

Article

Product Type, Rice Variety, and Agronomic Measures Determined the Efficacy of Enhanced-Efficiency Nitrogen Fertilizer on the CH₄ Emission and Rice Yields in Paddy Fields: A Meta-Analysis

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Abstract: Enhanced-efficiency nitrogen fertilizer (EENF) is a recommend nitrogen fertilizer for rice production because of its advantage on improving nitrogen use efficiency. However, its efficacy on CH₄, the dominant greenhouse gas, emission from rice fields showed great variation under field conditions. And the factors influencing its efficacy are still unclear. We synthesized the results of 46 field studies and analyzed the impact of product type, rice variety, and primary agronomic measures (rice cropping system, nitrogen (N) application rate, and water management options) on the effectiveness of EENF on the CH₄ emission and rice yield. Overall, EENF, including inhibitors (IS) and slow/control-released fertilizer (S/CRF), significantly reduced CH₄ emission by 16.2% and increased rice yield by 7.3%, resulting in a significant reduction in yield-scaled CH₄ by 21.7%, compared with conventional N fertilizer. Nitrapyrin, DMPP (3,4-dimethylpyrazole phosphate), and HQ (Hydroquinone) + Nitrapyrin showed relative higher efficacy on the mitigation of CH₄ emission than other EENF products; and HQ showed relative lower efficacy on rice yield than other EENF products. The reduction in CH₄ emission response of hybrid rice varieties to IS and S/CRF was greater than that of inbred rice varieties. IS significantly reduced the CH₄ emission and increased the rice yield under all three rice cropping systems, and showed the highest efficacy in the late rice season of double rice cropping system. Whereas, S/CRF did not significantly reduce the CH₄ emission from rice seasons of single rice cropping system and rice-upland crops rotation system. IS did not reduce the CH₄ emission when N application rate less than 100 kg ha⁻¹, and S/CRF did not affect the CH₄ emission when N application rate less than 100 kg ha⁻¹ or above 200 kg ha⁻¹. Continuous flooding was unfavorable for IS and S/CRF to mitigate CH₄ emission and enhance rice yield. These results emphasized the necessary to link EENF products with rice varieties and agronomic practices to assess their efficacy on CH₄ emissions and rice yield.

Keywords: enhanced efficiency nitrogen fertilizer; methane; yield; meta-analysis; *Oryza sativa* L.

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1. Introduction

Increasing crop yields with less greenhouse gas (GHG) emission is a great challenge in future crop production. Rice is one of the most important staple foods, which feeding around 3 billion world population. Rice planting area and production was 1.67×10^8 ha and 7.82×10^8 t respectively, accounting for 23.0% and 26.4% of the total cereals around the world in 2018 [1]. However, rice production was also considered to be an important agricultural source of CH₄ emission, which were responsible for 17.6% of global agricultural CH₄ emission [1]. Global demand for rice is expected to increase over 50% by 2050 [2]. It is a great challenge to meet future rice demand with less CH₄ emission.

Chemical nitrogen (N) fertilizer plays a vital role in enhancing rice yield in the past 50 years [3]. The fertilizer N input in rice production was 507.5 Tg around the world during

1961 and 2010 [4]. There is a great concern whether massive N input may stimulate CH₄ emission from rice fields. The effects of N fertilizer on CH₄ emission from rice fields were complex. N fertilizer can affect all the three processes of CH₄ production, oxidation, and transport in the soils, and the effects are either positive or negative on CH₄ emission from rice fields [5]. On the one hand, fertilizer N can prompt the growth of rice plant and then increase the substrate carbon supply for methanogenic bacteria or favor the transportation of CH₄ from soil to atmosphere [6,7]. On the other hand, fertilizer N can stimulate the growth and activities of methanotrophic bacteria and increase CH₄ oxidation [8]. The net effect of N fertilizer on CH₄ emission was affected by N source and agronomic measures [9].

Enhanced efficiency nitrogen fertilizers (EENF) are developed to improve the N use efficiency by regulating the release of fertilizer N to better meet crop needs and thereby reduce N losses to the environment [10–12]. The main products of EENF are polymer-coated slow or control release fertilizer (S/CRF) and common N fertilizer combined with nitrification inhibitor (NI), urease inhibitor (UI), and double inhibitors of UI + NI (DI). Previous meta-analysis mostly focused on the effectiveness of EENF on N₂O emission from agricultural fields [13–16]. As in rice fields, CH₄ accounted nearly 90%, far more than N₂O, to the total global warming potential (GWP). However, it is still difficult to draw a general conclusion on the effect of EENF on CH₄ emission from rice fields because the performance of EENF on CH₄ showed great variety under field conditions. Previous field experiments showed that EENF significantly reduced [17], or significantly increased [18], or did not affect [19] CH₄ emission from rice fields as compared with normal N fertilizer. Thus, it's necessary to make a quantitative and systemic analysis to identify the factors influencing the efficiency of EENF on the mitigation of CH₄ emission from rice fields. Additionally, EENF affected both the CH₄ emission and rice yields. An integrate assessment on the efficacy of EENF on the CH₄ emission and rice yields was beneficial for the balance of CH₄ mitigation and rice yields enhancement.

