Cowan, Nicholas; Bhatia, Arti; Drewer, Julia; Jain, Niveta; Singh, Renu; Tomer, Ritu; Kumar, Vinod; Kumar, Om; Prasanna, Radha; Ramakrishnan, Bala; Kumar, Dinesh; Bandyopadhyay, Sanjoy K.; Sutton, Mark; Pathak, Himanshu. 2021. **Experimental comparison of continuous and intermittent flooding of rice in relation to methane, nitrous oxide and ammonia emissions and the implications for nitrogen use efficiency and yield.**

The definitive version was published in *Agriculture, Ecosystems and Environment*, 319, 107571. https://doi.org/10.1016/j.agee.2021.107571

The definitive version is available at https://www.elsevier.com/

Experimental comparison of continuous and intermittent flooding of rice in relation to methane, nitrous oxide and ammonia emissions and the implications for nitrogen use efficiency and yield

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Keywords: India, Urea, greenhouse gases, leaf colour chart, integrated fertilizer

Abstract

Intermittent flooding (IF) of rice has been encouraged as an approach to reduce water use and methane emissions compared with continuous flooding (CF), but may involve trade-offs. This study compared the contrasting effect of IF and CF flooding regimes on emissions of methane (CH_4), nitrous oxide (N_2O) and ammonia (NH_3), nitrogen use efficiency (NUE) and yield. A split plot design was used which assessed the effects of four different fertiliser types. The results suggest that converting from CF to IF irrigation does lower CH_4 emissions (by approximately 18%); however, this comes at a cost. IF irrigation resulted in a significant decrease in grain yield, regardless of fertiliser type (6.1% in this study) and also a significant decrease in NUE (a drop of 22.5 % when compared to CF). IF irrigation also resulted in a small, but statistically significant (t-test $p < 0.01$) increase in N_2O emissions. Difference in NH_3 emission between the flooding regimes was not statistically significant. Our study concludes that conversion from CF to IF irrigation methods may well reduce overall global warming potential of greenhouse gas emissions from rice production; however, yield penalties and nitrogen pollution are likely to increase as a result. LCC based application of NCU may lower the yield scaled GHG emissions under CF irrigation and NH_3 loss in IF irrigation.

Introduction

Rice farming is one of the largest wide scale agricultural activities on Earth, with an estimated global production of approximately 782 million tonnes of rice harvested in the year 2018 (FAOSTAT, 2020). The population of India is largely dependent on rice as a staple crop and as a commercial export, and contributes to approximately 26.6% of the global annual production (FAOSTAT, 2020). A total of 44.5 million hectares of land in India is used to grow rice (13.5 % of all land cover), with the vast majority converted to flooded or heavily irrigated paddies to increase productivity (Gupta et al., 2016a). Although highly productive, rice paddies also contribute largely to emissions of the powerful greenhouse gases methane (CH_4) and nitrous oxide (N_2O) (Akiyama et al., 2005; Denman et al., 2007; Bhatia et al., 2012a; Gupta et al., 2015). In addition, rice production contributes to air pollution in the form of ammonia (NH_3) emissions, and water pollution in the form of pesticides, nitrate (NO_3) and phosphorus compounds (Maraseni et al., 2009; He et al., 2018; Tayefeh et al., 2018; Wang et al., 2018).

CH_4 is of particular importance when considering the environmental footprint of rice paddies, which are estimated to emit 25 to 100 Tg CH_4 yr^{-1}, accounting for approximately 10% of global anthropogenic emissions of CH_4 (Ciais et al., 2014, Denman et al., 2007; Ehalt et al., 2001). There is still a large degree of uncertainty over the true magnitude of CH_4 emissions at the global scale as regional weather differences and management practices can vary conditions that drive the biogenic processes of methanogens (methane emitting microorganisms) which favour warm anaerobic conditions such as those found in tropical wetlands. As intensively managed rice paddies regularly receive large quantities of nitrogen rich mineral and organic fertilisers, N_2O emissions are also associated with rice production (Akiyama et al., 2005; Datta et al 2009; Qin et al., 2009; Bhatia et al., 2013a). Based on IPCC Tier 1 emission factors, approximately 1% of the nitrogen applied to crops as fertiliser is expected to be lost in the form of N_2O (IPCC, 2014). However, emissions of N_2O are also dependant on fertiliser type, microbial populations and regional and management factors that affect the microbial processes of nitrification and denitrification (Bhatia et al., 2010; Butterbach-Bahl et al., 2013; Griffis et al., 2017; Cowan et al., 2020, Malyan et al., 2021a). Efficient management of N in cropped soils is the required for N_2O mitigation and climate change adaptation (Pathak et al., 2016).

Reducing atmospheric concentrations of GHGs is required if we are to meet the Paris Agreement target of keeping global warming below 1.5 degrees globally (Nisbet et al., 2020). Due to the relatively short lifetime of CH_4 in the atmosphere (approximately 9 years), reductions in CH_4 could have a significant impact on short term trends in global warming (Dlugokencky et al., 2011; Collins et al., 2018). Reducing concentrations of N_2O is important in the longer term, as it has an expected lifetime of approximately 116 years (Prather et al., 2015), thus mitigation efforts would take several decades to reduce concentrations effectively. Reducing the environmental impacts of rice production is an important step in mitigating emissions of GHGs at the global scale, and some success has been achieved in reducing GHG emissions by changing management practices. Altering fertiliser application methods (Yao et al., 2017; Bhatia et al., 2012b, Malyan et al., 2019, Kriti et al., 2020; Malyan et al., 2021b), improving straw management (Pathak et al., 2006), seeding/planting methods (Bhatia et al., 2013b, Jain et al 2014), and application of carbon storage methods (e.g. Allen et al., 2019; Liu et al., 2015), bio inoculants (Malyan et al., 2021b; Rani et al., 2021) can drastically reduce overall GHG budgets associated with rice paddy farming. However, mitigation efforts are also fraught with difficulty, and often result in instances of ‘pollution swapping’, in which one environmental aspect is improved at the cost of another (Dragosits et al., 2008; Weller et al., 2014). As CH_4 emissions from rice paddies are largely the result of anaerobic conditions in the soil due to regular flooding, one approach to reduce emissions has been to limit the time in which the paddies remain flooded (i.e. intermittent versus continuous flooding). This approach has seen CH_4 emissions reduced significantly, but at the cost of increasing N_2O emissions as the anaerobic conditions that result in CH_4 emissions also prevent the process of nitrification which produces N_2O (Akiyama et al., 2005; Abao et al., 2000; Cai et al., 1997; Weller et al., 2014). Under IF, a total water saving of 47.5-49.3% was observed by Oo et al. (2018) as compared to CF with no significant impact on rice yield. Pathak et al. (2003) reported that CH_4 emission from rice reduced by 25.4% on changing the irrigation from saturated (or CF) to IF; however, N_2O increased by 16.7%. Hou et al. (2005) also observed a 24.2% reduction in seasonal CH_4 emissions under IF compared to CF, with a simultaneous increase of 23.7% in N_2O emissions. During the rice growth period when the paddy field was submerged, N_2O emissions were low in CF, while in IF, due to frequent alteration between dry and wet soil conditions, N_2O emissions increased (Zhang et al., 2018). Gupta et al. (2016b) reported that the GWP fell by 11.4% when irrigation management was changed from CF to IF, with a slight decline in rice yield, however, the overall greenhouse gas budget was significantly reduced.

