

Greenhouse gas (N₂O and CH₄) fluxes under nitrogen-fertilised dryland wheat and barley on subtropical Vertosols: risk, rainfall and alternatives

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Abstract. The northern Australian grains industry relies on nitrogen (N) fertiliser to optimise yield and protein, but N fertiliser can increase soil fluxes of nitrous oxide (N₂O) and methane (CH₄). We measured soil N₂O and CH₄ fluxes associated with wheat (*Triticum aestivum*) and barley (*Hordeum vulgare*) using automated (Expts 1, 3) and manual chambers (Expts 2, 4, 5). Experiments were conducted on subtropical Vertosol soils fertilised with N rates of 0–160 kg N ha⁻¹.

In Expt 1 (2010), intense rainfall for a month before and after sowing elevated N₂O emissions from N-fertilised (80 kg N ha⁻¹) wheat, with 417 g N₂O-N ha⁻¹ emitted compared with 80 g N₂O-N ha⁻¹ for non-fertilised wheat. Once crop N uptake reduced soil mineral N, there was no further treatment difference in N₂O. Expt 2 (2010) showed similar results, however, the reduced sampling frequency using manual chambers gave a lower cumulative N₂O. By contrast, very low rainfall before and for several months after sowing Expt 3 (2011) resulted in no difference in N₂O emissions between N-fertilised and non-fertilised barley. N₂O emission factors were 0.42, 0.20 and –0.02 for Expts 1, 2 and 3, respectively. In Expts 4 and 5 (2011), N₂O emissions increased with increasing rate of N fertiliser. Emissions were reduced by 45% when the N fertiliser was applied in a 50 : 50 split between sowing and mid-tillering, or by 70% when urea was applied with the nitrification inhibitor 3,4-dimethylpyrazole-phosphate.

Methane fluxes were typically small and mostly negative in all experiments, especially in dry soils. Cumulative CH₄ uptake ranged from 242 to 435 g CH₄-C ha⁻¹ year⁻¹, with no effect of N fertiliser treatment. Considered in terms of CO₂ equivalents, soil CH₄ uptake offset 8–56% of soil N₂O emissions, with larger offsets occurring in non-N-fertilised soils.

The first few months from N fertiliser application to the period of rapid crop N uptake pose the main risk for N₂O losses from rainfed cereal cropping on subtropical Vertosols, but the realisation of this risk is dependent on rainfall. Strategies that reduce the soil mineral N pool during this time can reduce the risk of N₂O loss.

Additional keywords: 3,4-dimethylpyrazole-phosphate (DMPP), ENTEC, *Hordeum vulgare*, *Triticum aestivum*.

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Introduction

Direct greenhouse gas (GHG) emissions from Australia's agricultural sector total 81 Mt carbon dioxide equivalents (CO₂-e) annually, or 15% of net national GHG emissions of 547 Mt CO₂-e (Commonwealth of Australia 2015b). The agriculture sector is the primary source of emissions of both methane (CH₄), essentially associated with meat and wool production, and nitrous oxide (N₂O), predominantly associated with grain cropping (Dalal *et al.* 2003). Methane emissions from enteric fermentation (i.e. grazing animals) account for ~70% of all agricultural emissions, and N₂O a further 15–20%. Concerns over the impacts of increasing GHG concentrations in the atmosphere and resultant effects on global warming and climate

change have prompted the Australian agricultural sector to sponsor research into methodologies for improved GHG mitigation. These methodologies will then be incorporated into industry plans for environmentally sustainable production that maintains or increases farm profitability and market access (Rodriguez *et al.* 2003; Gunasekera *et al.* 2007; Blumenthal *et al.* 2008).

The concentration of N₂O in the atmosphere is increasing, largely because of increased anthropogenic N inputs into the soil. Emissions of N₂O from the soil originate from the biological processes of nitrification and denitrification, which utilise inorganic N from any source (Bremner 1997). Susceptibility to N₂O loss is primarily determined by the

interaction between the rate of supply of inorganic N, plant demand for N, soil properties, and environmental conditions (Dalal *et al.* 2003). Of particular concern are N₂O emissions associated with fertiliser N inputs in combination with soil moisture.

The Australian Government publishes quarterly national inventories of the sources and magnitude of GHG emissions (Commonwealth of Australia 2015b) as well as comprehensive guidelines on how the emissions are calculated (Commonwealth of Australia 2015a). For the inventories, emissions of N₂O associated with grain cropping are calculated by using an emissions factor (EF), which is the proportion of N input subsequently emitted to the atmosphere as N₂O, applied to estimated amounts of N fertiliser and other N inputs (IPCC 2006). Australia uses a country-specific EF of 0.2% for N fertiliser used in rainfed cropping (Commonwealth of Australia 2015a), a value based on an analysis by Shcherbak and Grace (2014) of recent Australian field research.

Those same Australian studies indicate that the percentage of fertiliser N applied to grain crops and emitted as N₂O varies substantially. The array of values reflects, among other factors, rate of fertiliser N, crop type, tillage practice, stubble management, soil texture, soil pH, and environment – particularly rainfall and temperature (Barker-Reid *et al.* 2005; Barton *et al.* 2008, 2010, 2013; Li *et al.* 2008; Officer *et al.* 2010; Wang *et al.* 2011; Schwenke *et al.* 2015). An analysis of Australian work in which conservation tillage was used indicates an overall average EF of 0.28% from a range 0.01–0.77%. The EFs for subtropical dryland cropping in northern New South Wales (NSW) and southern Queensland (average 0.48%) were higher than for the remainder of Australian grain-growing areas (average 0.07%).

Li *et al.* (2008) suggested that it was inappropriate to use a single default EF to estimate N₂O emissions associated with grain cropping, with crop type, management and environmental factors needing to be taken into account in the calculations. Nitrous oxide is emitted episodically, largely in association with rainfall events. For example, there were 8–10 spikes of N₂O emissions during the 3 years of field monitoring in the study by Wang *et al.* (2011), with the spikes much greater in magnitude for N-fertilised treatments than for unfertilised treatments. Those authors concluded that emissions mainly occurred when the water-filled pore space (WFPS) was >50% and the daily air temperature was >10°C. Other studies have also reported temporal patterns of N₂O emissions (Barton *et al.* 2008, 2011; Officer *et al.* 2010; Schwenke *et al.* 2015). Therefore, the occurrence of rainfall episodes coinciding with other conditions conducive to high N₂O emissions will determine the EF for any particular situation.

From an industry point of view, an emissions intensity index (EI) can be a more effective tool than EF for comparing management options to optimise both crop yield and N₂O emissions (Scheer *et al.* 2012). The EI is calculated as the ratio of N₂O emitted to grain produced. Simply aiming to minimise N₂O emissions with no regard to continued profitable grain production will produce strategies that are unlikely to be adopted by grain growers. Instead, using a yield-scaled emissions approach such as EI should ensure that proposed N₂O-mitigation strategies are both agronomically efficient and

economically profitable (Van Groenigen *et al.* 2010). Substantially more data from direct field measurements of N₂O emissions are needed so that EFs and EIs can be applied that are at least more specific to region, crop type and soil (Ogle *et al.* 2014).

