al. (1992) found that once NO_3^- was denitrified and unavailable for plant growth, soil redox levels declined to levels similar to urea and ammonium sulfate treatments. However, since NO_3^- is generally not recommended in rice systems due to the potential for large denitrification losses, our analysis did not include NO_3^- studies but rather focused on urea and ammonium sulfate. In general, studies have demonstrated that these two fertilizers have similar effects on rice productivity and N uptake (e.g. Bufogle et al., 1998), provided S does not limit plant growth. The cost of each fertilizer and the high N content of urea (urea contains 46% N versus 21% for ammonium sulfate) probably favor the use of urea over ammonium sulfate. However, these factors and others would need to be considered before making recommendations on the use of ammonium sulfate to mitigate GHG emissions.

3.2.1. CH_4 emissions

The average N rate used across studies in data set 2 was 154 kg N ha^{-1}. Ammonium sulfate reduced CH_4 emissions by 40% (95% CI: −50% to −30%) compared to urea applied at the same rate (Fig. 3). The reason for lower CH_4 emissions with ammonium sulfate is most likely related to the addition of sulfate (see Section 3.5). Methane reductions were generally greater at

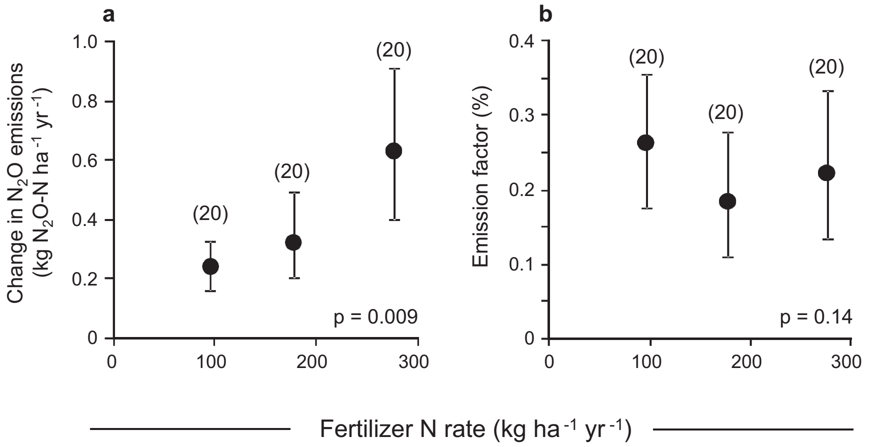

Fig. 2. The effect of inorganic N additions on N_2O emissions relative to when no N fertilizer was applied, expressed as absolute difference in emissions (a) and as emission factor (b). The number in parentheses indicates the number of observations used in the meta-analysis. Error bars represent 95% confidence intervals.

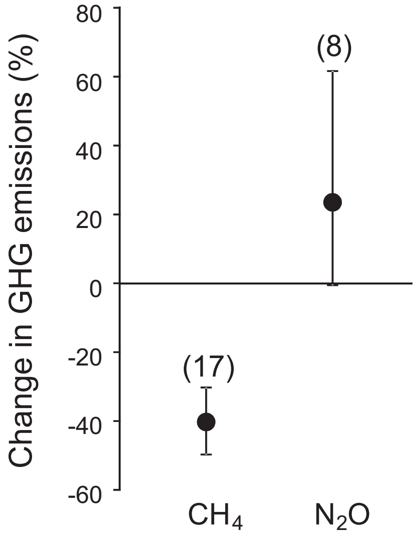

Fig. 3. The effect of replacing urea fertilizer with ammonium sulfate at the same N rate on CH_4 and N_2O emissions. The number in parentheses indicates the number of observations used in the meta-analysis. Error bars represent 95% confidence intervals.

high ammonium sulfate N rates (data not shown), as may be expected based on the relationship between sulfate additions and CH_4 emissions (see Section 3.5); however this relationship was not significant and more studies are required to quantify this relationship.