In this study, we hypothesized that the efficacy of EENF on CH₄ emission and rice yield is highly dependent on the changes of agronomic practices. Therefore, we conducted a meta-analysis to: (1) evaluate the effects of EENF on CH₄ emission and rice yields compared with conventional N fertilizer in rice fields; (2) evaluate the impacts of product type, rice variety, and agronomical measures, including cropping system, fertilizer N application rate, and water management, on the efficacy of EENF.

2. Materials and Methods

2.1. Data Collection

We used ISI-Web of Science and Google Scholar to extensively search peer-reviewed papers published before April 2021 that reported the effects of EENF on CH₄ emissions and rice yields. The keywords used in literature search were “nitrification inhibitor”, “urease inhibitor”, “slow/control-released fertilizer”, “CH₄”, “rice yield”, and “paddy fields”. To select suitable studies, we used the following five criteria: (1) studies must be conducted in rice fields with at least three replications, pot or incubation experiments were excluded; (2) the treatment (EENF) and control (conventional N fertilizer) must have the same N application rate, rice varieties, and farmland management options; (3) CH₄ must be measured by the closed static chamber for the whole rice growing season; (4) rice yield was reported; (5) fertilizer application methods, experimental duration, and water management practices were clearly recorded. Based on the above criteria, a total of 46 papers (including 194 comparisons) were selected for analysis. Details of the selected studies and the data collected are listed in (Table 1).

EENF was classified as two groups (inhibitors (IS) and slow/control-released fertilizer (S/CRF) based on their action mode in this analysis (Table S1). IS was further categorized into three sub-groups: nitrification inhibitor (NI), urease inhibitor (UI), urease and nitrification inhibitors (UI + NI). The detailed information of products of IS and S/CRF used in selected studies were listed in (Table S1). In present analysis, the most commonly used NIs were DMPP (3,4-dimethylpyrazole phosphate), DCD (dicyandiamide), Nitrapyrin,

and Neem (including neem oil, neem cake, and nimin); and the most tested UI products were HQ (Hydroquinone) and NBPT (N-(N-butyl) thiophosphoric triamide). Other NI and UI products, such as Karanjin (3-methoxy furano-2', 3', 7, 8-flavone), MHPP (methyl 3-(4-hydroxyphenyl) propionate), and NPPT (N-(N-Propyl) thiophosphoric triamide), were tested only in one or two studies. The S/CRF products used in selected studies were divided into two groups: polymer-coated and sulphur-coated fertilizers, according to the coating materials.

Table 1. The studies used in the meta-analysis to evaluate the impacts of EENF on CH₄ emission and rice yield.

Id	Country	Number of Comparisons	Type of EENF	Reference	Id	Country	Number of Comparisons	Type of EENF	Reference
1	China	2	UI + NI	[20]	24	China	4	NI	[21]
2	China	2	UI + NI	[22]	25	China	12	NI, S/CRF	[17]
3	China	10	UI, NI, UI + NI	[23]	26	China	2	S/CRF	[24]
4	China	2	NI	[25]	27	India	8	NI	[26]
5	China	4	UI + NI, S/CRF	[27]	28	Vietnam	4	UI	[28]
6	China	2	NI, S/CRF	[29]	29	China	7	NI	[30]
7	China	8	NI, UI + NI, S/CRF	[31]	30	China	4	UI + NI, S/CRF	[32]
8	China	2	UI, S/CRF	[33]	31	China	8	NI, UI + NI, S/CRF	[34]
9	China	6	UI, S/CRF	[35]	32	China	12	NI, S/CRF	[36]
10	China	2	UI, S/CRF	[37]	33	Indonesia	6	NI, S/CRF	[38]
11	China	6	UI + NI, S/CRF	[39]	34	China	4	S/CRF	[19]
12	China	3	NI, UI + NI, S/CRF	[40]	35	China	1	S/CRF	[41]
13	China	14	NI, S/CRF	[42]	36	China	3	NI, UI + NI	[43]
14	China	2	UI, S/CRF	[44]	37	China	1	UI + NI	[45]
15	China	4	S/CRF	[46]	38	China	2	S/CRF	[47]
16	China	1	S/CRF	[48]	39	India	2	NI, S/CRF	[49]
17	China	1	S/CRF	[50]	40	China	9	UI, NI, UI + NI	[51]
18	India	2	NI	[52]	41	China	4	S/CRF	[53]
19	India	3	NI	[54]	42	China	4	S/CRF	[55]
20	India	2	NI	[56]	43	Philippines	1	S/CRF	[57]
21	India	4	UI, NI	[58]	44	China	2	S/CRF	[59]
22	China	3	UI + NI	[60]	45	China	1	S/CRF	[61]
23	India	6	NI	[18]	46	India	2	NI	[62]

Rice variety and three agronomic practices (cropping system, N fertilizer application rates, and water management options). Rice variety was divided into two groups: hybrid variety and inbred variety. N application rates was divided into three levels: ≤ 100 kg ha⁻¹, 100–200 kg ha⁻¹, ≥ 200 kg ha⁻¹. Cropping system was classified as four groups: rice season of SRS (single rice cropping system), rice season of RUS (rice-upland crops rotation system), early rice season of DRS (double rice cropping system), and late rice of DRS (double rice cropping system). Water management methods during rice growing season was grouped into three categories: continuous flooding, intermittent flooding, and un-flooding.