One common form of pollution swapping observed in other crop systems is that of reducing N_2O emissions at the cost of releasing ammonia (NH_3) into the atmosphere (e.g. Lam et al., 2016). Unlike emissions of CH_4 and N_2O, volatilisation of NH_3 is largely physiochemical driven, and largely dependent on temperature and humidity. Elevated NH_3 concentrations in the atmosphere, as a result of emissions after wide scale nitrogen fertiliser application can result in increased particulate matter (PM) in cities, especially when elevated NH_3 comes in contact with high nitrate and sulphate concentrations, typically emitted from traffic and burning materials in large megacities cities in Asia (Saraswati et al., 2019; Wang et al., 2015). The resulting formation of $PM_{2.5}$ and PM_{10} aerosols can result in serious impacts on human health such as cardiovascular and respiratory problems (Bittman et al., 2013). Pollution swapping that results in an increase in NH_3 emissions is possible when microbial inhibitors such as nitrification inhibitors are used with urea fertiliser (Lam et al., 2016: Zaman et al., 2009). These inhibitors typically work by reducing the rate at which microbes can consume reactive nitrogen in soils, thus allowing increased uptake by crops. However, by increasing the duration in which the nitrogen is present in the soil, the likelihood that ammonium compounds will volatilise into NH_3 into the atmosphere increases. Although microbial inhibitors widely used in

India, such as neem oil, have been shown to potentially reduce N_2O emissions in rice paddies (e.g. Majumdar et al., 2000, Malla et al., 2005, Gupta et al., 2016b), the impacts of these inhibitors on NH_3 emissions is still largely unknown, as studies have been limited by methodology available. Where NH_3 emissions are quantified from rice paddies, it has been estimated that up to 44% of nitrogen applied can be lost in the form of NH_3volatilisation (e.g. Fillery and Datta, 1986). However, the commonly used NH_3 chamber flux methodology is associated with high measurement uncertainties due to the "sticky" properties of NH_3 gas and the likely resultant underestimation of NH_3 emissions.

Although CH_4 emissions have been widely studied in rice paddies across Asia, there is less regional information on the emissions of N_2O and NH_3, especially from studies where pollution mitigation efforts have been carried out (Móring et al., 2021). In this study, we aim to add to this knowledge by investigating emissions of CH_4, N_2O and NH_3 as a result of two rice paddy irrigation methods (continuous and intermittent flooding regimes), and four fertiliser types; prilled urea, neem coated urea, neem coated urea applied according to leaf colour index charts and a 50:50 farmyard manure and neem coated urea and bio fertiliser mix. We aim to establish the environmental costs and benefits of each of these management regimes, as well as the impact that each has on the overall yield of a rice crop in conditions typical to the trans Indo-Gangetic plains (IGP) region.

Methods

<u>Experimental site and soil</u>

A field experiment was conducted growing rice in kharif (rainy season) during 2016 in a silty clay loam (Typic Ustochrept) soil at the experimental farm of the Indian Agricultural Research Institute, New Delhi, India. The site is located in the Indo-Gangetic alluvial tract at 28°40' N and 77°12' E, at an altitude of 228 m above mean sea level. The climate of the region is subtropical and semi-arid. Approximately 80% of the annual rainfall (750 mm) typically occurs from July to September. The soils are classified as well drained, with the groundwater table at approximately 6.6 m and 10 m deep during the rainy and dry seasons, respectively. The mean maximum and minimum temperatures from July to October are 35°C and 18°C, respectively. The alluvial soil of the experimental site had a bulk density of 1.38 g cm^{-3}, pH (1:2 soil:water) of 8.01, organic carbon of 4.2 g kg^{-1} and total N of 0.24 g kg^{-1}. Rainfall and temperature data were collected from the nearby meteorological laboratory, located 300 meters from the experimental site, using the tipping bucket method for rainfall measurements, and a shielded thermometer placed at 1.5 m to measure air temperature (Figure 1).

Crop management and treatments

Rice was grown using two irrigation regimes of continuous flooding (CF) and intermittent flooding (IF) irrigation in a split plot design with five separated nitrogen treatments (Table 1), each with three replicates. These irrigation methods aimed to mimic common practice in the region. Each replicated plot measured 6 m by 7 m. Rice (variety Pusa 44) was raised in a nearby nursery and 30 days old seedlings were transplanted in to the puddled fields on 12-13th July 2016 at a spacing of 20 x 15 cm. Irrigation events occurred throughout the growing period via the basin irrigation technique. Each irrigation event increased the depth of the water in the plots by approximately 0.5 to 2 cm, varying each time (Figure 1d). Twenty-five irrigations were applied for the continuous flooding treatment (CF), whereas fifteen irrigations were applied under the intermittent flooding (IF) treatment. Irrigation was applied when fine cracks developed on the soil surface in the IF treatment. The five fertiliser treatments shown in Table 1 were:

Control (CON) plots received no nitrogen. Neem coated urea (NCU) with 120 kg N ha^{-1} applied (50% 15 days after transplanting, 25% at maximum-tillering, and 25% at flowering). Integrated treatment (FYM) with 120 kg N ha^{-1} applied (50% of N in the form of farmyard manure applied ten days prior to rice transplanting, 50% of N as neem coated urea applied in three splits of 50:25:25. The roots of the rice seedlings were dipped for two hours before they were transplanted in the biofertiliser culture comprising of mix of cyanobacterial strains—*Anabaena torulosa, Nostoc* *carneum, Nostoc piscinale* and *Anabaena doliolum* which have a symbiotic association with *Azolla*. Leaf colour chart (LCC) based NCU application (30 kg N ha^{-1} of neem coated urea was applied 15 days after transplanting and subsequently all application of neem coated urea were 30 kg N ha^{-1} based on LCC readings of level 4 on a IRRI notified leaf colour chart. The LCC readings were taken at weekly intervals from 10 randomly selected topmost fully expanded leaves starting at 21 days after transplanting. When the LCC value of six out of ten leaves fell below the critical level, 30 kg N ha^{-1} of urea was top dressed on the same day. Prilled urea (PRI) with 120 kgN ha^{-1} was applied (50% 15days after transplanting, 25% at maximum-tillering, and 25% at flowering). A basal dose of 26 kg P ha^{-1}, 50 kg K ha^{-1} and 10 kg Zn ha^{-1} was applied to all the treatments.

Plant sampling and estimation of yield

Vegetation samples were collected during harvest to estimate the biomass of crops. Rice yields were determined from one square meter of area in each plot in triplicate. The grains were separated from the straw, dried, and weighed. Grain moisture was determined immediately after weighing and sub-samples were dried in an oven at 65 °C for 48 hours. The dried grain and biomass samples were ground and used to estimate the total N content using the Kjeldahl method (Page et al. 1982). Plant nitrogen content was calculated separately for (i) grain and (ii) stem and leaf. Nitrogen use efficiency (NUE) was calculated after subtracting the equivalent nitrogen content of the control plots under the same irrigation method for (i) the total harvest of the entire plant (Harvest NUE) and (ii) the grain harvest (Grain NUE). Thus, NUE reported in this study represents the additional effects on yield that the fertiliser application has, above that measured in the control plots.