Apart from soils used for wetland rice cultivation, agricultural soils are typically considered a sink, not a source, of atmospheric CH₄, but limited availability of data means that CH₄ uptake by soil microorganisms is currently not considered in Australian GHG inventory calculations (Dalal *et al.* 2008). Methanotrophic activity tends to be greater in forest soils than grasslands, with dryland arable soils typically having much lower uptake potential (Le Mer and Roger 2001). Conditions favouring greater CH₄ uptake by cultivated soils include low WFPS, temperatures >10°C, greater aeration, more gas-diffusion pathways (less compaction), non-acidic pH and low salinity (Dalal *et al.* 2008). Fine-textured soils typically have low CH₄ oxidation rates due to their low porosity and high water retention, which combine to restrict diffusion of CH₄ into the soil profile (Dutaur and Verchot 2007). However, long-term no-till management that improves soil structure can enhance gas diffusivity and CH₄ uptake (Plaza-Bonilla *et al.* 2014). The addition of ammonium to soils through fertilisers may temporarily inhibit CH₄ uptake through competition between some methanotrophic groups and ammonium oxidisers for oxygen in the soil atmosphere. Long-term N-fertiliser use can also cause long-lasting reductions in methanotrophic activity (Hütsch *et al.* 1993). Chemical additives used to inhibit soil nitrification may either enhance (Weiske *et al.* 2001) or inhibit (Syamsul Arif *et al.* 1996) soil CH₄ uptake.

Globally, CH₄ uptake in cultivated soils averages 0.92 kg CH₄-C ha⁻¹ year⁻¹ across a range of boreal, temperate and tropical climates (Dutaur and Verchot 2007). Soil CH₄ flux data from cultivated Australian soils are available for tropical sugarcane soils in Queensland (Weier 1999; Denmead *et al.* 2010), temperate winter crops on a sandy soil in Western Australia (Barton *et al.* 2010, 2013), and subtropical winter wheat on a clay soil (Wang *et al.* 2011). There is a need for substantially more field-based data on CH₄ fluxes from a diversity of soil types, climatic conditions and potentially influential management factors. Such data would be used in national GHG inventories and, where CH₄ uptake exceeds CH₄ emission, might be used to offset some of the N₂O emissions produced during the same cropping period (Wang *et al.* 2011).

We report data from five experiments conducted during a 2-year period in northern NSW, in which we used both automated and manual chambers to monitor fluxes of N₂O and CH₄ associated with the production of N-fertilised wheat and barley. The automated chamber system provides high temporal-measurement resolution of GHG fluxes that can be readily related to changes in soil factors, particularly temperature and moisture. Chamber numbers, however, are restricted (in our case to 12), in turn restricting the number of treatments and/or replicates that can be monitored at any one time. On the other hand, manual chambers deployed at a particular site or experiment need not be as restricted in number and may therefore prove useful in assessing potential emissions-reducing management options.

Materials and methods

Five field-plot experiments were conducted in the winter cropping seasons of 2010 and 2011. Expts 1, 2 and 3 were at the Tamworth Agricultural Institute (31.152°S, 150.982°E) near Tamworth, NSW. Expt 4 (31.484°S, 150.177°E) and Expt 5 (31.171°S, 150.806°E) were on nearby commercial farms. All experiments were on neutral–alkaline Vertosols (Isbell 2002) of medium–heavy clay content.

Experiments 1 and 3: automated chambers in wheat (2010) and barley (2011)

The site for Expts 1 and 3 was described by Schwenke *et al.* (2015), along with field methods of soil and plant sampling, laboratory analysis, monitoring of soil–water content and environmental conditions, and data interpretation.

Plots were 12 m long and 6 m wide. The experimental crops were wheat (*Triticum aestivum* cv. Crusader) in 2010 and barley (*Hordeum vulgare* cv. Shepherd) in 2011. All plots were sown with a no-till planter at a row spacing of 0.25 m. Wheat was sown on 27 July 2010. The previous crop (2009) was chickpea (*Cicer arietinum*). Wheat plots were machine-harvested on 15 December 2010. Following the weed-free summer–autumn fallow, barley was sown on 27 June 2011 and it was harvested on 16 December 2011. Rates of applied N fertiliser were 0 or 80 kg N ha⁻¹ (wheat) and 0 or 60 kg N ha⁻¹ (barley). Rates were calculated as the projected crop N demand minus the pre-sowing soil mineral N supply as determined by soil-core testing to 1.5 m depth (Herridge 2011). Urea-N was side-banded at sowing at a 0.1-m offset to each plant row and a soil depth of 0.05–0.1 m. Weeds, insect pests and plant diseases were controlled chemically by using appropriate compounds at approved rates when necessary. The 2010 wheat and 2011 barley were grown within a larger crop rotation trial organised as a randomised complete block design with four replicates.

Fluxes of N₂O and CH₄ were measured in three of the four replicates. One chamber (0.5 m by 0.5 m by 0.15 m high) was deployed in each treatment of three replicate plots from July 2010 to June 2011 for wheat, and from June 2011 to July 2012 for barley. Chambers were secured to bases pushed 0.1 m into the soil. Each base covered two crop rows and two N-fertiliser bands. During crop growth, chambers were moved weekly to new locations within each plot to minimise the impact of the chamber on plant growth. Chamber height was increased with extensions so that the chamber covered the crops as they grew, to include N₂O emitted through plant transpiration (Chang *et al.* 1998). At maturity, plants growing within the chamber bases were hand-harvested, the grain was removed, and the plant residues were returned to the same base.

We used a 12-chamber automated gas-measuring system (Scheer *et al.* 2011) on four treatments within the larger rotation trial. Data from only two of the four treatments are presented in this paper. The automatically operated chambers in the first replicate were closed for 60 min, during which time four separate samples of air from the chamber headspace were collected at 15-min intervals. Samples were analysed immediately in an *in-situ* gas chromatograph (8610C; SRI Instruments, Torrance, CA, USA) fitted with an electron-capture detector for N₂O measurement and a flame-ionisation

detector for CH₄ measurement. After the closure period, the chambers in the first replicate opened and those in the second replicate closed for 60 min, followed by the chambers in the third replicate 60 min later. After 180 min, the cycle restarted, giving eight measurements per chamber per day.

The N₂O and CH₄ concentrations in the four air samples from each chamber during each closure period were regressed against closure time. For N₂O fluxes, we used the HMR routine, developed by Pedersen *et al.* (2010), which selects the most appropriate model for flux estimation based on the data from each measurement period. The routine first fitted a non-linear model to the data. Where this fit was not statistically significant, the linear model was then fitted. If neither model was statistically significant, a slope of zero was assigned. For CH₄ fluxes, we used linear regression, with a slope of zero assigned where $r^2 < 0.8$. The slope of the selected regression was used in the calculation of N₂O and CH₄ fluxes (Schwenke and Haigh 2016). Chamber temperature was measured by using a thermocouple probe in one chamber in each replicate set of four. Excessive heat (>55°C) within a chamber triggered a cessation of the current measurement and the chambers opened. Similarly, chambers opened and measurements were suspended when rainfall intensity exceeded 0.4 mm in 5 min. Altogether, ~25% of all possible measurement opportunities (eight per day) in Expts 1 and 3 were missed through heat, rainfall, equipment removal for planting or harvesting, or equipment servicing or breakdown. Cumulative N₂O and CH₄ emitted during the experiment were calculated by linear interpolation between daily average fluxes.