3.2.2. N_2O emissions

Urea and ammonium sulfate additions potentially affect N_2O emissions because they have different nitrification rates and have opposite effects on soil pH (Burger and Venterea, 2011). Our meta-analysis results indicate that replacing urea with ammonium sulfate fertilizer led to a marginally significant increase in N_2O emissions by 24% (Fig. 3). In a meta-analysis of many different crops, Bouwman et al. (2002) reported that urea and ammonium sulfate use resulted in similar N_2O emissions; however their analysis was not restricted to side-by-side comparisons. Given the relatively few studies that our analysis was based on, further studies are required to quantify the effect of N sources on N_2O emissions from rice systems.

3.3. Enhanced-efficiency N fertilizers and GHG emissions (dataset 3)

Enhanced-efficiency N fertilizers (EENF) include N fertilizers with nitrification and urease inhibitors as well as slow-release N fertilizers. They are applied to increase N use efficiency and minimize N losses associated with ammonia volatilization, nitrification and leaching (Snyder et al., 2009). In rice systems EENF have been shown to be effective for improving N use efficiency in dry seeded systems (e.g. Norman et al., 1989) or when there is a delay between N application and flooding (Wells et al., 1989; Carreres et al., 2003).

Nitrification inhibitors are compounds that delay bacterial oxidation of NH_4^+ and include compounds such as dicyandiamide (DCD), thiosulfate, calcium carbide, and neem (various products including nimin from the Indian neem tree – *Azadirachta indica*). Urease inhibitors such as hydroquinone are compounds that delay the hydrolysis of urea by suppressing the enzyme urease which transforms amide-N in urea to ammonium hydroxide and ammonium ions (Li et al., 2009). Finally, coated or encapsulated N fertilizers are conventional soluble mineral N fertilizers with a protective, water insoluble coating to control dissolution, nutrient release and duration of release.

3.3.1. CH_4 emissions

Results of our meta-analysis which included all EENF products shows that CH_4 emissions were reduced by 15% (95% CI: −21% to −9%) and that the use of DCD alone reduced CH_4 emissions by 18% (95% CI: −25% to −12%) (Table 2). Rates of DCD application ranged from 10 to 30 kg ha^{-1} (mean of 14 kg ha^{-1}) and represented 10–25% of the N added (mean of 12%). There was no relationship between DCD rate and CH_4 reduction (data not shown); however, lower DCD rates than those used in these studies may not have the same effect on CH_4 emissions. For the other EENF products evaluated, encapsulated calcium carbide reduced CH_4 emissions by the greatest amount (−25%, Table 2). Only two field studies evaluated this product (Lindau et al., 1993; Malla et al., 2005); however Bronson and Mosier (1991) reported that encapsulated calcium carbide reduced CH_4 emissions in a pot study. The other types of EENF had limited effect on CH_4 emissions; however the number of studies evaluating each of these products was small, preventing definitive conclusions (Table 2).

The question remains why DCD, and possibly other EENF, reduce CH_4 emissions. In upland aerobic soils NH_4^+ inhibits CH_4 oxidation and methanotroph growth (Schimel, 2000). Thus, in such soils DCD (or other EENF) prevents nitrification, thereby conserving NH_4^+ which in turn inhibits the oxidation of CH_4 (Bronson and

Table 2
Summary of results on relative effect of various enhanced-efficiency N fertilizers (EENF) on N_2O and CH_4 emissions in rice systems. A meta-analysis was only conducted on dicyandiamide (DCD) due to the limited number of observations for the other products. The change in GHG emissions is an EENF treatment compared to a N fertilizer treatment at the same rate without EENF.