Collection and analysis of greenhouse gas samples and fluxes

Collection of greenhouse gas samples was carried out using the static chamber technique (e.g. Bhatia et al. 2005). Transparent chambers of 50 cm x 30 cm x 100 cm (length x width x height) were made of 6 mm thick acrylic sheets. An aluminium soil base frame (channel) of 15 cm height and 5 cm internal diameter placed in the field and was used with each chamber. The channels were inserted at 10 cm depth in the soil and stayed in situ for the duration of the experiment. They were filled with water to make the system airtight. The chambers were placed over the rice plants on the sampling days. A small rotary fan and a glass thermometer were also attached to each chamber. Gas samples were drawn through a silicone septum on top of the chamber with a 50 ml syringe attached to a hypodermic needle (24 gauge) at 0, 30, and 60 minutes for both CH_4 and N_2O. Syringes were made air tight with a 3-way stopcock. Headspace volume inside the chambers was recorded to calculate concentrations of N_2O-N and CH_4-C. Concentrations of CH_4 in the gas samples was analysed using a gas chromatograph (GC) fitted with a flame ionization detector (FID)(GC 8A Series, Shimadzu) and N_2O samples were analysed using a GC with electron capture detector (ECD)(Hewlett Packard 5890 Series II) as per Pathak et al., (2002, 2003). Gas standards of 2 and 5ppm for CH_4 and 500 and 1000ppb for N_2O were used as calibration standards.

Fluxes of N_2O and CH_4were calculated as:

$$F = \frac{dC}{dt} . \frac{\rho V}{A} \quad \text{(Eq. 1)}$$

where F is the gas flux from the soil (nmol m^{-2} s^{-1}), dC/dt is the rate of change in the concentration in time in nmol mol^{-1} s^{-1} estimated by linear regression, ρ is the density of air in mol m^{-3}, V is the volume of the chamber in m^3 and A is the ground area enclosed by the chamber in m^2.

A smoothing approach via a general additive model (GAM) was used to gap-fill flux data and estimate cumulative fluxes of N_2O and CH_4 for the duration of the measurement period. This accounted for temporal patterns at a range of time scales and nonlinear responses to environmental variables, implemented using the mgcv package in the R software (Wood, 2006). The GAM was fitted to the flux data, using the same model terms for both the N_2O and CH_4 data, but run separately. The terms included were temperature, water depth, and time since fertilisation. The

GAM allows for non-linearity by fitting a smooth response with cubic splines. The degree of smoothing is optimised by the algorithm, but was also adjusted subjectively, such that the model was not over-fitting to noise in the data. Uncertainty was quantified by simulating 2000 replicate time series from the GAM, given the uncertainty in the fitted parameters, to estimate the posterior distribution. The quantiles of this posterior distribution provided the 95% confidence interval at each predicted time step (Marra and Wood, 2012).

Estimation of ammonia volatilisation losses

Transparent static chambers measuring 18 cm x 18 cm x 30cm (length x width x height) were placed on soil base frames inserted in between the rows of rice plants in the plots for one hour (two replicates per treatment, separate bases than used for the GHG measurements). The volatilised ammonia gas inside the chamber was bubbled through 0.01N boric acid solution containing mixed indicator (methyl red and bromocresol green) using a vacuum pump with a flow rate of 3 l min^{-1} for 3.5 minutes. The volatilised ammoniacal N was determined by the titration of boric acid solution with 0.001 N sulphuric acid as per Bremner (1965). The mass of ammonia measured per unit area of soil enclosed was then estimated as:

$$\mathrm{N} = (S_{vol} \times 28.014) \div A \qquad \text{(Eq. 2)}$$

where N is NH_3-N in mg m^{-2}, $S_{(vol)}$ is amount of 0.001 N sulphuric acid consumed in (ml), the constant 28.014 is the molecular weight of NH_3-N (g mol^{-1}) multiplied by 2 (two moles of NH_3 react with one mole of sulphuric acid) and A is the soil area covered by the chambers (m^2).

In lack of an effective model by which to interpolate between measurement dates, we used a locally weighted smoothing (LOESS) function to estimate cumulative emissions of NH_3. This was implemented by the geom_smooth function in the R package “ggplot2” with a span of 0.25. The advantage of this method is that it was able to estimate an uncertainty to the fitted model. Due to the sticky properties of NH_3, the chamber method is limited in terms of calculating fluxes as NH_3 gas will also attach to the chamber walls during measurements, thus underestimating fluxes to some degree. However, the concentration measurements provided by the method does allow for a relative comparison of NH_3 emissions expected from the different treatments in this experiment, and remains a valid tool to carry out these comparisons under the circumstances of working in rice paddies with limited access to power if the above concerns are taken into account.

Results

Grain and Biomass Yield

The mean dry harvest yields of the full rice plant (grain, stem and leaf) collected from the plots varied between 1,515 and 1,869 g m^{-2}, and the harvests from the different fertiliser and irrigation treatments yielded broadly similar values with no consistently outstanding treatment effect (Table 2). This was also true for the mass of grain harvested for each of the treatment types (dry), with the exception of the CON plots which had considerably lower yield. Dry grain yield for the CON plots was 327 and 307 g m^{-2} for the CF and IF treated fields, respectively, while all other grain yields exceeded at least 440 g m^{-2}. The grain yield was significantly higher in the CF plots than that harvested in the IF plots (t-test $p = 0.01$) with mean yields of 516 and 467 g m^{-2}, respectively.

N content and Nitrogen use efficiency

The total N content of the crops grown in the CF plots was higher than the respective treatment plots in the IF fields in all cases. This difference was most notable in the N content of the grain, while the N content in the stem and leaf segments were comparable in magnitude. In the case of the LCC treated plots in the CF fields, the N content of the stem and leaf exceeded 0.55%, by far the largest value observed in all of the plots. The grain NUE was the highest in LCC plots in both IF and CF. The harvest nitrogen use efficiency (NUE, the % of N applied used by the crop harvest minus the N content of the control plots) was significantly higher in the CF plots than the IF plots (t-test $p = 0.03$), with peak efficiency achieved by the LCC treated CF plots at 64.5% of applied nitrogen. By contrast, the lowest NUE observed was for FYM treated plots in the IF fields with an NUE of only 23.6% (Figure 4a).

Greenhouse gas fluxes

Fluxes of N_2O measured from the plots varied from 0.08 to 1.31 nmol m^{-2} s^{-1}. Observed fluxes typically increased in the days immediately after a fertiliser application, and remained elevated during the growing period, with the exception of the CON plots which remained near zero throughout the experiment (Figure 2a). Cumulative N_2O emissions from the different plots were broadly similar throughout the experiment, although emissions from the fertilised IF plots were significantly larger than those calculated for the CF plots in all cases, (t-test $p<0.01$) with mean cumulative flux values of 1.11 and 1.38 kg N_2O-N ha^{-1} for CF and IF plots, respectively (Table 3, Figure 4b).