Aboveground plant and grain samples (two 0.5-m rows per plot) were collected before harvest by hand-cutting, then dried at 70°C for 48 h, weighed and analysed for total N concentration (%N) by combustion analysis (EA1112; Thermo Finnigan, San Jose, CA, USA). Grain protein was calculated by multiplying grain %N by a factor of 5.7. All results for grain yield and protein were standardised to a moisture content of 12% before treatments were compared. After harvest, all plant residue material from a plot was distributed evenly across that same plot.

Surface and subsurface samples (0–0.1 and 0.1–0.2 m) for soil mineral N (ammonium and nitrate) were collected in a cross-row transect of five 0.05-m-diameter cores per plot. For deeper samples (0.2–0.3, 0.3–0.6, 0.6–0.9, 0.9–1.2 and 1.2–1.5 m), two cores were collected per plot. Surface and subsurface samples were collected approximately monthly and deeper cores at pre-sowing and post-harvest. Soil bulk density was determined by the small-core volumetric-ring method (Cresswell and Hamilton 2002). Soil–water content was determined by gravimetric analysis at each time of soil sampling. Ammonium-N and nitrate-N in filtered (Whatman 42) soil extracts (2 M KCl) that were prepared on the day of sampling were determined by standard colourimetric analyses with a flow injection analyser (Lachat Instruments, Loveland, CO, USA). Soil moisture was also monitored by using a site-calibrated ThetaProbe ML2x soil moisture sensor (Delta-T Devices, Burwell, UK) at 0.05 m depth in the soil within each chamber.

Weather conditions measured at the site included ambient air temperature and relative humidity (Tinytag Plus 2: TGP-4500; Gemini Data Loggers, Chichester, UK), daily rainfall

(RainLogger; RainWise, Trenton, ME, USA), and soil temperature at 0.05 and 0.15 m depths (Tinytalk II; Gemini Data Loggers).

Experiment 2: manual chambers in wheat
(Tamworth, 2010)

Experiment 2 was adjacent to Expts 1 and 3. Plots were 12 m long and 2 m wide. Wheat (cv. Crusader) was sown on 27 July 2010. The experiment was part of a larger, randomised complete block experiment with four replicates. Results presented here are for 4-m-wide plots that grew chickpea in 2009 and were then divided in half lengthwise, with one half receiving N fertiliser in 2010 and the other half no N fertiliser. Emissions of N₂O and CH₄ were measured weekly on average (range 1–16 days between samplings) during the first 2 months, then every 12 days on average for the remainder of the year. Crop agronomy, and soil and plant sampling, were conducted as described for Expt 1. Manual measurements of GHG emission were described previously (Schwenke *et al.* 2015). The chambers were the same dimensions as the automated chambers used in Expt 1 and included plants. Chamber bases were inserted 0.1 m into the soil and remained in place throughout the experiment but chambers were removed after sampling. Upon chamber closure, 18-mL air samples were collected in pre-evacuated 12-mL glass Exetainer vials (Labco, UK) after 0, 30 and 60 min. All samples were later analysed using a laboratory gas chromatograph with detectors similar to those used in Expt 1.

Experiment 4: manual chambers in wheat
(Spring Ridge, 2011)

Wheat (cv. EGA Gregory) was sown on a Black Vertosol on 21 June 2011 and harvested on 5 December 2011. Plots were 9 m long and 1.5 m wide (5 rows at 0.3-m spacing). Nitrogen fertiliser treatments were: 0, 40, 80 and 160 kg N ha⁻¹ applied as urea side-banded at sowing; a split urea application (40 kg N ha⁻¹ at sowing + 40 kg N ha⁻¹ as broadcast urea at Z31, mid-tillering; Zadoks *et al.* 1974) and 80 kg N ha⁻¹ of DMPP (3,4-dimethylpyrazole-phosphate) coated urea (ENTECTM, Incitec-Pivot Fertilisers, Melbourne, Australia) at sowing. All treatments were replicated four times within a randomised block design.

Fluxes of N₂O and CH₄ were measured by using manual chambers on 14 occasions during crop growth. Chambers were 0.25-m-diameter PVC cylinders positioned centrally over the fertiliser band, then pushed into the ground to a depth of 0.1 m, leaving 0.2 m above the soil surface. At the time of sampling, a lid fitted with a rubber O-ring was placed on the top of each chamber. Several chambers were sampled immediately after fitting the lids to give an average ambient gas concentration that was used for that day's flux calculations. Using pre-evacuated, 12-mL glass Exetainer (Labco, Lampeter, UK) vials, we collected 20 mL chamber air through a rubber septum in the chamber lid at 0, 30 and 60 min post-closure. These samples were analysed as for Expt 2. Cumulative N₂O emitted during the experiment was calculated by multiplying the average daily flux rate of consecutive samples by the number of days between those consecutive sample collections. However, where consecutive samples were collected at more

than 3 days apart, the intervening daily fluxes were calculated by halving each previous day's flux. High-temporal resolution data from a previous auto chamber experiment at the site showed that this calculation avoided overestimating fluxes during extended dry periods after rainfall events and dry periods leading up to a wet period with high fluxes (Schwenke *et al.* 2015). Cumulative fluxes of CH₄ were calculated by linear interpolation between sampling days.

Daily rainfall was measured at the site using a tipping-bucket rain logger (RainWise). Soil was sampled to 1.5 m depth at eight locations across the trial area before sowing, then approximately monthly to 0.1 m in each plot during the crop's growth. Samples were processed and analysed for mineral N as in Expt 1. Biomass was measured at plant maturity (Z99) by collecting all aboveground plant matter in two 0.5-m lengths of row per plot. Cut samples were dried at 70°C for 48 h then weighed and analysed for %N as per Expts 1 and 3.

Experiment 5: manual chambers in barley
(Bithramere, 2011)

Barley (cv. Shepherd) was sown on a Red Vertosol on 9 June 2011 and harvested on 30 November 2011. Plots were 9 m long and 1.5 m wide (five rows at 0.3-m spacing). Nitrogen fertiliser treatments were 0, 30, 60 and 90 kg N ha⁻¹ applied as urea side-banded at sowing, a split urea application treatment (30 kg N ha⁻¹ at sowing + 30 kg N ha⁻¹ as broadcast urea at Z31, mid tillering), and 60 kg N ha⁻¹ of DMPP-coated urea at sowing. All treatments were replicated four times within a randomised block design.

Fluxes of N₂O and CH₄ were measured on 13 separate occasions during the crop growth as in Expt 4. Plant and soil samples were also collected and analysed as in Expt 4.

N₂O emission factors and emission intensity

Emission factors for N₂O were calculated by first subtracting the N₂O emitted from the non-N-fertilised crop from that emitted by the N-fertilised crop, then dividing the net amount by the fertiliser N applied. In Expts 1–3, this was calculated for the crop-only period (EF_{crop}, sowing–harvest) and for the full year after N fertiliser application (EF_{year}). In Expts 4 and 5, EF was calculated for the crop period only. The N₂O EI (g N₂O-N t⁻¹ grain) was calculated as the cumulative N₂O emitted over the measurement period, divided by the grain yield from the same plot.

Non-CO₂ GHG balance

Using the cumulative N₂O and CH₄ emission totals, an annual non-CO₂ GHG balance was calculated for each treatment in each trial as follows:

$$\begin{aligned} \text{Non-CO}_2 \text{ GHG balance (kg CO}_2\text{-e ha}^{-1}\text{year}^{-1}) \\ &= (298 \times \text{kg N}_2\text{O-N ha}^{-1}\text{year}^{-1} \times 44/28) \\ &+ (25 \times \text{kg CH}_4\text{-C ha}^{-1}\text{year}^{-1} \times 16/12) \end{aligned}$$

The conversion factors of 298 and 25 were used to convert N₂O and CH₄, respectively, to CO₂-e (Forster *et al.* 2007).