Product	Action[a]	Relative effect on GHG emissions					
		N_2O			CH_4		
		n[b]	%	95% CI/SE[a]	*n*[b]	%	95% CI/SE[c]
All products	–	21	−28	−39 to −17	20	−15	−21 to −9
DCD	NI	9	−29	−40 to −20	8	−18	−25 to −12
Thiosulfate	NI	2	−21	13	1	5	–
Neem[d]	NI	4	−12	3	4	−7	6
ECC[e]	NI/SR	1	−29	–	2	−25	11
Polyon 12	SR	1	−97	–	1	−4	–
Hydroquinone	UI	1	−4	–	1	12	–

[a] Mode of action: nitrification inhibitor (NI), slow-release (SR) and urease inhibitor (UI).
[b] *n* denotes total number of field observations.
[c] The 95% upper and lower confidence interval (CI) is given for DCD while the standard error (SE) is provided for other products with more than one observation.
[d] Neem products such as neem oil, neem cake and nimin.
[e] Encapsulated calcium carbide.

Mosier, 1994). As discussed in Section 3.1.1, in flooded soils this is not the case, as NH_4^+ has been shown to stimulate CH_4 oxidation (Bodeleir and Laanbroek, 2004). Furthermore, in flooded anaerobic soils, nitrification is not likely to occur and mineral N in the soil will remain as NH_4^+ regardless of whether an EENF is present or not. Therefore, the effect of DCD is likely not due to its effect on soil NH_4^+ concentrations. It is possible, as found by Xu et al. (2000), that DCD and hydroquinone enhance CH_4 oxidation in the root rhizosphere which leads to a reduction in CH_4 emissions.

3.3.2. N_2O emissions

The EENF products discussed here limit substrate N for nitrification and denitrification by various modes of action and thus reduce the potential for N_2O emissions (Subbarao et al., 2006; Prasad and Power, 1995). Indeed, our meta-analysis suggests that on average, EENF reduced N_2O emissions by 28% (95% CI: −39 to −17) and DCD reduced N_2O emissions by 29% (95% CI: −40% to −20%) (Table 2). These results for DCD are consistent with those of Akiyama et al. (2010), who reported that DCD reduced N_2O emissions by 36% (95% CI = −43% to −24%) in rice systems.

Although there is limited data available for EENF products other than DCD, they all appeared to reduce N_2O emissions. However, there was a high degree of variability in the reduction of emissions, which ranged from 4% to 97% (Table 2). This variation may be due to the EENF product, how it was applied, or how the rice system was managed. Akiyama et al. (2010) found that the relative reduction in N_2O emissions from the use of EENF products was similar between rice and upland systems.

While EENF can reduce GHG emissions, these products are costly and it needs to be determined if they also improve N use efficiency in rice systems to justify their use. It has been shown that EENF can increase N use efficiency under some circumstances (Norman et al., 1989; Carreres et al., 2003; Wells et al., 1989). In the studies used in our analysis, N-use efficiency was not evaluated, although some authors reported yield increases (Ghosh et al., 2003; Li et al., 2009) or lower soil NO_3^- content (Ghosh et al., 2003; Kumar et al., 2000) due to EENF applications.

3.4. Nitrogen placement and GHG emissions (dataset 4)

Fertilizer N can either be applied to the soil surface or incorporated into the soil prior to planting. Incorporating N into the soil is often recommended as it places the nitrifiable N fertilizer into a reduced soil layer, which limits nitrification, denitrification, and volatilization rates and has been shown to enhance N use efficiency (Linquist et al., 2009).

Only four studies have directly compared the effects of N placement on GHG emissions in rice systems (Table 1). Placing fertilizer N deep into the soil reduced CH_4 emissions on average by 40% in continuously flooded rice systems but led to a small increase in rainfed systems (Table 3). Methods of N incorporation varied among studies: Schutz et al. (1989) incorporated urea and ammonium sulfate N to a depth of 20 cm while Setyanto et al. (2000) did not provide the depth of placement when comparing the deep placement of urea tablets with a surface urea application. Few mechanisms have been proposed to explain these results. First, deep placement of N concentrates fertilizer-NH_4^+ into localized areas or bands. This process has been shown to stimulate CH_4 oxidation by soil methanotrophs and reduce overall CH_4 emissions (Bodelier et al., 2000a,b). This effect of localized placement may be similar to the high N rates discussed in Section 3.1.1 (Fig. 1). Second, deep placement of N may promote rice root growth in deeper soil layers where CH_4 production is greater (Kruger et al., 2001). The increased oxygen availability in the rhizosphere would likely enhance CH_4 consumption in deeper soil layers, thereby decreasing overall emissions (Gilbert and Frenzel, 1998).