Fluxes of CH_4 measured from the plots varied from -6.9 to 144 nmol m^{-2} s^{-1}. Measurements in all plots, including the CON plots, observed a gradual rise in CH_4 emissions during the growing season, peaking in the period between late August and early September before falling back to pre-transplanting magnitude (Figure 2b & Figure 2c). The largest peaks in emissions were observed in the FYM plots for both the IF and CF plots, which resulted in considerably larger cumulative CH_4 emissions when compared to the other treatments (Table 3). Cumulative CH_4 emissions from the FYM treatments were 53.5 and 39.6 kg CH_4-C ha^{-1} for the CF and IF plots, respectively. This compares to a range of 20.0 to 28.3 kg CH_4-C ha^{-1} for all other treatments and control plots. Cumulative CH_4 emissions measured from the control plots were comparable to the fertilised plots, with the exception of the FYM treatments. Methane emissions were significantly lower with application of NCU as compared to PRI under IF (Table 3). A comparison of cumulative CH_4 emissions measured from the different irrigation methods (with the exception of the FYM plots) reveals that emissions were significantly higher from the CF plots than the IF plots (t-test p = 0.05), with mean cumulative emissions of 33.5 and 27.15 kg CH_4-C ha^{-1}, respectively.

Global warming potential (GWP) was estimated for the plots using values provided from the IPCC 2014, Fifth Assessment Report (IPCC, 2104) (i.e. molar volume multiplied by 265 for N_2O and 28 for CH_4 for a 100-year time horizon). Using cumulative emissions for both N_2O and CH_4, the CO_2 equivalent (CO_2eq) is presented in Figure 3c and Table 3. A comparison of GWP between the plots shows that CO_2eq is dominated by the contribution from CH_4. This comparison also highlights the large contribution to the GWP of the control plots without fertiliser application, which are comparable in magnitude to the other treatments with the exception of the FYM plots. After control plot values have been subtracted, emissions of CO_2eq from the FYM plots are estimated to be 905 and 637 kg CO_2-C ha^{-1} under CF and IF, respectively. These are significantly higher than the other treatments, with CO_2eq estimates ranging from 96 to 233 kg CO_2-C ha^{-1} once control plot values have been subtracted. This large difference is entirely attributable to the higher CH_4 emissions from the FYM plots (Figure 4c). The GWP under the two flooding methods was significantly different for the control, FYM and NCU plots (Table 3).

Ammonia volatilisation

Total collection of volatilised NH_3 collected in the chambers ranged from 0 to 154 mg N m^{-2} d^{-1}. Measured NH_3 concentrations peaked after each fertiliser application, with the largest emissions observed after applications to the NCU treated CF plots (Figure 3a). With the exception of the CON plots, all plots observed a marked increase in NH_3 concentrations during the measurement period (Table 4). Cumulative emission estimates suggest that between 27.2 and 32.9 kg of NH_3-N are lost from the fertilised plots over the measurement period, resulting in NH_3 EFs ranging from 22.9 to

27.4%. The lowest EF for NH_3 was 22.7% (PRI) in CF and 22.9% (LCC) under IF. Mean cumulative NH_3 EFs are similar at 24.7 and 24.8% for the CF and IF plots, respectively, with no statistical significance between the different methods (t-test p =0.46). Interpolation uncertainty for NH_3 fluxes as estimated using the LOESS fit is approximately the same order of magnitude as differences observed between the two irrigation methods (Figure 3b, Figure 4d).

Discussion

Our results suggest that nitrogen fertiliser type is not a powerful driver of yields in rice paddies if the amount of fertiliser applied is the same, but that there was a significant difference in grain yields when comparing continuous flooding (CF) and intermittent flooding (IF) methods (Figure 4a). The average of the dry grain yield from the harvests was significantly higher in the CF plots than the IF plots (t-test p = 0.01), suggesting that a conversion from CF to IF farming would reduce grain yield by approximately 6.1%. Published literature on the effects that more water efficient irrigation systems have on yields varies, with many studies showing that less water intensive methods generate similar or occasionally increased yield as CF fields (e.g. de Avila 2015; Thakur et al., 2018; Massey et al., 2014; Nugroho et al., 1994). However, there is also strong evidence to show that intermittent flooding can consistently reduce grain yield (e.g. Eriksen et al., 1985, Jain et al 2016, Carrijo et al., 2017). The consensus among many rice farmers is that the CF method is more productive (Carrijo et al., 2017), and our study supports this. Rather than a particular irrigation method controlling rice yields, it is likely that water depth is the true factor in determining the success of the crops. In various experiments, water depth varies widely, and in some experiments using water-saving irrigation methods, the threshold of water in the paddies at which rice production is impacted may not be reached. The depth of water in which rice is most productive has been estimated as 5 to 10 cm (Talpur et al., 2013), although this will vary dependant on other site and crop specific variables.

In our experiment, water depth in the IF paddies reached zero, or near-zero multiple times, thus this critical threshold was likely breached several times, consequently yields were impacted. A further meta-analysis of the available data would be required to establish best practice for both saving water, and keeping grain yields similar or higher than CF methods.

Although the total mass of fresh weight harvest was comparable for the different treatments, the NUE varied drastically between the plots as the N content was significantly different among the treatments in grain and biomass. The highest N content in grain was in FYM plots in CF and in LCC plots in IF. The NUE of the different fertilisers varied from 23.6 to 64.5%, and was significantly higher in the CF plots than the IF plots (t-test $p = 0.03$).The NUE of the crops is typical of values recorded in other NUE experiments (e.g. Chen et al., 2015; Cassman et al., 1993; Zhang et al., 2018b), however, depending on practice, rice harvests can see N recovery rates vary from as much as 5 to 96% (Peng et al., 2006). The NUE was significantly higher in the CF plots than the IF plots (t-test $p = 0.03$), with mean NUEs of 51.3 and 28.8%, respectively. Theoretically, the slower release of N via the neem coated urea, and the use of leaf colour charts to apply less N per application, spread over regular intervals was expected to increase plant NUE in our experiment as crops would have better access to nitrogen throughout the growing season. This appeared successful in the CF LCC plot in which the highest NUE was recorded at 64.5% of the applied N; however, this was not found in the IF plots in which the LCC plots recorded a much lower NUE of 28.4%. Even though among the IF plots, the N content in grain was the highest in LCC, no significant increase was observed in the grain and biomass yield over NCU plots which led to a lower NUE for the LCC plots in IF. Significantly higher total biomass yield was recorded for NCU plots in IF compared to all other treatments.

Cumulative N_2O emissions from the fertilised IF plots were significantly larger than those calculated for the CF plots (t-test $p < 0.01$) with EFs ranging between 0.56% and 0.70% (Figure 4b).These values fall below the default estimates of 1% of applied N released as N_2O used by the IPPC Tier 1 approach for mineral fertiliser application (IPCC, 2014), although agree well with emissions expected from urea and organic fertiliser emissions presented in other studies which are typically in the range from 0.4% to 0.9% (e.g. Cowan et al., 2020; Islam et al., 2018; Thorman et al., 2020; Yue et al., 2019). The neem oil coating in NCU acting as nitrification inhibitor (Kumar et al., 2007) likely lowered the N_2O emissions by 8.6% and 4.8% in NCU compared to PRI, in CF and IF, respectively, but the difference was not significant. Gupta et al. (2016b) reported a significant decrease in N_2O emissions using neem oil coated urea compared to prilled urea in transplanted continuously flooded rice. The use of LCC resulted in an additional 30 kg N fertiliser application, however, the N_2O emissions were not higher and were at par with other fertiliser treatments. The LCC method has been reported to be more efficient in increasing N-use efficiency (Bhatia et al., 2012b) as demand-driven N application results in higher N uptake by the crop and increases NUE. In this experiment, the LCC based N fertilizer application also had significantly higher NUE in CF plots.