Statistical analyses

Statistical comparisons of treatment results were made using the REML with spatial analysis procedure in GENSTAT 16th edition (VSN International Ltd, Hemel Hempstead, UK).

Individual treatment means were tested for difference using the least significant difference (l.s.d.) test at a probability level of $P=0.05$. Possible correlations between daily gas fluxes and environmental factors (air temperature, soil

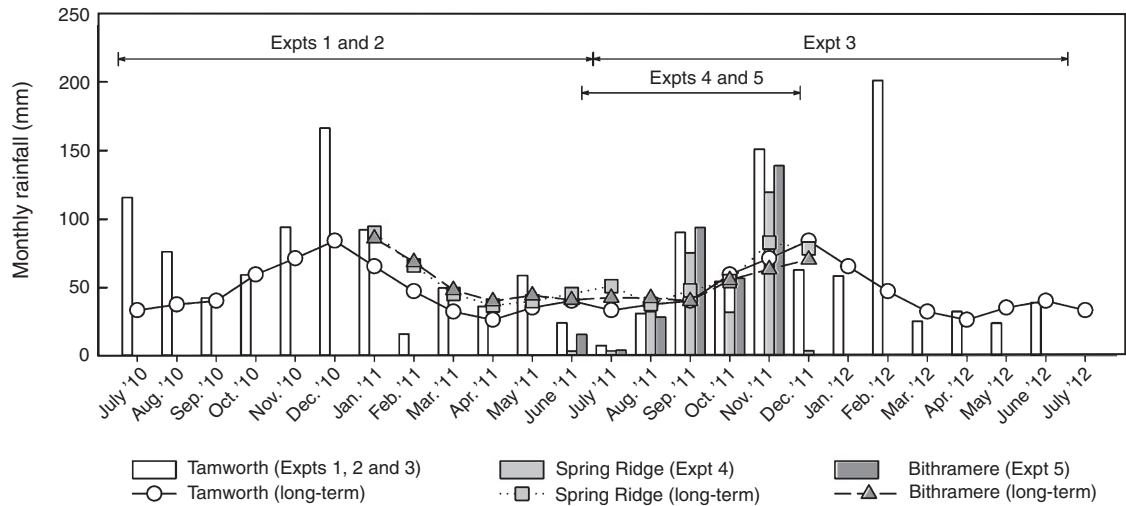


Fig. 1. Monthly rainfall at the five experimental sites (bars) and long-term monthly rainfall (symbols) from nearby recording stations. Totals for Expts 4 and 5 include only rainfall after sowing and before harvesting, not the entire month as in Expts 1–3.

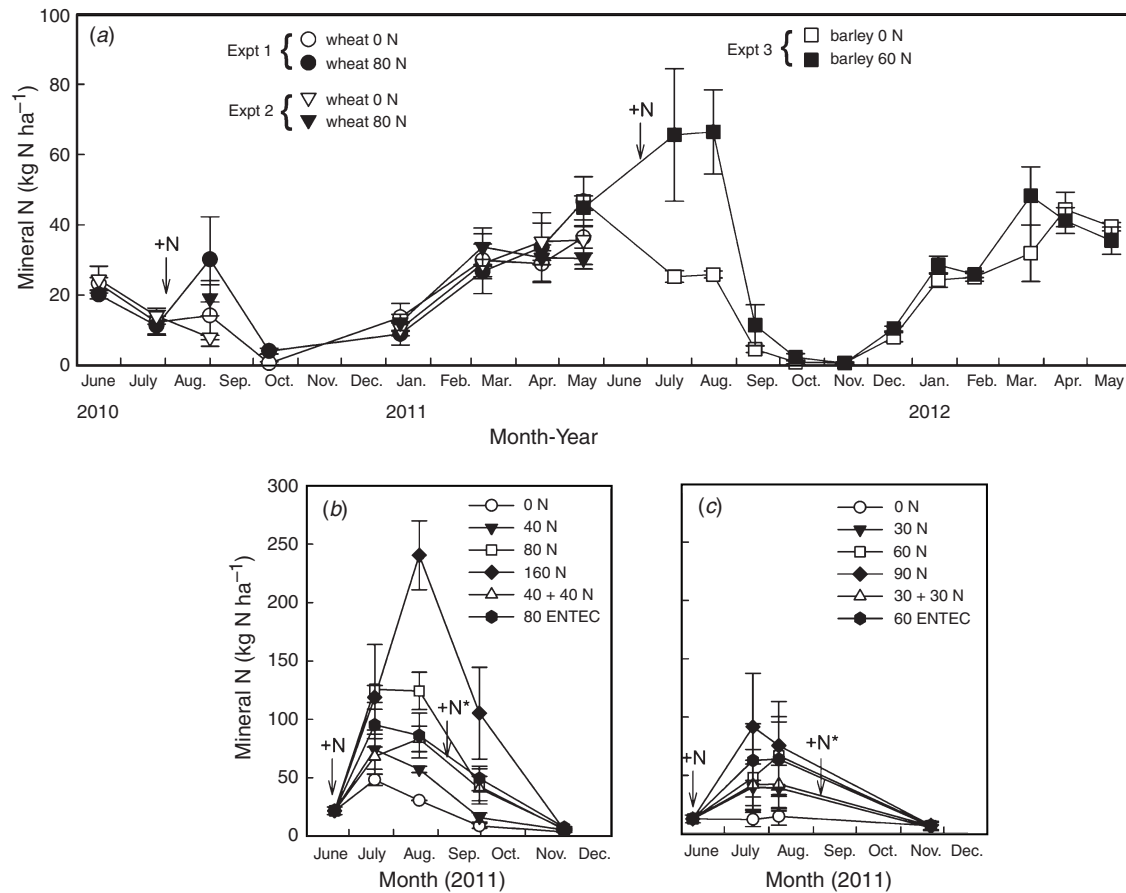


Fig. 2. Surface soil mineral N in (a) Expts 1–3 (0–0.2 m), (b) Expt 4 (0–0.1 m), and (c) Expt 5 (0–0.1 m). Treatments refer to kg N ha⁻¹ as standard urea applied at sowing or as a split application, or DMPP-coated urea (ENTEC) applied at sowing.

temperature at depths of 0.05 and 0.15 m, rainfall and WFPS) were investigated by using the multiple linear regression procedure in GENSTAT 16th edition.

Results

Rainfall

Monthly rainfall deviated considerably from long-term averages at the experimental sites (Fig. 1). At the Tamworth site, rainfall in the weeks preceding sowing of Expts 1 and 2 was three times the long-term July average for the site (93rd percentile), and continued at a high intensity into August (86th percentile). Rainfall throughout the remainder of the growing season was near normal until harvest in December when the monthly total was double the long-term average (94th percentile). By contrast, there was minimal rainfall before, during and for 2 months after the sowing of Expts 3, 4 and 5 in June–July 2011 (33rd and 16th percentiles). Only in September and November 2011 were the monthly rainfalls well above average (86th and 91st percentiles).