In rainfed systems on the other hand, deep soil placement of fertilizer N did not decrease CH_4 emissions (Setyanto et al., 2000; Rath et al., 1999). This difference in response may be due to water management which in rainfed fields can vary from year to year. Setyanto et al. (2000) found that total CH_4 emissions were substantially reduced across all N rates when drainage events occurred in the rainfed system, which may have also affected the response of CH_4 emission to N placement (urea tablets increased CH_4 emissions by 16–20%). In the other rainfed study (Rath et al., 1999), urea supergranules were placed only 5 cm deep which was relatively shallow compared to the deep N placement in some of the continuously flooded studies (e.g. 20 cm deep – Schutz et al., 1989).

Only Suranto et al. (1998) evaluated the effect of N placement on N_2O emissions. They assessed a broadcast N application of urea with three splits versus a single application of a urea tablet incorporated at a depth of 15 cm in both continuously flooded and intermittently flooded systems. On average, across water treatments, deep placement of N increased N_2O emissions by approximately 15% in both systems (Table 3). This effect has been observed in other upland crop systems (Fujinuma et al., 2011) and is explained, in part, by concentrating nitrifiable fertilizers when N fertilizers are placed deep which increases the potential for N_2O production (Burger and Venterea, 2011).

Table 3
The change in CH_4 and N_2O emissions resulting from deep N applications relative to surface N applications. Studies were grouped by water management practices and means for each GHG were calculated using the total number of observations.

Water management	Number of studies	Total observations	Change in emissions (%)	Standard error
CH_4				
Continuous flood	2	4	−39.7	10.9
Rainfed	2	3	11.2	7.8
N_2O[a]				
Continuous flood	1	2	18.0	10.7
Intermittent irrigation	1	2	13.1	8.9

[a] All N_2O results are from a single study (Suranto et al., 1998).

Overall, deep N placement represents a relatively simple change in management practices that can increase N use efficiency and appears to have potential for CH_4 mitigation. Future research that accounts for the combined effects of N placement on CH_4 and N_2O emissions should be a priority.

3.5. *Sulfate and GHG emissions (dataset 5)*

The use of sulfate containing fertilizers or amendments has been proposed as a means of mitigating CH_4 emissions. In natural systems, Pennock et al. (2010) found that annual CH_4 emissions from a freshwater wetland declined when the concentration of $SO_4{}^{2-}$ in the water increased. Segers (1998) summarized that sulfate can reduce overall CH_4 emissions by both suppressing methanogenesis as well as contributing to anaerobic CH_4 oxidation. Three possible mechanisms as to how sulfate (and other electron acceptors) could suppress methanogenesis were proposed. First, the reduction of electron acceptors could reduce substrate concentrations to a value that is too low for methanogenesis. Second, the presence of electron acceptors could result in a redox potential that is too high for methanogenesis. Third, electron acceptors could be toxic for methanogens.

We evaluated the effects of non-N sulfate containing products (gypsum, phosphogypsum, $NaSO_4$, K_2SO_4) on GHG emissions because N rate affects emissions of CH_4 (Fig. 1) and N_2O. Sulfate at average rates of 208 and 992 kg S ha^{-1} reduced CH_4 emissions by 28% (95% CI: −37% to −19%) and 53% (95% CI: −62% to −43%), respectively (Fig. 4a). These data suggest that the effect of sulfate on reducing CH_4 emissions is rate dependent and this is confirmed by a regression analysis (Fig. 4b). Relatively high rates of sulfate are required to obtain significant reductions in CH_4 emissions. For example, to reduce CH_4 emissions by 40% the regression indicates about 500 kg S ha^{-1} is required. Furthermore, it appears that sulfate can mitigate CH_4 emissions by up to 60%, but beyond this threshold further sulfate additions have limited effect. This plateauing effect is also supported by results from individual studies within this analysis that assessed different rates of the same S source (Fig. 4b). Of particular interest is the study by Lindau et al. (1998), who reported little to no difference in CH_4 emissions when gypsum and phosphogypsum were applied at rates ranging from roughly 500–1500 kg SO_4-S ha^{-1}.