Cumulative CH_4 emissions from the plots were broadly similar (CON plots included), with the exception of the FYM treatments. Cumulative emissions for the FYM treatments were approximately double that of the other fertiliser applications using the same irrigation method (Figure 4c). Taking emissions of the CON plots into account, emissions of CO_2eq related to the FYM applications were considerably larger than the other treatments, resulting in an additional 1,014 and 743 kg CO_2-C ha^{-1} from the CF and IF plots, respectively. Emissions associated with the other fertilisers ranged from 208 to 360 kg CO_2-C ha^{-1} once the control plot values were subtracted. Higher emissions from organic fertiliser applications such as FYM have been reported before in similar studies (e.g. Jain et al., 2000; Pathak et al., 2003; Pandey et al., 2014), and our experiment provides further evidence that adding carbon rich organic materials such as animal waste to rice paddies will substantially increase CH_4 emissions. Significantly lower emissions of CH_4 measured in NCU compared to PRI under IF may be due to the presence of Nimin in the neem oil coating which has been reported to increase the methanotrophic bacterial population in the soil, thus increasing CH_4 oxidation and reducing fluxes (Datta and Adhya, 2014).

Cumulative CH_4 emissions measured from the CF plots (excluding FYM) were approximately 18% larger than the IF plots (t-test p = 0.05), with mean cumulative emissions of 26.2 and 22.2 kg CH_4-C ha^{-1} for the two irrigation methods, respectively. Our observations of increased N_2O and decreased CH_4 in the IF plots are consistent with similar studies (Yagi et al., 1996; Jain et al., 2000; Cai et al., 1997). Although we do report a degree of pollution swapping as a result of switching from CF to IF irrigation methods, a comparison of GWP between the rice paddy plots shows that CO_2eq is dominated by the contribution from CH_4. This comparison also highlights the large CO_2eq emissions from the control plots that did not receive fertiliser application, with GWP emissions from the CF and IF CON plots of 720 and 621 kg CO_2eq ha^{-1}. With the exception of the FYM treatments, differences in GWP of the NCU, LCC and PRI methods were all comparable in magnitude in terms of both N_2O and CH_4 emissions. However, if the gains in economic yield benefit are taken into account, LCC based NCU application resulted in a significant reduction in the yield scaled GWP which is the global warming potential per kg of economic yield (Table 3).

Measurements of NH_3 emissions are notoriously difficult to carry out in remote locations. Although the NH_3 measurement method deployed in this experiment has its weaknesses, we are still able to meaningfully assess the magnitude of NH_3 losses. What is clear from the measurements carried out in this study is that a large amount of the applied N is lost as volatilised NH_3 in the plots. Using a basic analysis, EFs of NH_3 (emissions minus the control) ranging from 22.8 to 27.4% of the applied N was estimated to have been lost from the plots. The LCC based N application of NCU did not significantly impact the NH_3 losses compared to NCU applied through traditional split application, even though NH_3-N volatilized from the LCC plots from IF and was significantly lower than from the PRI plots (Table 4). These estimates compare well with some studies (e.g. Hayashi et al., 2008; Datta et al., 2012; Wang et al., 2018) in which NH_3 emissions are reported in the region of 10 to 25%. However, it is difficult to compare studies directly due to varying meteorological conditions which drive NH_3 volatilisation and large uncertainties in the majority of methods used to measure NH_3

fluxes. Theoretically, our measurements could be underestimating the flux of NH_3 due to losses on the surface of walls of flux chambers; however, contamination of the acid traps as a result of high atmospheric concentrations could also result in overestimation. Regardless, our results show that NH_3 emissions peak after fertiliser application in the paddies compared with the low emissions measured in the CON plots, and that relatively large N losses occur due to NH_3 volatilisation. We recommend further research in this area to determine the true magnitude of these N losses, which are sizable enough to cause harm both environmentally and economically.

Overall, the change in irrigation method from CF to IF led to a significant reduction in grain yield and harvest NUE. The GWP was, however, reduced by the change in irrigation method from CF to IF for FYM and NCU treatments. The yield scaled GWP was lower in CF with LCC based fertiliser N application.

Conclusions

Our conclusions are mixed regarding the economic and environmental costs and benefits of the different fertiliser types and irrigation methods. The different applications of urea and neem coated urea showed little difference in terms of yield, GHG and NH_3 response, with most significant differences between the plots being observed between the different irrigation methods. In terms of grain yield, conventional flooding (CF) irrigation methods performed better than the intermittent flooding (IF) in this study. The NUE of the crops in the CF plots was higher overall than those in the IF fields, and grain yields were 6.3% lower in the IF fields. However, GHG and NH_3 emissions were also larger from the CF plots, especially in the case of FYM application, which resulted in an additional loss of 905 kg CO_2eq ha^{-1} in the form on non-GHG gases during the measurement period resulting in higher yield scaled greenhouse emissions. Emissions of CH_4 dominated the CO_2eq emissions for all plots, but emissions of CH_4 were lower in the IF plots when compared to CF. Although the IF plots produced less CH_4, slightly more N_2O was produced, resulting in a small amount of trade off. The use of LCC based N application may result in an increase in NUE and lower yield scaled greenhouse gas emissions from the conventionally practiced continuous flooding method of irrigation in rice grown in this region. Realistically, CH_4 reductions are a far more important target for future mitigation efforts as CH_4 emissions make up approximately 78 to 94% of the total CO_2eq from the rice paddies in this study. Measurements of NH_3 from the plots could not determine decisive differences between the treatments; however, our measurements do show that emissions of NH_3 from rice paddies are not trivial, ranging from approximately 22.8 to 27.4% of applied N.

We recommend that further studies deploy more advanced methods where possible to better determine the temporal behaviour of GHG emissions during the intermittency of flooding events (such as auto chambers or eddy covariance) to capture peak events that irregular sampling may miss. We also recommend the use of more advanced NH_3 measurement methodology where possible to fully determine the nature of NH_3 emissions from rice paddies for which there are few studies reported in the literature.

Acknowledgements

The authors also want to thank the Director ICAR-Indian Agricultural Research Institute, New Delhi, India for providing facilities for conducting this research. The experiments were carried out within Newton-Bhabha Virtual Centre on Nitrogen Efficiency of Whole-cropping Systems for improved performance and resilience in agriculture (NEWS India-UK) jointly between India and the UK and funded by the Department of Biotechnology (DBT), Government of India for funding of the Indian part of this research and the Biotechnology and Biological Science Research Council (BBSRC) for the UK part of this research (grant reference BB/N013492/1). Additional financial assistance was also received from the National Initiative for Climate Resilient Agriculture Project (NICRA-IARI/12-115). This work was also supported by the UK Natural Environment Research Council (NERC) as part of the

South Asia Nitrogen Hub (SANH) (NE/S009019/1), supported through UKRI Global Challenges Research Fund.