Total in-crop (sowing–harvest) rainfall was 476, 476, 380, 303 and 338 mm for Expts 1–5, respectively. However, much of the above-average rainfall recorded in November 2011 occurred just before harvest and thus did not benefit crop production; for example, 86 mm rainfall occurred in the final week before harvest at Expt 5. During the post-harvest fallow to the end of the 12-month emissions-measuring period, Expts 1 and 2 had an additional 315 mm rainfall, and Expt 3 an additional 400 mm.

Soil mineral N

Pre-sowing mineral N concentrations (0–1.5 m) were uniform across the sites used for Expts 1–3 (data not shown). Post-harvest sampling to 1.5 m depth showed no significant treatment effects on mineral N at any depth in the soil profile.

In all experiments, treatment effects of N fertiliser application on surface-soil mineral N (0–0.1 and 0–0.2 m) were evident for 1–3 months after application (Fig. 2), depending on the experimental conditions. In Expts 1 and 2 (Fig. 2a), soil mineral N in the surface declined between June and July 2010 as a result of the intense rainfall and waterlogging conditions between these sample times. Although sampling in late August 2010 showed significant treatment differences in soil mineral N, levels were much less than expected considering the amount of N applied; therefore, much of the applied N had been either lost or taken up by the crop. The next sampling in October found little remaining evidence of treatment effects. Following harvest in December 2010, soil mineral N increased in all treatments during the 6-month fallow period, with no effect of the N fertiliser application in July 2010.

Mineral N in the surface soil of Expt 3 (Fig. 2a) showed a large effect of fertiliser N throughout the dry period until September 2011, when rainfall and crop uptake reduced available N to nil by November 2011. Mineralisation of soil organic matter and crop residues rapidly replenished soil mineral N during the summer fallow, but no significant effects of the N fertiliser applied in June 2011 were detected post-harvest.

Surface soil mineral N in Expts 4 and 5 (Fig. 2b, c) showed effects of the fertiliser N applied at sowing throughout crop growth. However, treatment differences had disappeared by harvest. In Expt 4, the strategies of split N (40 + 40 kg N ha⁻¹) and DMPP-coated urea (80 kg N ha⁻¹) applications tended to reduce soil mineral N, particularly the ammonium component (not shown), in samples collected during July and August 2011 compared with the same rate of N added as urea at sowing (80 kg N ha⁻¹). These apparent trends were not statistically significant ($P > 0.05$). In September 2011, despite similar total mineral-N levels, the treatment with DMPP-coated urea had

Table 1. Crop N uptake, grain yield, grain protein and crop-residue N in Expts 1–3

Grain yield and protein data are presented from machine-harvest, and N-removal data from hand-harvests. For each parameter, comparisons are between nil-N and N-applied treatments within experiments: * $P < 0.05$; n.s., no significant difference ($P > 0.05$)

	Expt 1 wheat		Expt 2 wheat		Expt 3 barley	
	0	80	0	80	0	60
Crop N uptake (kg N ha ⁻¹)	136	147n.s	161	174n.s	75	106*
Grain yield (t ha ⁻¹)	3.1	3.0n.s.	3.2	3.0n.s.	3.7	3.8n.s. ^A
Grain protein (%)	13.5	14.1b*	13.7	13.9n.s.	10.6	13.2*
N removed in grain (kg N ha ⁻¹)	55	57n.s.	58	56n.s.	60	77*
Crop residue N (kg N ha ⁻¹)	54	66n.s.	53	74n.s.	16	29n.s.

^AA significant yield difference was found in hand-harvest results, with 0N = 3.6 t ha⁻¹ and 60N = 4.1 t ha⁻¹.

Table 2. Effects of rate of fertiliser N applied as urea on biomass, grain yield and grain protein of wheat in Expt 4

Within rows, means followed by the same letter are not significantly different ($P > 0.05$)

	N fertiliser rate (kg N ha ⁻¹)					
	0	40	80	160	40 + 40 split	80 DMPP-coated
Dry matter (Z99) (t ha ⁻¹)	11.2a	15.1b	15.4b	14.0b	15.3b	15.8b
Grain yield (t ha ⁻¹)	4.4a	5.3b	5.6c	5.2b	5.2b	5.3b
Grain protein (%)	10.5a	11.2b	11.9c	12.5d	12.0c	11.7c

Table 3. Effects of rate of fertiliser N applied as urea on biomass, grain yield and grain protein of barley in Expt 5
Within rows, means followed by the same letter are not significantly different ($P>0.05$)

	N fertiliser rate (kg N ha ⁻¹)					
	0	30	60	90	30+30 split	60 DMPP- coated
Dry matter (Z99) (t ha ⁻¹)	6.0a	7.6b	8.9b	9.9c	9.9c	9.2c
Grain yield (t ha ⁻¹)	2.8a	3.6ab	4.4bc	4.9c	4.8c	4.6c
Grain protein (%)	6.7a	8.0 ab	9.3bc	10.3c	8.7bc	10.1c

significantly more ammonium-N than the urea at sowing and the split N treatments, demonstrating its effectiveness in delaying nitrification. For Expt 5, there were no significant N treatment effects on soil mineral N at any sampling date.

Crop production, N uptake and grain yield

Nitrogen uptake by the wheat and barley in Expts 1 and 2 was not affected by N fertiliser, whereas in Expt 3, N fertiliser resulted in significantly higher crop N uptake (Table 1). Crop (aboveground) residue N was similarly unaffected by N fertiliser in Expts 1 and 2 but was higher with N application in Expt 3 (Table 1).