2.2. Data Analysis

In this meta-analysis, we analyzed three effect sizes, including CH₄ emission (kg ha⁻¹), rice yield (t ha⁻¹), and yield-scaled CH₄ emission (kg t⁻¹). The effects of EENF on CH₄, rice yield and yield-scaled CH₄ were evaluated by the response ration (lnR) [63]:

$$\ln R = \ln \left(\frac{X_t}{X_c} \right) \quad (1)$$

where the X_t and X_c represent the measured values of the treatment (EENF) and control (conventional N fertilizer), respectively. It is important to note that only studies that included one-to-one comparisons were used for analysis. Furthermore, the mean response ratio was calculated by the following formula:

$$RR = \sum(\ln R \times W_i) / \sum W_i \quad (2)$$

In Formula (2), the W_i was the weighting factor and estimated by following equation [15]:

$$W_i = n \times f \quad (3)$$

where n and f represent the numbers of replications of the treatment and the flux measurements per month, respectively. The percentage change in each index was calculated according to Equation (4):

$$\text{Change (\%)} = (e^{RR} - 1) \times 100 \quad (4)$$

where RR denotes the mean effect size of the response ratio in Equation (2), and e is the natural base number.

We used the Metawin2.1 software (Version 2.1. Sinauer Associates, Sunderland, MA, USA) for this meta-analysis, along with a random effects model and bootstrapping using 4999 iterations to calculate the mean effect size and 95% convenience interval (CI) [64,65]. Mean effect sizes were considered to be significantly different only when the 95% CI did not overlap.

3. Results and Discussions

3.1. Overall Effect of EENFs

Overall, EENF significantly reduced CH_4 emission by 16.2%, and significantly increased rice yield by 7.3%, resulting in a significant reduction in yield-scaled CH_4 by 21.7%, compared with conventional N fertilizer (Figure 1). IS and S/CRF did not present significant difference on CH_4 , rice yield, and yield-scaled CH_4 emission. The effect sizes of IS and S/CRF on rice yield were close to the results of previous meta-analysis [66,67]. The effect of IS and S/CRF on rice yield did not show significant relationship with their effects on CH_4 emission (Figure S1). Both IS and S/CRF significantly reduced the yield-scaled CH_4 emission.

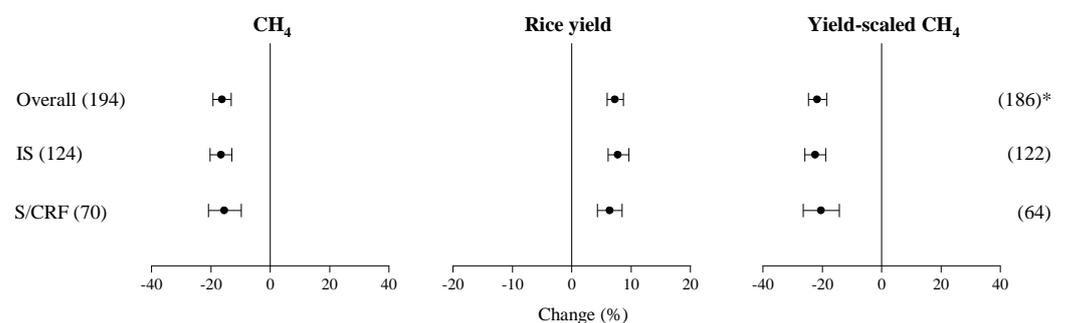


Figure 1. Overall effects of EENF on CH_4 , rice yield, and yield-scaled CH_4 emission from rice fields. * the number of comparisons for rice yield and yield-scaled CH_4 , which is less than that for CH_4 , because 4 studies did not report rice yield. All error bars represented 95% confidence intervals.

3.2. Differences among EENF Products

The effect size of the different EENF products differed significantly (Figure 2). Nitrapyrin and DMPP were more effective than DCD and Neem on the mitigation of CH_4 emission. Nitrapyrin and DMPP significantly reduced the CH_4 emission by 29.2% and 26.8% compared with conventional N fertilizer, respectively. DCD and Neem did not significantly affect the CH_4 emission. This was possibly because that Nitrapyrin and DMPP

were more effective than DCD and Neem to inhibit the transformation of NH_4^+ to NO_3^- in the soil because of their less mobility and slower degradation rate [68,69]. NH_4^+ is benefit to promote the CH_4 oxidation in rice fields [43]. Thus, stronger inhibition of Nitrapyrin and DMPP on the nitrification process may greatly strengthen the oxidation of CH_4 and result in more reduction in CH_4 emission from rice fields. All four NI products significantly increased the rice yield. Nitrapyrin showed the highest efficacy on the mitigation of yield-scaled CH_4 emission, followed by DMPP.