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Table 1 Nitrogen fertiliser treatment details. FYM = farmyard manure, NCU = Neem coated urea, LCC = leaf colour chart, CF = continuous flooding, IF = Intermittent flooding

#	Name	Fertiliser applied
1	CON	No nitrogen fertiliser was applied
2	FYM	50% N through FYM + 50% N through NCU+ Bio fertiliser (120 kg N ha^{-1})*
3	LCC	Leaf Colour Chart (LCC) based NCU application (150 kg N ha^{-1} in CF and 120 kg N ha^{-1} in IF)
4	NCU	100% N through NCU (120 kg N ha^{-1})
5	PRI	100% N through Prilled urea (120 kg N ha^{-1})

* Indicates the rate of N fertiliser applied in each treatment

Table 2 Yield harvest data from three replicate plots for each fertiliser and irrigation treatment. Mean values reported for fresh harvest biomass.

Treatment	Total Biomass ($g\ m^{-2}$)	Grain yield ($g\ m^{-2}$)	N Content Stem & Leaf (%)	N Content Grain (%)	N Content Total ($kg\ ha^{-1}$)	Harvest NUE (%)	Grain NUE (%)
CF							
CON	1,515	327*	0.249	1.588	81.5		
FYM	1,868*	502*	0.387	1.894*	147.9*	55.4*	27.6*
LCC	1,688	533*	0.553*	1.783*	158.9*	64.5*	30.6*
NCU	1,634	504*	0.331	1.743	125.3	36.5	25.7
PRI	1,714	524*	0.415*	1.732	140.1*	48.9*	28.4*
IF							
CON	1,582	307	0.276	1.496	81.1		
FYM	1,618	476	0.334	1.499	109.5	23.6	21.1
LCC	1,637	478	0.331	1.608	115.2	28.4	22.9
NCU	1,869*	469	0.332	1.579	120.5	32.8	21.3
PRI	1,749	446	0.359	1.588	117.6	30.4	18.4

* Indicates a statistically significant increase when compared to the same fertiliser treatment applied to the alternate irrigation regime.

Table 3 Cumulative fluxes are presented for N_2O and CH_4 emissions measured from the plots. A general additive model (GAM) as described in the text was used to interpolate between measurement dates using available meteorological data to estimate cumulative fluxes and provide 95% confidence intervals of the fitted prediction. The global warming potential (GWP) of N_2O and CH_4 emissions are presented as CO_2 equivalent (CO_2eq), using values provided from the IPCC 2014, Fifth Assessment Report (IPCC, 2014). Yield scaled GWP represented by grain yield, as reported in Table 2.

	N_2O Flux (kg N_2O-N ha^{-1})		CH_4 Flux (kg CH_4-C ha^{-1})		N_2O + CH_4 GWP (kg CO_2-C ha^{-1})		Yield scaled GWP (kg CO_2-C kg^{-1})
Treatment	Cumulative	95% C.I.	Cumulative	95% C.I.	Cumulative	95% C.I.	
CF							
CON	0.4	0.39-0.42	24.1*	22.4-25.7	720*	632-808	0.22
FYM	1.12	1.07-1.17	53.5*	52.3-54.6	1625*	1565-1685	0.32*
LCC	1.09	1.05-1.14	25	23-27	824	725-923	0.15
NCU	1.07	1.03-1.12	28.3*	26.7-29.9	914*	799-1029	0.18*
PRI	1.17	1.11-1.23	27.2*	25.4-28.9	894	790-998	0.17
IF							
CON	0.61*	0.59-0.63	19.7	18.8-20.6	621	574-668	0.21
FYM	1.31*	1.23-1.39	39.6	37.6-41.5	1258	1156-1360	0.26
LCC	1.37*	1.28-1.46	24.5	22.7-26.2	842	748-936	0.18*
NCU	1.38*	1.28-1.49	20	18.8-21.3	717	581-853	0.15
PRI	1.45*	1.37-1.53	24.6	22.7-26.6	853	748-958	0.19

* Indicates a significant increase when compared to the same fertiliser treatment applied to the alternate irrigation regime.

Table 4 Cumulative emissions of NH_3 calculated from measurement data using LOESS interpolation between points. An assumption is made that the NH_3 collected by the acid traps in the chamber is representative of NH_3 volatilised from the surface during the measurement period.

Treatment	NH_3 Emission Cumulative (kg NH_3-N ha^{-1})	NH_3 EF %	95% C.I.
CF			
CON	2.8		
FYM	27.4	22.8	1.4
LCC	31.6	26.4	2.0
NCU	32.1	26.7	3.1
PRI	27.2	22.7	1.5
IF			
CON	3.7		
FYM	28.6	23.8	1.5
LCC	27.5	22.9	1.6
NCU	30.3	25.2	2.0
PRI	32.9	27.4*	2.0

* Indicates a significant increase when compared to the same fertiliser treatment applied to the alternate irrigation regime.

Legends of Figures

Figure 1 (a) Mean daily air temperature (min and max shaded), (b) mean daily relative humidity, (c) cumulative daily rainfall and (d) water depth of the continuously (black) and intermittently (red) flooded paddies are presented for the field site during the period in which measurements took place (12/07/16 to 21/10/16).

Figure 2 Mean daily fluxes of (a) N_2O and (b) CH_4 are presented in nmol m^{-2} s^{-1}. Global warming potential of the cumulative emissions of N2O and CH4 during the experiment are presented in kg of CO_2eq (c).A general additive model (GAM)as described in the text was used to interpolate between measurement dates using available meteorological data to estimate cumulative fluxes and provide 95% confidence intervals of the fitted prediction (line/shaded). Fertiliser dates for all plots are shown (vertical lines) with additional dates included for LCC applications only (green vertical lines).

Figure 3(a) Emissions of NH_3 measured using transparent chambers are shown for each fertiliser treatment type for both the conventional and intermittently flooded plots. (b) The difference between the interpolated data is presented, coloured red when CF plots emissions are higher and blue where IF emissions are higher. Fertiliser dates for all plots are shown (vertical lines) with additional dates included for LCC applications only (green vertical lines).

Figure 4 Bar plots highlight differences in (a) NUE, (b) N_2O EFs, (c) GWP and (d)NH_3 EFs observed for the different fertiliser types and irrigation regimes in the experiment. Error bars represent the 95% confidence interval in the estimated values.