Sulfur is a component of a number of fertilizer products. Ammonium sulfate is a commonly used N fertilizer (see Section 3.2). Single superphosphate is a commonly used P fertilizer which contains approximately 14% S Adhya et al. (1998) found that single superphosphate inhibited CH_4 emissions in a pot study and they attributed this decline to the S content in the P fertilizer. Potassium sulfate is a commonly used K fertilizer and contains about 18% S. If these fertilizer products are applied at rates to meet common N–P–K requirements of a rice crop, the mitigation effect will likely be relatively small due to the small amount of sulfate. In contrast, gypsum contains about 19% S and is sometimes used as a soil amendment in sodic soils where it is applied in relatively large quantities (e.g. 5 Mg ha^{-1} – Yaduvanshi and Swarup, 2005). Such rates will likely have a large effect on CH_4 emissions.

Apart from studies involving ammonium sulfate, there are few studies on the effect of sulfate on N_2O emissions. In one field study, Kumar et al. (2000) reported a small (8%) but significant reduction in N_2O emissions from rice systems when thiosulfate was added to urea versus no thiosulfate. However, this study did not report how much thiosulfate was added. Based on the analysis comparing ammonium sulfate with urea (Fig. 3), sulfate additions may increase N_2O emissions.

3.6. *Farmyard manure and GHG emissions (dataset 6)*

Farmyard manure (FYM) is an important nutrient source for many rice systems. In the studies used for our analysis, FYM formed all or part of the total N rate and increased CH_4 emissions by 26% (95% CI: 12–47%) when compared to a treatment receiving only urea N at the same total N rate (Fig. 5a). A regression analysis of these studies found that the effect of FYM on CH_4 emissions was not related to the total amount of FYM-N that was added (data not shown). Such a relationship would be expected, given that higher FYM-N rates would generally correspond to greater carbon inputs to the soil. The lack of a significant rate effect is likely explained by the variation between studies in FYM source and how it is handled prior to application. These details are often unreported and should be a requirement in future studies. This is important as the handling and processing of FYM has been shown to strongly affect CH_4 emissions. For instance, Chen et al. (2011) showed that composting FYM lead to a 75% reduction in CH_4 emissions relative to uncomposted FYM. Several studies have also reported that the addition of composted straw reduced CH_4 emissions relative to fresh straw (Corton et al., 2000; Yagi and Minami, 1990). Corton et al. (2000) attributed this to a lower C:N ratio in the composted straw (6–10) than in the fresh straw (25–45). However, a complete assessment of the effect of composted materials must also consider the GHG generated during the composting process which can be highly variable depending upon the material and how it is composted (i.e. aerobically or anaerobically) (Brown et al., 2008).

Only three studies (6 observations) have evaluated the effect of FYM on N_2O emissions in rice systems through side-by-side comparisons. In these studies FYM-N represented 25–100% of the total N rate. We found no significant effect on N_2O emissions when FYM was used instead of mineral N fertilizer (Fig. 5a). In other studies on upland soils, Akiyama et al. (2004) found that emissions relative to urea-N applications varied by the type of FYM applied. Since FYM is an important input for many rice systems, a better understanding of how FYM source, processing and application can affect GHG emissions is needed.