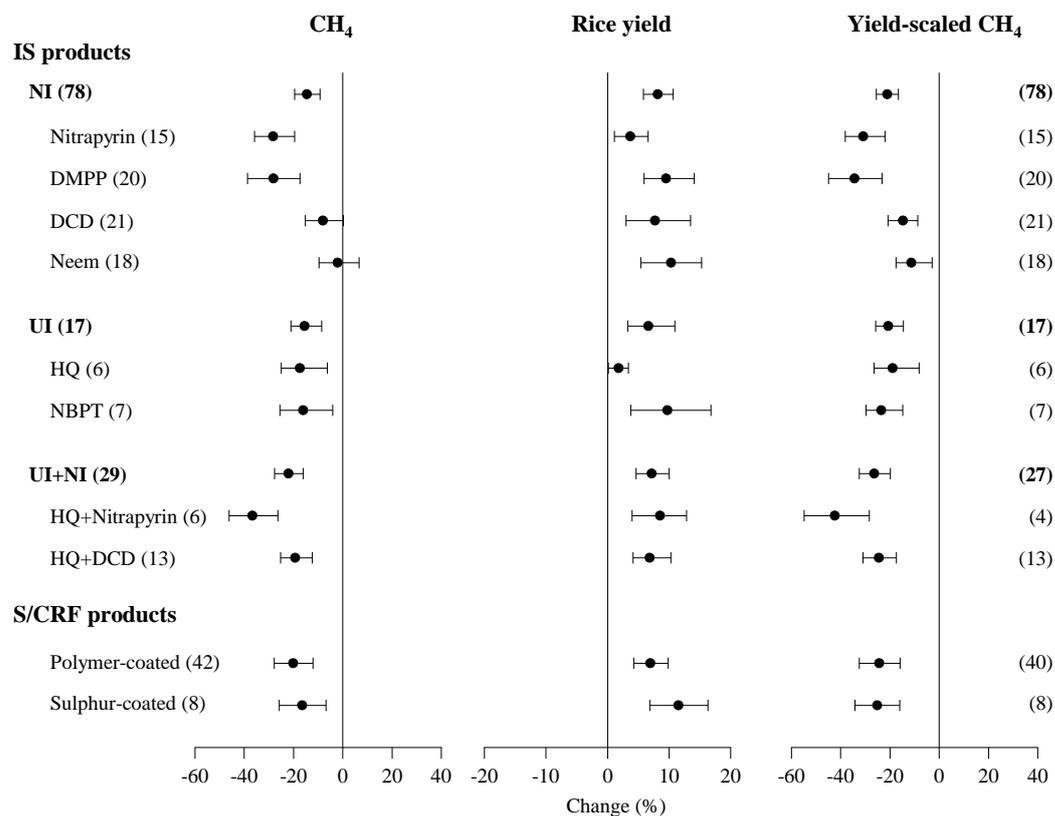


Figure 2. Effects of EENF products on CH_4 , rice yield, and yield-scaled CH_4 emission from rice fields.

As for the UI products, HQ and NBPT significantly reduced the CH_4 emission and significantly increased rice yield compared with conventional N fertilizer. The effect size of NBPT on rice yield was significantly higher than that of HQ. This was possibly because that NBPT was more effective for increasing N uptake and dry matter accumulation by rice plants due to its higher efficacy to inhibit urea hydrolysis and N loss as ammonia volatilization than HQ [70,71]. Dual application of HQ with nitrapyrin or DCD had an intermediate effect on CH_4 emission and rice yields related to separate application of these inhibitors. Combination of inhibitors can improve the efficacy of less effective products. For example, Dual application of HQ + nitrapyrin and HQ + DCD increased more rice yields than separate application of HQ as compared with conventional N fertilizer. HQ + DCD significantly reduced the CH_4 emission, while separate application of DCD did not significantly reduce the CH_4 emission, as compared with conventional N fertilizer.

3.3. Impacts of Rice Varieties

The efficacy of EENF on CH_4 emission presented significantly difference among rice varieties (Figure 3). IS significantly reduced 23.6% of the CH_4 emission from the rice fields cultivated hybrid rice varieties compared with conventional N fertilizer, which was significantly higher than that of inbred rice varieties (8.2%). The main pathway of rice varieties influencing CH_4 emission was the regulation of rice plants on belowground CH_4 production and oxidation [72]. Rice varieties allocating more photosynthetic carbon, an