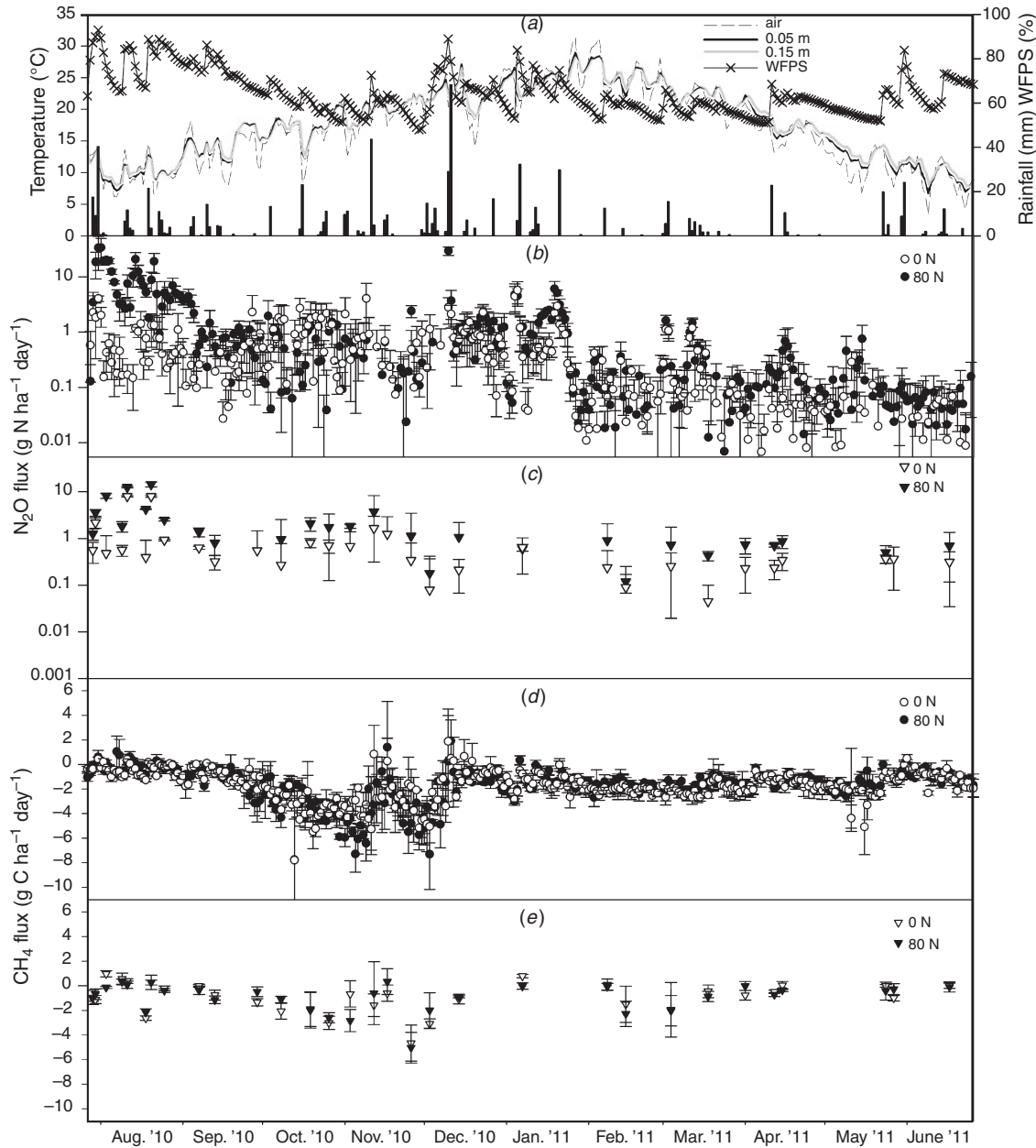


Fig. 3. Expts 1 and 2. Daily measurements of (a) rainfall, air and soil (0.05 and 0.15 m) temperatures, and water-filled pore space (WFPS); N₂O flux in (b) Expt 1 and (c) Expt 2; and CH₄ flux in (d) Expt 1 and (e) Expt 2. Data in (b)–(e) are mean daily results (\pm standard error) of the three treatment replicates. Treatments refer to kg N ha⁻¹.

In 2010, wheat grain yields were reduced because of late sowing caused by rain delays, waterlogging after sowing, a late frost coinciding with flowering, and rainfall during crop maturation (Table 1). These factors led to low harvest indices of 0.26 (Expt 1) and 0.22 (Expt 2). There was no significant effect of N fertiliser on grain yields in either experiment, but grain protein contents were high and, in Expt 1, were significantly increased with added N fertiliser.

Crop production in 2011 (Expt 3) was reduced by low available soil water at sowing and very dry conditions for the first 2 months post-sowing (Fig. 1). As a result, crop biomass was below that of 2010, although grain yields were similar across the two seasons (Table 1). The 2011 harvest index was 0.42. Fertiliser N addition in 2011 significantly increased yield in hand-harvested samples (although not in machine-harvested results), grain protein, and grain N removal (Table 1).

In Expts 4 and 5, mature crop biomass, grain yield and grain protein were increased by N fertiliser above the nil N treatment. In Expt 4, although all fertiliser N treatments produced similar biomass, 80 kg N ha⁻¹ applied at sowing produced the highest grain yield, higher than the treatments with split N or the DMPP-coated urea with the same amount of N applied (Table 2). All three 80 kg N ha⁻¹ strategies gave similar grain protein results, whereas the 160 kg N ha⁻¹ rate significantly increased grain protein. The treatments with split N application and DMPP-coated urea did not influence grain yield or grain protein in Expt 5 but did result in greater

mature biomass than the equivalent N rate all applied at sowing (Table 3).

Daily N₂O fluxes

In general, N₂O emissions were very low, interspersed with brief periods of higher emission activity after heavy rain fell on saturated soils with either freshly decomposing crop residue or recently added N fertiliser. Daily N₂O fluxes (g N₂O-N ha⁻¹ day⁻¹) averaged 1.0 in Expt 1 (range -1.7 to 33.5), 1.6 in Expt 2 (range -1.8 to 14.4), 0.6 in Expt 3 (range -1.0 to 33.0), 4.2 in Expt 4 (range -1.7 to 26.5), and 9.1 in Expt 5 (range -0.7 to 118.4).

Nitrous oxide fluxes in the first 2 months after N application were greater in the N-fertilised treatments of Expts 1 and 2 than in the corresponding nil-N treatments (Fig. 3*b, c*). Sowing and N fertiliser application on 27 July 2010 was followed by 68 mm rainfall over 3 days on an already-saturated soil, so soil WFPS remained >70% for much of the first 2 months post-sowing (Fig. 3*a*). From October 2010 onwards, the soil dried as the crop grew and N₂O emissions remained low, with no difference in daily N₂O flux between N-fertilised and non-fertilised treatments. In November and December 2010, isolated heavy rainfall events temporarily increased WFPS and N₂O emission, but only for 1–2 days. Post-harvest N₂O emissions were very low, with daily fluxes only temporarily exceeding 1 g N₂O-N ha⁻¹ day⁻¹ following significant rainfall. Daily N₂O emissions