3.7. *Green manure and GHG emissions (dataset 7)*

Green manures (GrM) are used in many agricultural systems as a source of N fertilizer, with most GrM crops capable of fixing

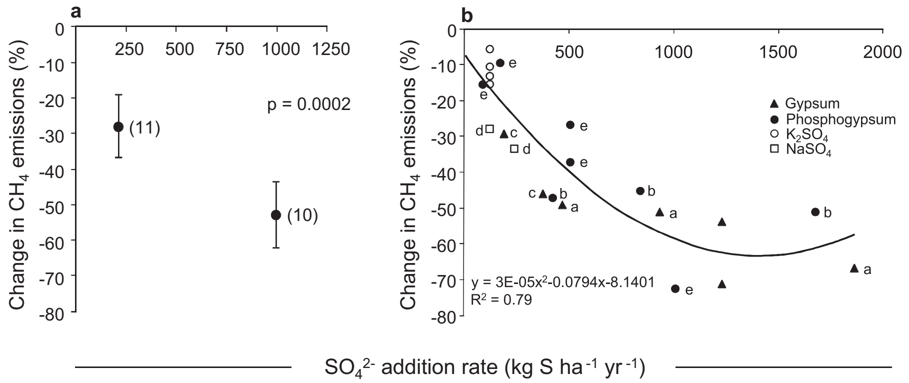

Fig. 4. (a) A meta-analysis showing the effect of non-N sulfate additions on CH_4 emissions. The number in parentheses indicates the number of observations used in the meta-analysis and error bars represent 95% confidence intervals. (b) A regression analysis of the same data used in the meta-analysis. The same letter next to a set of data points indicates the same study and S source (a, b = Lindau et al., 1998; c = Lindau et al., 1994; d = Lindau et al., 1993; e = Corton et al., 2000).

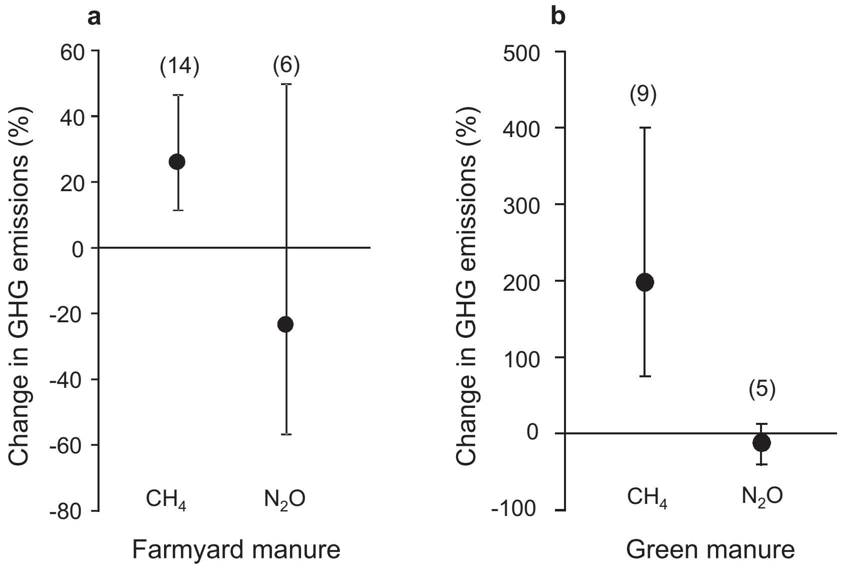

Fig. 5. The change in CH_4 and N_2O emissions from the addition of farmyard manure (a) and green manure (b). For the analysis of the effect of green manure only *Sesbania rostrata* studies were included. The number in parentheses indicates the number of observations used in the meta-analysis. Note the difference in the *Y*-axis between the graphs. Error bars represent 95% confidence intervals.

atmospheric N_2. In rice systems a GrM crop is generally grown prior to the rice crop and incorporated into the soil before planting. Different GrM species can have variable effects on CH_4 emissions (Adhya et al., 2000); therefore in our meta-analysis we only included studies on *Sesbania* which was the most evaluated GrM crop. Addition of *Sesbania* increased CH_4 emissions by 192% (95% CI: 71–396%) (Fig. 5b). A linear regression showed no significant relationship between N input from GrM and the relative effect of GrM on CH_4 emissions (data not shown). The lack of a significant relationship may be due to differences in GrM management between studies. For example, the C:N ratio of *Sesbania* varies depending on when it is harvested (Kumar et al., 2007) which in turn affects the amount of carbon substrate available for CH_4 production.