important substrate for belowground CH₄ production, to aboveground than belowground organs were benefit to reduce the CH₄ production in paddy soils [73]. Hybrid rice varieties had larger leaf area index and more efficient translocation of carbohydrates to aboveground parts, including culm, leaf sheath, and spikelets, than ordinary inbred rice varieties [74], which may mitigate the substrate carbon for belowground CH₄ production. Additionally, hybrid rice varieties had larger root biomass and higher root activity that can release more oxygen into the soil compared with ordinary rice varieties [75,76]. The total copy number of functional genes related to CH₄ oxidation (*pmoA* genes) in the rhizosphere were higher for hybrid rice varieties than ordinary inbred rice varieties [77]. The growth rate and N uptake were higher for hybrid than inbred rice varieties [78]. IS stabilized the fertilizer N in the soil, which may further prompt the growth the hybrid rice varieties and strengthen their positive effects on inhibiting CH₄ production and on enhancing CH₄ oxidation. This was supported by the results of rice yield (Figure 3). IS tended to increase more rice yield for hybrid than inbred rice varieties. The mitigation of IS on yield-scaled CH₄ emission was significantly higher for hybrid (29.2%) than inbred (13.5%) rice varieties.

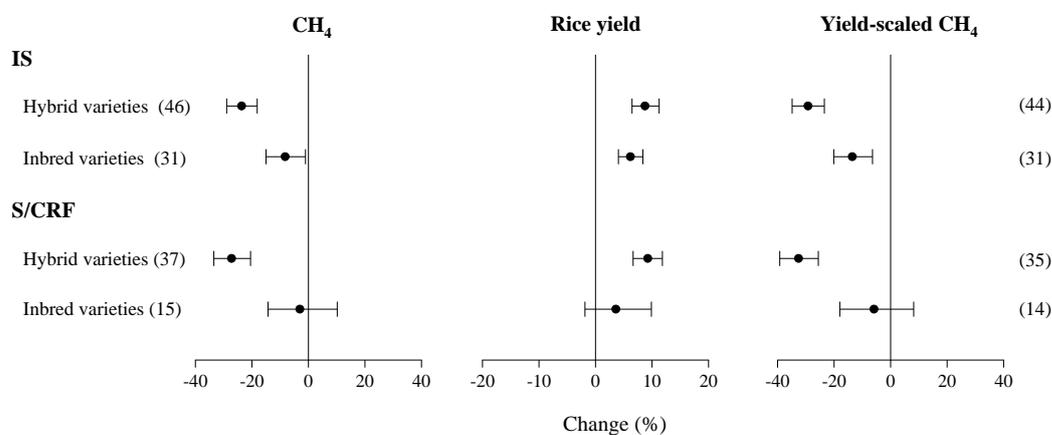


Figure 3. Impacts of rice variety on the efficacy of IS and S/CRF on CH₄, rice yield, and yield-scaled CH₄ emission from rice fields.

Similarly, S/CRF presented significantly higher efficacy for hybrid than inbred varieties. S/CRF significantly reduced the CH₄ emission by 27.2% and significantly increased rice yield by 9.3% for hybrid varieties compared with conventional N fertilizer, which were close to the effect size of IS. However, S/CRF did not significantly affect the CH₄ emission and rice yield for inbred varieties. The average N application rates for four subgroups in Figure 3 were 170.1 kg ha⁻¹ for IS-Hybrid varieties, 171.7 kg ha⁻¹ for IS-Inbred varieties, 192.3 kg ha⁻¹ for S/CRF-Hybrid varieties, and 193.7 kg ha⁻¹ for S/CRF-Inbred varieties, respectively. The average fertilizer N application rate for the subgroup of S/CRF-Inbred varieties was close to the optimal N rate for inbred varieties [79,80]. S/CRF may not further prompt the growth of inbred varieties as compared with conventional N fertilizer. Relative higher N application rate may weaken the efficacy of S/CRF on the CH₄ emission and yield of inbred varieties.

3.4. Impacts of Cropping Systems

We analyzed four rice seasons of three typical rice cropping systems (SRS, RUS, and DRS). DRS has two rice cropping seasons: early and late rice seasons. As shown in Figure 4, IS is more effective on the mitigation of CH₄ emission from late rice season of DRS than other rice seasons. The CH₄ emission from late rice season of DRS was reduced 40.6% by IS, which was significantly higher than that of other three rice seasons. Previous studies have reported that the CH₄ emission density was significantly higher for the late rice of DRS than the rice seasons of other cropping systems, which was primarily attributed to the abundant fresh crop straw incorporated into the soil followed immediately flooding in the late rice season [81]. Speedy anaerobic decomposition of fresh residue of early rice

greatly stimulated the CH₄ emission from late rice season [82,83]. Rice straw has a high carbon/nitrogen ratio (commonly between 60–100), the decomposition of rice straw needed sufficient N supply [84]. IS slowed down the urea hydrolysis and nitrification, and then decreased the N supply for straw decomposition, which may greatly mitigate the CH₄ production from straw decomposition [82]. IS significantly increased the yield of late rice of DRS by 13.0%, which was significantly higher than its efficacy on the rice yield of SRS and RUS. This was possibly because that the rice growing days of late rice (88 days) were shorter than that of SRS (122 days) and RUS (119 days). The delayed release of NH₄⁺ by IS was commonly less than 100 days [85,86]. Therefore, IS may regulate the N supply better match with rice crop demand in short growth duration.