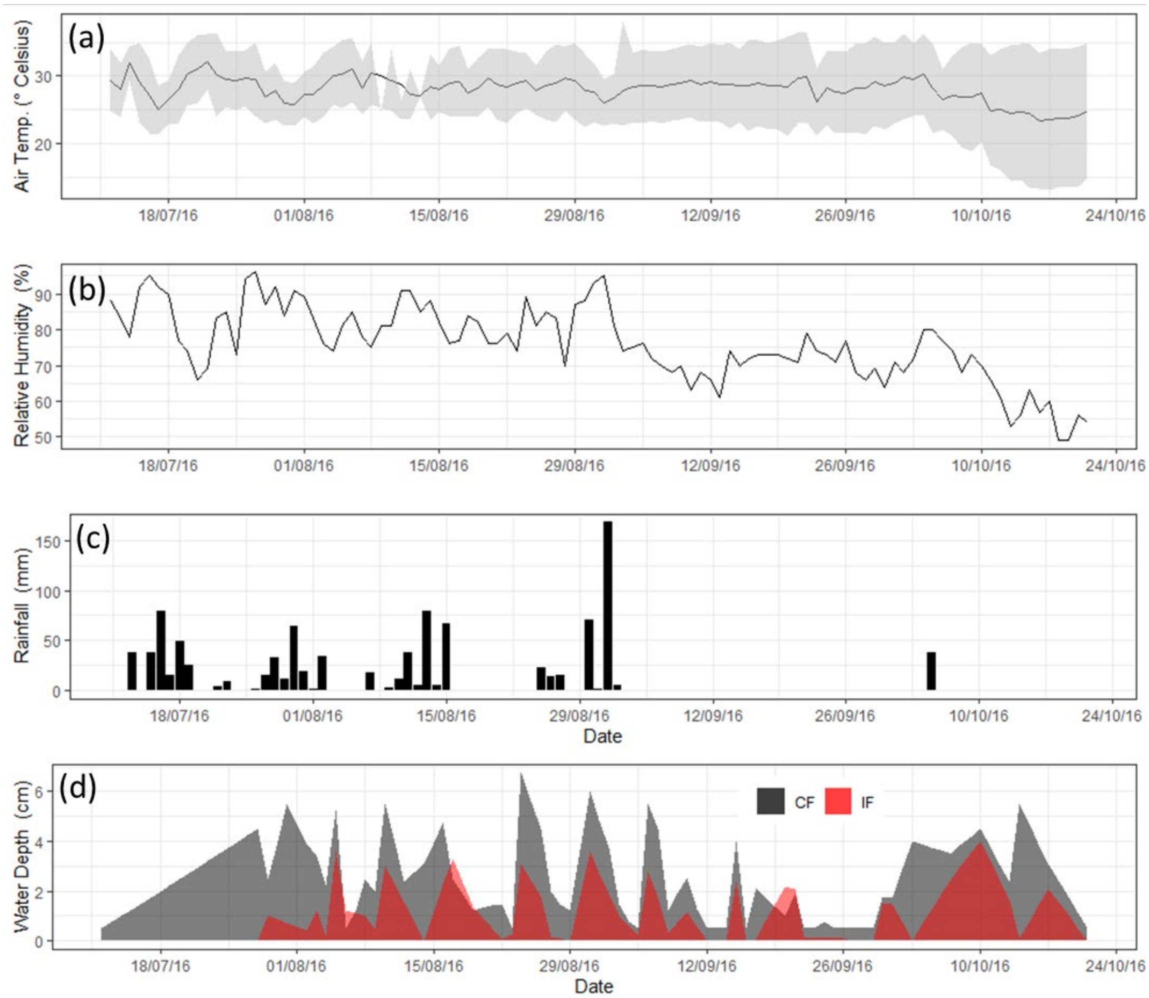
(a)
Air Temp. (° Celsius)
30
20
18/07/16
01/08/16
15/08/16
29/08/16
12/09/16
26/09/16
10/10/16
24/10/16
(b)
Relative Humidity (%)
90
80
70
60
50
(c)
Rainfall (mm)
150
100
50
0
Date
(d)
Water Depth (cm)
6
4
2
0
CF
IF
Date

Figure 1

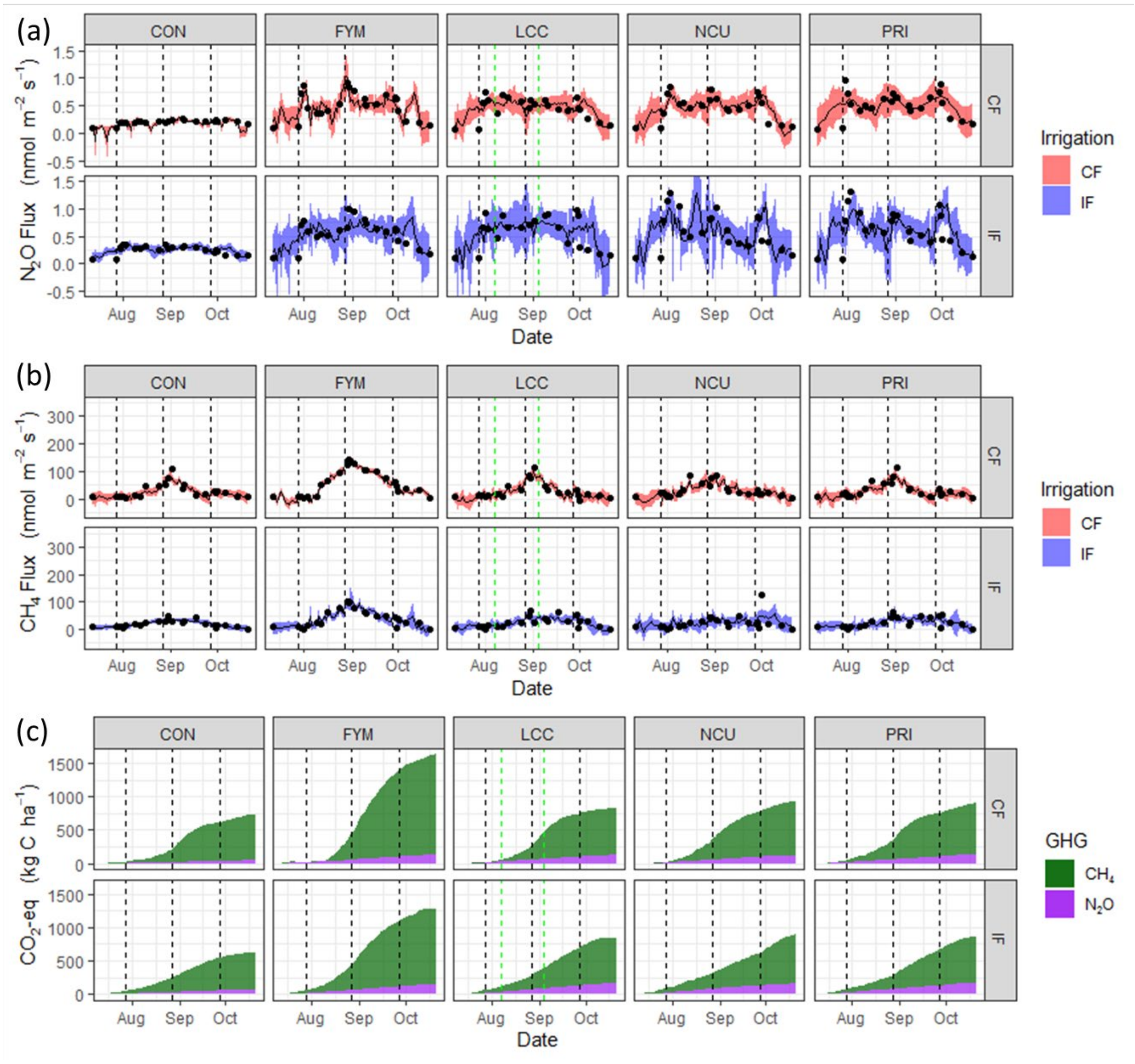
(a)
CON
FYM
LCC
NCU
PRI
CF
IF
N$_2$O Flux (nmol m^{-2} s^{-1})
1.5
1.0
0.5
0.0
-0.5
Aug
Sep
Oct
Date
Irrigation
CF
IF
(b)
CH$_4$ Flux (nmol m^{-2} s^{-1})
300
200
100
0
(c)
CO$_2$-eq (kg C ha^{-1})
1500
1000
500
0
GHG
CH$_4$
N$_2$O