Other GrM crops have been evaluated on a limited basis and even fewer studies have compared GrM sources side-by-side. In one such study, Adhya et al. (2000) compared *Azolla caroliniana* to *Sesbania* and found that *Azolla* reduced CH_4 emissions by half at similar N rates (40 kg N ha^{-1}). *Azolla* is different from other GrM crops, as it is a free floating aquatic fern which can either be incorporated into the soil at the beginning of the season (similar to other GrM crops) or grown alongside rice. Bharati et al. (2000) reported that *Azolla* alone or in combination with urea reduced CH_4 emissions relative to urea alone at the same total N rate. These two studies indicate there is potential to use *Azolla* as a GrM source with reduced CH_4 emissions.

Another common GrM is Chinese milk vetch (*Astragalus sinicus*). In the two studies that evaluated Chinese milk vetch, no comparisons were made at similar N rates. These studies compared vetch additions to a treatment with no N (Lee et al., 2010; Shang et al., 2011) or to a urea N treatment of a different N rate (Shang et al., 2011). Lauren et al. (1994) evaluated purple vetch (*Vicia benghalensis*) and found that at similar N rates purple vetch increased CH_4 emissions by 70%, on average, relative to when urea was applied alone.

Only a limited number of observations have examined the effect of *Sesbania* on N_2O emissions. Based on these studies, *Sesbania* had no effect on N_2O emissions (Fig. 5b) when compared to a treatment with the same N rate applied as urea.

4. Summary and conclusions

We analyzed results from field studies that assessed the effect of various fertilizer management options on either CH_4 or N_2O emissions. There are cost considerations for all of these options that need to be taken into account when assessing the economic viability of a system. Our results clarify contradicting reports in the literature regarding the effect of N input on CH_4 emissions. Results show that the effect of inorganic fertilizer N on CH_4 emissions depends on rate of N application: low N rates of either urea or ammonium sulfate increase CH_4 emissions relative to when no N is applied while high N rates (typically beyond crop demand) decrease CH_4 emissions. At N input rates generally needed for optimal yields there was no effect of N rate on CH_4 emissions. Therefore, to minimize the yield-scaled GWP intensity of rice systems, the goal should be to provide an adequate amount of N to achieve optimal yields. We determined the inorganic fertilizer-induced N_2O emission factor for flooded rice systems to be 0.22%, which is lower than reported in previous reviews. Ammonium sulfate reduced CH_4 emissions relative to urea but it also tended to increase N_2O emissions. The use of the nitrification inhibitor DCD resulted in both lower CH_4 and N_2O emissions. While promising in terms of reducing GWP, the effect of DCD at improving N-use efficiency or yields remains unclear in rice systems and the economics of its use need to be considered. Limited data suggest that deep placement of N fertilizer reduces CH_4 emissions but may increase N_2O emissions. FYM increased CH_4 emissions by 26% while the use of the GrM *Sesbania* increased CH_4 emissions by 192%. Neither FYM nor GrM had a significant impact on N_2O emissions. Limited research suggests that there are differences between GrM species. Sulfate additions reduced CH_4 emissions; however a relatively large amount of sulfate is required to achieve substantial benefits and the benefits of sulfate additions appear to plateau at CH_4 emission reductions of 60%. Further research is required to determine the effect of sulfate on N_2O emissions in flooded rice systems.

Our analysis has focused on the effect of single fertilizer management practices on GHG emissions; further research should aim at quantifying the effects of combining mitigation options (i.e. deep placement of ammonium sulfate). Furthermore, due to data limitations we analyzed the effects of various fertilizer management options on CH_4 and N_2O emissions separately; however, when developing mitigation strategies to reduce GWP in rice systems both CH_4 and N_2O emissions must be considered.

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