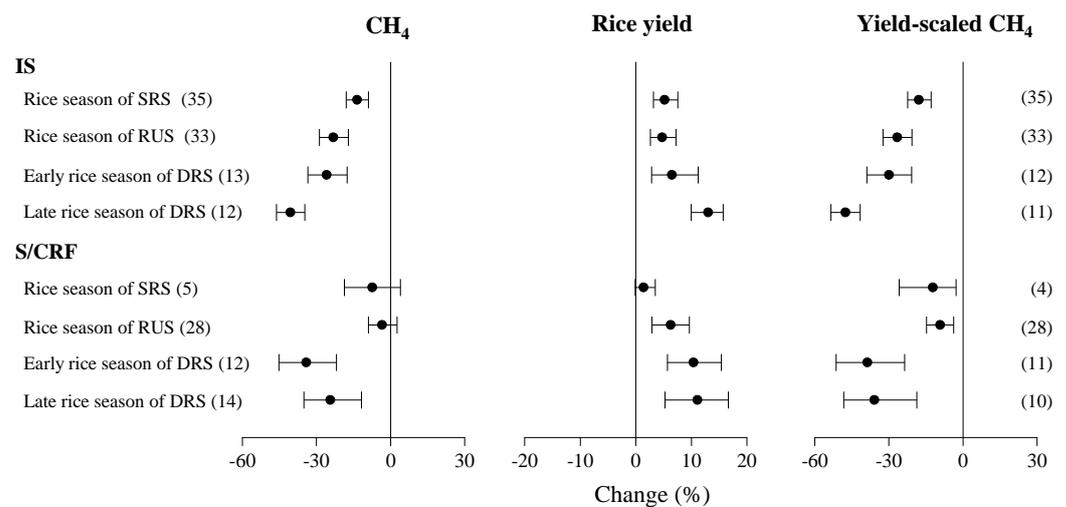


Figure 4. Impacts of cropping system on the efficacy of IS and S/CRF on CH₄, rice yield, and yield-scaled CH₄ emission from rice fields.

S/CRF also performed better in double rice system than other two rice systems (Figure 4). S/CRF significantly reduced the CH₄ emission from the early rice season and late rice season of DRS, but did not affect the CH₄ emissions from the rice seasons of SRS and RUS. This was possibly because that DRS primarily located in tropical and southern sub-tropical regions, the CH₄ production potential and emission density were higher than SRS and RUS attributed to the higher temperature during rice growing season [81]. The suppression of N supply by S/CRF may inhibit more CH₄ emission in DRS than SRS and RUS.

3.5. Impacts of Fertilizer N Application Rates

The efficacy of EENF on CH₄ emission and rice yield varied with fertilizer N application rates (Figure 5). The effect size of IS on CH₄ decreased with fertilizer N application rate (Figures 5 and S2, Supplementary Materials). IS did not affect the CH₄ emission when N application rates less than 100 kg ha⁻¹, but significantly reduced CH₄ emission when N application rates above 100 kg ha⁻¹. The N fertilizers used in rice fields are ammonium-based inorganic N fertilizer, which affects both the production and oxidation processes of CH₄ in rice soils [9]. On the one hand, ammonium-based N fertilizers can stimulate CH₄ production by stimulate the growth and activities of methanogenic bacteria and by promoting rice plant growth, thus increasing the organic carbon substrates (e.g., root exudates) supply for methanogenic bacteria [5]. On the other hand, NH₄⁺ released from N fertilizers can stimulate the CH₄ oxidation by enhance the growth and activities of methanotrophic bacteria especially in the rice rhizosphere [8]. The integrated effect of N fertilizer on CH₄ production and oxidation was varied with N application rates. We speculated that, when N application rate was less than 100 kg ha⁻¹, rice plants outcompete methanogenic and methanotrophic bacteria for fertilizer N due to limited N supply [87]. The inhibition of N

release by IS primarily benefit the rice uptake, and further strengthened the N limitation to methanogenic and methanotrophic bacteria. Thus, IS significantly increased the rice yield, but did not affect the CH₄ emission. When N application rates increased to above 100 kg ha⁻¹, the competition for N between rice and methanogenic and methanotrophic bacteria was alleviated. The suppressing of the nitrification of NH₄⁺ by IS may greatly enhance the growth and activities of methanotrophic bacteria, thus significantly reducing the CH₄ emission, as compared with conventional N fertilizer. Regard to rice yields, the positive effect of IS on rice yields decreased with N application rates (Figures 5 and S2). This was possibly because that the marginal effect of IS on promoting rice growth was decreased with N application rates.