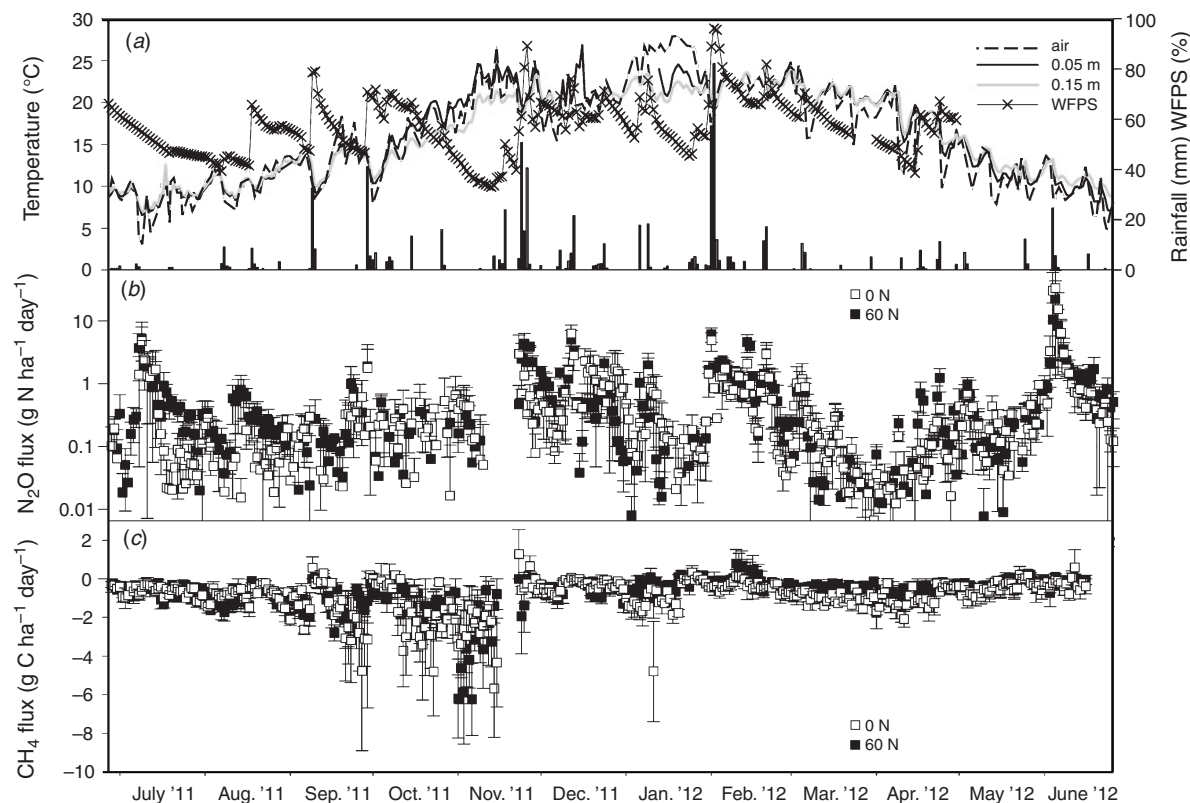


Fig. 4. Expt 3. Daily measurements of (a) rainfall, air and soil (0.05 and 0.15 m) temperatures, and water-filled pore space (WFPS); (b) N₂O flux (log scale); and (c) CH₄ flux. Data in (b) and (c) are mean daily results (\pm standard error) from three replicates of the two fertiliser-N treatments. Treatments refer to kg N ha⁻¹.

measured in Expt 2 were generally similar to those in Expt 1 (Fig. 3c).

During the June–December 2011 crop period of Expt 3, there were only 7 days when soil WFPS exceeded 70% (Fig. 4a). It was not until February 2012 that more than 3 consecutive days showed soil WFPS >70%. As a result, daily N_2O fluxes were low throughout the year of measurement, with only a single spike in daily N_2O flux $>10 \text{ g N}_2\text{O-N ha}^{-1} \text{ day}^{-1}$ during June 2012 (Fig. 4b). There was no measurable impact of N fertiliser addition on N_2O flux at any stage in Expt 3.

Daily N_2O fluxes in Expts 4 and 5 were low for the first half of the growing season (Fig. 5b, e) owing to dry conditions, with elevated emissions recorded only after heavy rainfall (28 mm for Expt 4, 45 mm for experiment 5; Fig. 5a, d) in the later stages of the experimental period. In Expt 4, rain in early September 2011 resulted in treatment differences in N_2O emissions. The 160 kg N ha^{-1} treatment produced significantly higher N_2O emissions than all other treatments for the remainder of the experiment. There were also two occasions in September when N_2O flux was significantly greater in the 80 kg N ha^{-1} treatment than the treatments with split N or DMPP-coated urea. In Expt 5, the large variation amongst replicates meant that there were no statistically significant differences between N

rate treatments on most sampling occasions. However, there was a consistent trend across sampling dates for N_2O fluxes in the order $90 \text{ kg N ha}^{-1} > 60 \text{ kg N ha}^{-1} > 30 \text{ kg N ha}^{-1} > \text{split N}$, $30 + 30 \text{ kg N ha}^{-1} > \text{DMPP-coated urea}$, 60 kg N ha^{-1} .

Daily CH_4 fluxes

Emissions of CH_4 were below the detection limit or negative across all experiments; therefore, for the majority of measurements there was a net uptake of atmospheric CH_4 . Daily CH_4 fluxes ($\text{g CH}_4\text{-C ha}^{-1} \text{ day}^{-1}$) averaged -1.7 in Expt 1 (range -7.8 to 1.9), -0.9 in Expt 2 (range -5.0 to 1.0), -0.8 in Expt 3 (range -6.2 to 1.3), -1.6 in Expt 4 (range -4.7 to 1.9), and -1.9 in Expt 5 (range -5.3 to 0.2).

Fluxes of CH_4 in Expts 1, 2 and 3 became increasingly negative as the crop-growing season progressed and the soil became drier (Figs 3d, e and 4c). Significant rainfall events and high soil WFPS in November 2010 and September 2011 coincided with less negative or positive CH_4 fluxes. In both years of measurement, the CH_4 fluxes reverted to mostly negative again as the soil dried. Fluxes of CH_4 were more stable and generally less negative during the post-crop fallow than during the cropping period. Methane flux and WFPS were