Figure 2

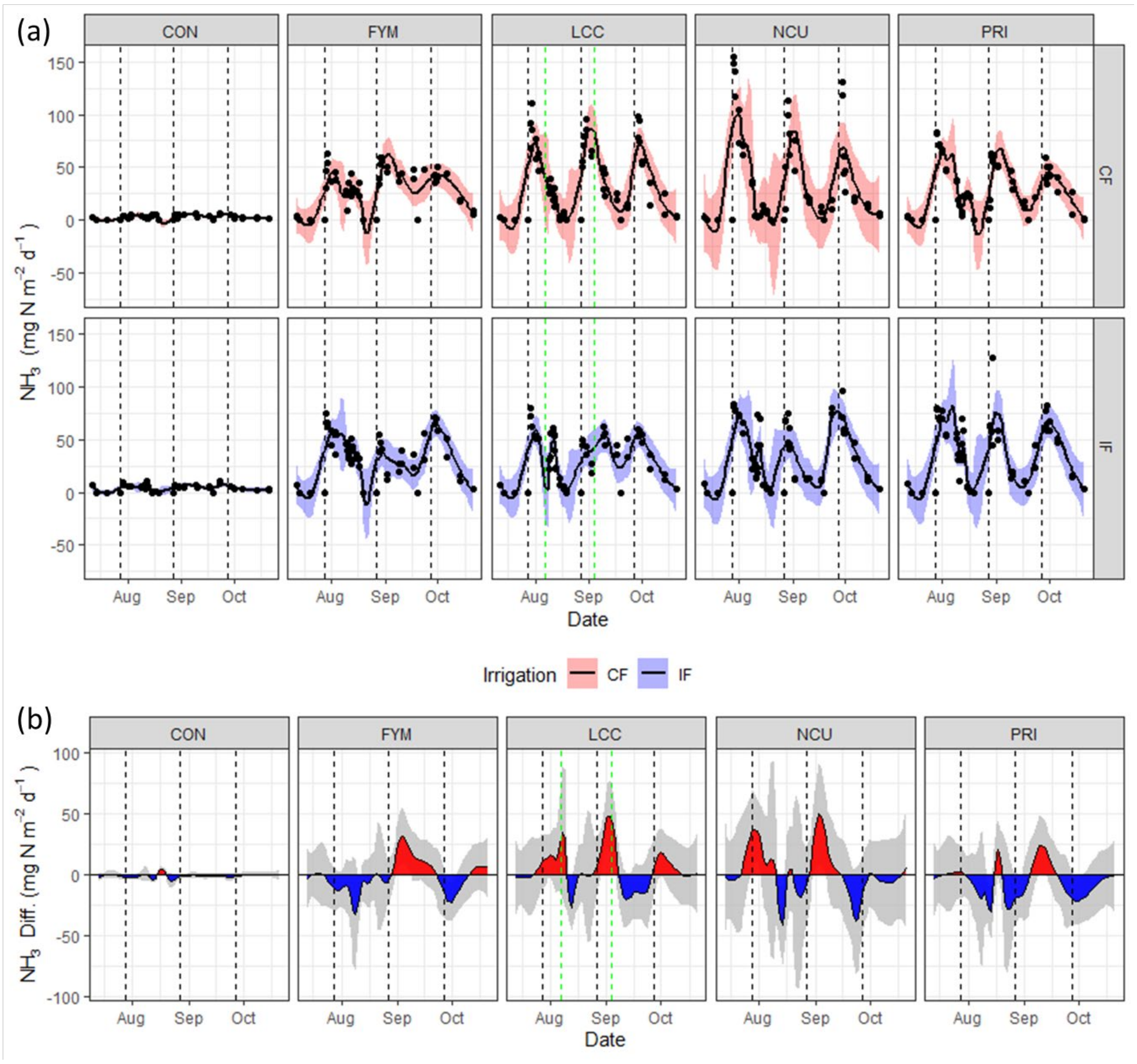
(a)
CON
FYM
LCC
NCU
PRI
CF
IF
150
100
50
0
-50
NH3 (mg N m-2 d-1)
Aug
Sep
Oct
Date
Irrigation
CF
IF
(b)
100
50
0
-50
-100
NH3 Diff. (mg N m-2 d-1)

Figure 3

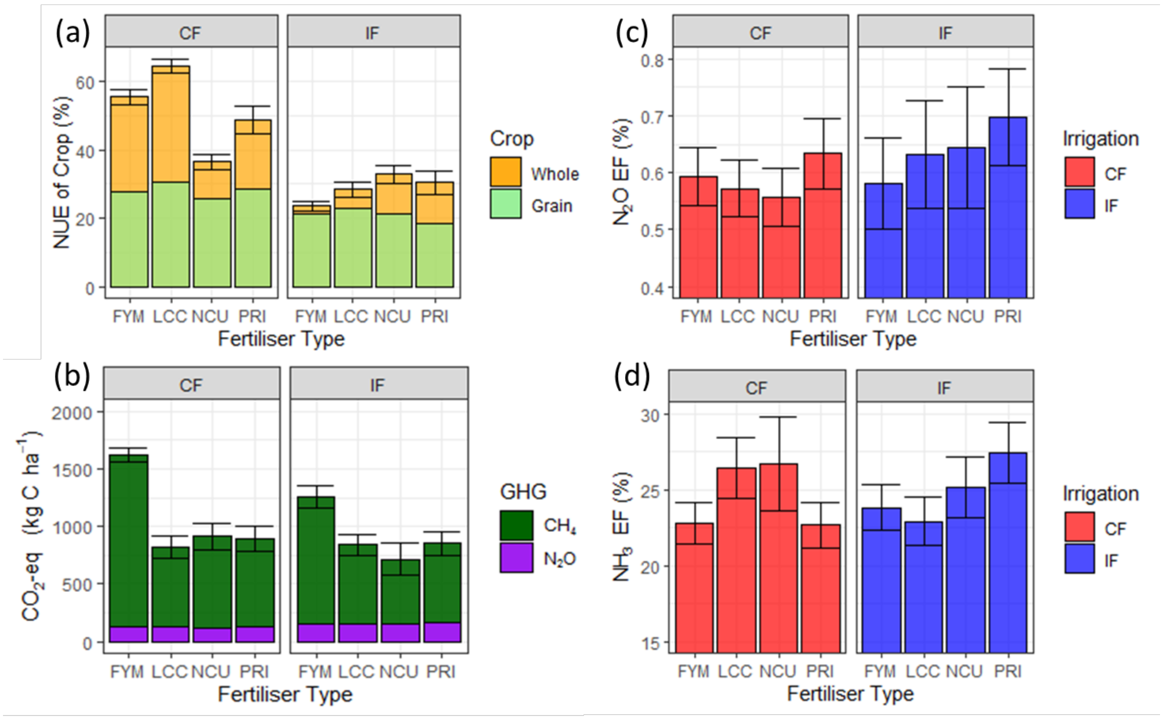

Figure 4 Bar plots highlight differences in (a) NUE, (b) N_2O EFs, (c) GWP and (d)NH_3 EFs observed for the different fertiliser types and irrigation regimes in the experiment. Error bars represent the 95% confidence interval in the estimated values.