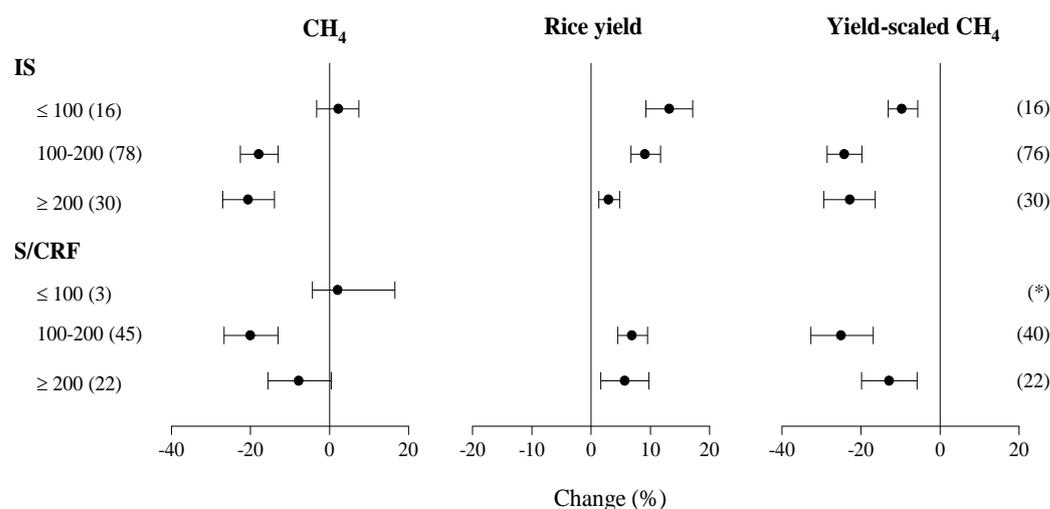


Figure 5. Impacts of N application rate on the efficacy of IS and S/CRF on CH₄, rice yield, and yield-scaled CH₄ emission from rice fields. * the number of comparisons for rice yield and yield-scaled CH₄ was less than three.

Similar as IS, S/CRF did not affect the CH₄ emission when N application rates less than 100 kg ha⁻¹, but significantly reduced the CH₄ emission when N application rates between 100 and 200 kg ha⁻¹, compared with conventional N fertilizer (Figure 5). However, different from IS, the effect of S/CRF on CH₄ emission was not significant when N application rates was increased to above 200 kg ha⁻¹. This may be due to the difference in action mode of IS and S/CRF. Previous studies reported that NH₄⁺ in the soils benefit the CH₄ oxidation [8]. IS inhibited the transformation of NH₄⁺ to NO₃⁻, thus greatly stimulated the CH₄ oxidation and reduced the CH₄ emission. While S/CRF only delayed the release of NH₄⁺. When N application rate was above 200, the N supply is sufficient for rice. The delayed released NH₄⁺ may not immediately absorbed by rice.

3.6. Impacts of Water Management Methods

The performance of IS on CH₄ emission also varied with water management methods (Figure 6). IS did not significantly affect CH₄ emission under continuous flooding compared with conventional N fertilizer. The positive effect of IS on CH₄ oxidation was limited by the presence of O₂ in the soils. CF inhibited the diffusion of O₂ into the soils [9], thus weakened the effect of IS on CH₄ emission. Decreasing flooding time during rice growing stage can enhance the positive effect of IS on CH₄ mitigation. The CH₄ emission was significantly reduced 24.9% by IS than conventional N fertilizer under intermittent flooding (Figure 6). However, excessively decreasing flooding time weakened the mitigation of IS on CH₄ emission. IS only reduced CH₄ emission by 7.9% under un-flooding, which was significantly lower than that under intermittent flooding (Figure 6). This was possibly because that the positive effect of IS on CH₄ oxidation was weakened under un-flooding condition. Firstly, the CH₄ production rate was greatly decreased when the soil was un-

flooded. Lower CH_4 concentration in the soil may reduce the CH_4 oxidation. Secondly, Methanotrophs can switch substrate from CH_4 to ammonia under un-flooding soils [88]. IS inhibited the nitrification processes and increased the ammonia in the soils, thus decreasing the CH_4 oxidation. The effect of IS on rice yield did not affect by water management methods. IS significantly increased the rice yields under three water management methods compared with conventional N fertilizer. And the yield-scaled CH_4 was significantly reduced by 10.3%, 29.5%, and 10.0% under continuous flooding, intermittent flooding, and un-flooding conditions, respectively.

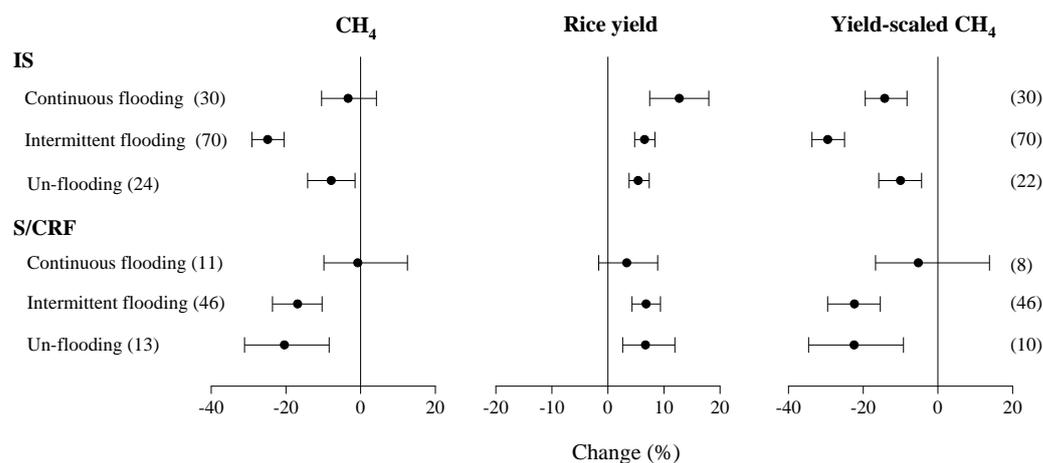


Figure 6. Impacts of water managements on the efficacy of IS and S/CRF on CH_4 , rice yield, and yield-scaled CH_4 emission from rice fields.

S/CRF significantly reduced the CH_4 emission by 16.9% and 20.4% and significantly increased the rice yield by 6.8% and 6.7% under intermittent flooding and un-flooding compared with conventional N fertilizer, respectively (Figure 6). However, its effect on CH_4 emission and rice yields was not significant under continuous flooding. The nutrients released from S/CRF was controlled by water penetration into the S/CRF through the coating [89]. Continuous flooding weakened the suppression of coating on the release of N from S/CRF, and then weakened the efficacy of S/CRF on CH_4 emission and rice yield. Thus, intermittent flooding and un-flooding were recommended for S/CRF to mitigate CH_4 emission and to enhance rice yield.

4. Study Limitations

In this meta-analysis, the impact of N form on the effectiveness of EENF on CH_4 emission was not considered, because nearly all of the N fertilizers used in the selected studies were urea. There was only one comparison of potassium nitrate and ammonium sulfate in selected studies, respectively. The efficacy of EENF on CH_4 emission may be affected by N form. Previous study reported that integrated application of DCD with urea was more effective on the mitigation of CH_4 emission than with potassium nitrate or ammonium sulfate [54]. Besides inorganic N fertilizer, organic fertilizers (e.g., crop residue and manure) are also widely used in paddy fields to provide organic N for the paddy soils. It is well known that organic fertilizer greatly stimulates the CH_4 emission from rice fields due to the abundant C supply [65,81,90]. Therefore, the effectiveness of inhibitors, such as DCD, DMPP, and HQ, on CH_4 emission may be weakened when they are applied with organic fertilizer because of the abundant C in organic fertilizer. Ref. [91] reported that HQ + DCD mitigated more CH_4 emission in crop straw removed fields than crop straw applied fields. Thus, more work needs to be done to investigate the effect of N form on the efficacy of EENF on CH_4 emission.

EENF can directly or indirectly affect the processes of CH_4 production and oxidation in many pathways. The mechanism that EENF regulates CH_4 emission is complex. Most previous studies only evaluated the effect of EENF on CH_4 emission, but did not

provide sufficient evidence (e.g., the change of C, N, and the activity of methanogens and methanotrophs in the soils) to elucidate the mechanism that how EENF influencing CH₄ emission from paddy fields [17,56,58,62]. In this study, we deduced the pathway that how product type, rice variety, and three agronomic measures influencing the CH₄ emission from rice fields based on limited evidence. Future field studies are needed to pay more attention to investigate the underlying mechanism how EENF affecting the CH₄ emission at biochemical and ecosystem levels.

5. Conclusions

Overall, EENF significantly mitigated CH₄ emission and increased the rice yields compared with conventional N fertilizer. Whereas, its performance was highly depended on product type, rice variety, and agronomic measures. Nitrapyrin and DMPP were more effective than DCD and Neem on the mitigation of CH₄ emission. IS and S/CRF were more effectively for hybrid rice varieties than inbred rice varieties in mitigating CH₄ emission and improving rice yield. The performance of IS on CH₄ emission and rice yield were more stable than S/CRF under different agronomic options. IS significantly mitigate the CH₄ emission under most agronomic options except when N application rate was less than 100 kg ha⁻¹ and under continuous flooding, and significantly increased rice yield under all agronomic options. S/CRF did not significantly affect CH₄ emission and rice yield in rice season of SRS, under continuous flooding, and when N application rate was less than 100 kg ha⁻¹ or above 200 kg ha⁻¹. These results could provide a good reference for the application of EENF in rice fields to mitigate CH₄ emission without yield reduction.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agronomy12102240/s1>. Figure S1: Response of CH₄ effect to yield effect under the addition of IS (a) and S/CRF (b); Figure S2: Response of CH₄, Yield and Yield-scaled CH₄ to the N application rates by the IS ((a), (b), (c)) and S/CRF((d), (e), (f)); Table S1: Categorization of enhanced efficiency nitrogen fertilizer (EENF) used in this meta-analysis.

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