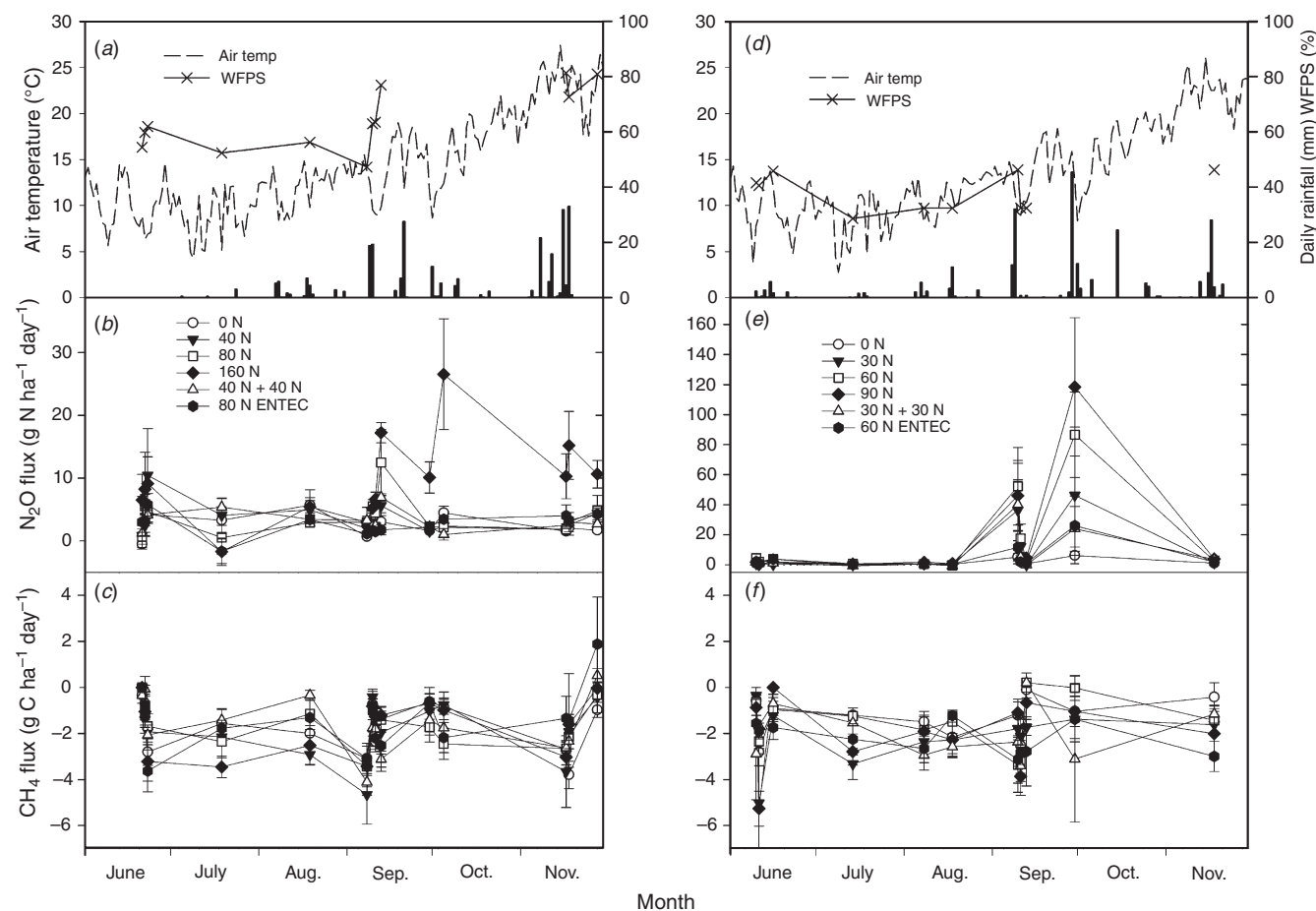


Fig. 5. Expts 4 (left, a–c) and 5 (right, d–f). Daily measurements of (a, d) rainfall, air temperature, and water-filled pore space (WFPS); (b, e) N_2O flux; and (c, f) CH_4 flux. Data in (b), (c), (e) and (f) are mean daily results (\pm standard error) of four replicates of six fertiliser-N treatments. Treatments refer to kg N ha^{-1} as standard urea applied at sowing or as a split application, or DMPP-coated urea (ENTEC) applied at sowing.

significantly positively correlated, with WFPS accounting for 33% of variation in CH₄ fluxes in Expt 1 ($P < 0.05$) and 23% in Expt 3 ($P < 0.05$). Addition of N fertiliser did not significantly affect CH₄ flux in Expts 1–3.

In Expts 4 and 5 (Fig. 5*c, f*), CH₄ flux appeared to be positively related to soil moisture, but incomplete sampling of soil moisture during these experiments meant that statistical correlations could not be calculated. There was no significant effect of N fertiliser rate or application strategy on CH₄ flux, except during one mid-September sampling in Expt 5. In that case, the treatment with DMPP-coated urea at 60 kg N ha⁻¹ had a significantly greater negative flux than treatments with 60 kg N ha⁻¹ or split N at 30 + 30 kg N ha⁻¹, both of which had slightly positive fluxes on the same date.

Cumulative N₂O emissions

Cumulative N₂O emissions for the year of measurement were significantly affected by N fertiliser application in Expts 1 and 2

(Fig. 6*a*) but not in Expt 3 (Fig. 6*b*). Most of the treatment effect in Expts 1 and 2 occurred during the first 2–3 months after N fertiliser application, with only sporadic additions to the cumulative total throughout the remainder of the measurement period.

For Expts 4 and 5, there was a clear trend for increasing cumulative N₂O emitted with increasing N rate (Figs 6*c, d* and 7*a, b*). DMPP-coated urea reduced N₂O emissions by 76% (Expt 4) and 65% (Expt 5) compared with treatments where the same rate of urea was applied (Fig. 7*a, b*). Similarly, the strategy of splitting N reduced N₂O emissions by 38% (Expt 4) and 51% (Expt 5) compared with treatments where the same rate of urea was applied all at sowing (Fig. 7*a, b*).

Cumulative CH₄ uptake

Most daily CH₄ fluxes were nil or negative, so the cumulative CH₄ emitted during the measurement periods was negative; that is, there was a net uptake of atmospheric methane by the

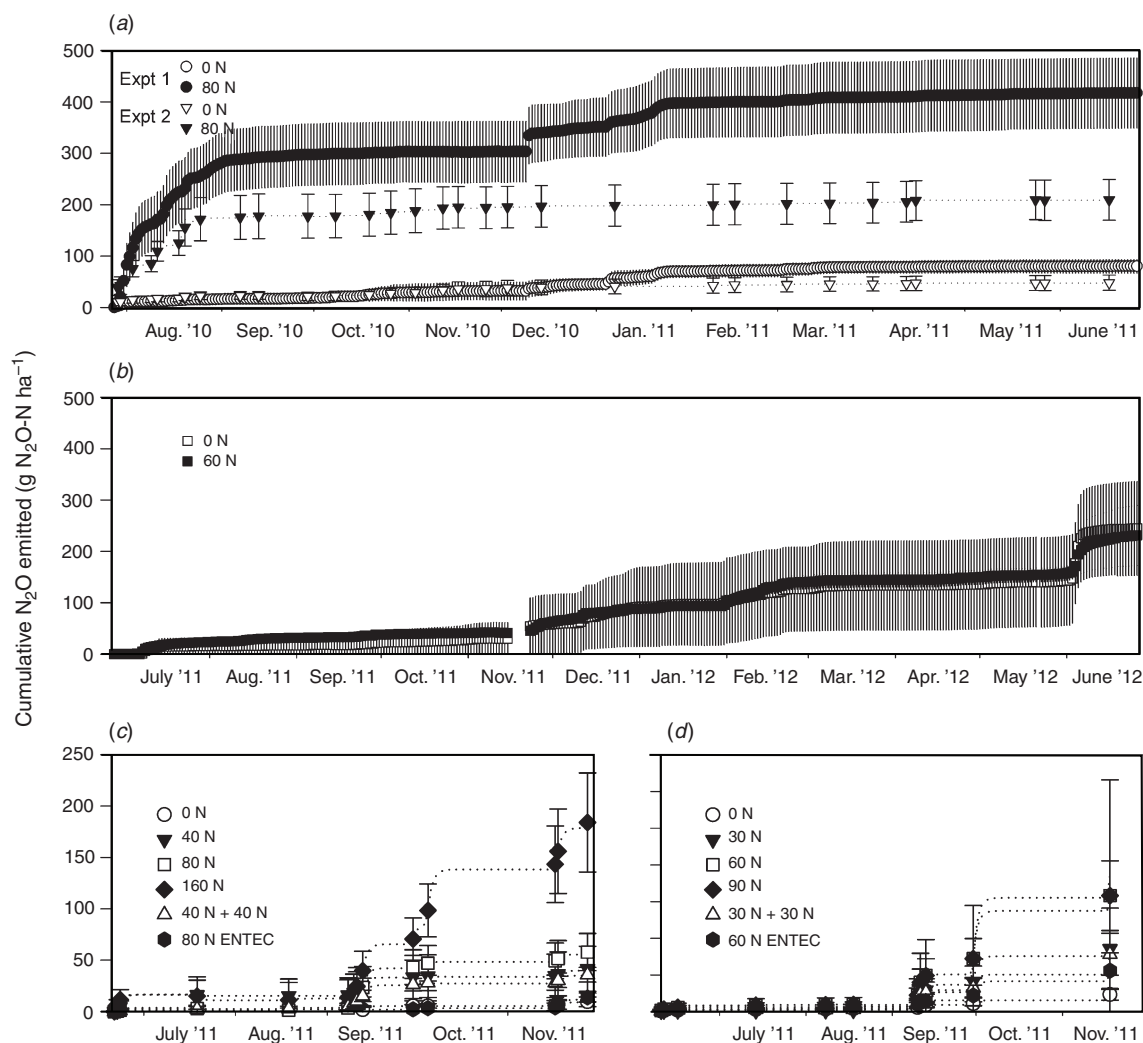


Fig. 6. Cumulative N₂O emitted in (a) Expts 1 and 2, (b) Expt 3, (c) Expt 4, and (d) Expt 5. Data are means (\pm standard error) of three (Expts 1–3) or four (Expts 4 and 5) replicates. Treatments refer to kg N ha⁻¹ as standard urea applied at sowing or as a split application, or DMPP-coated urea (ENTEC) applied at sowing.

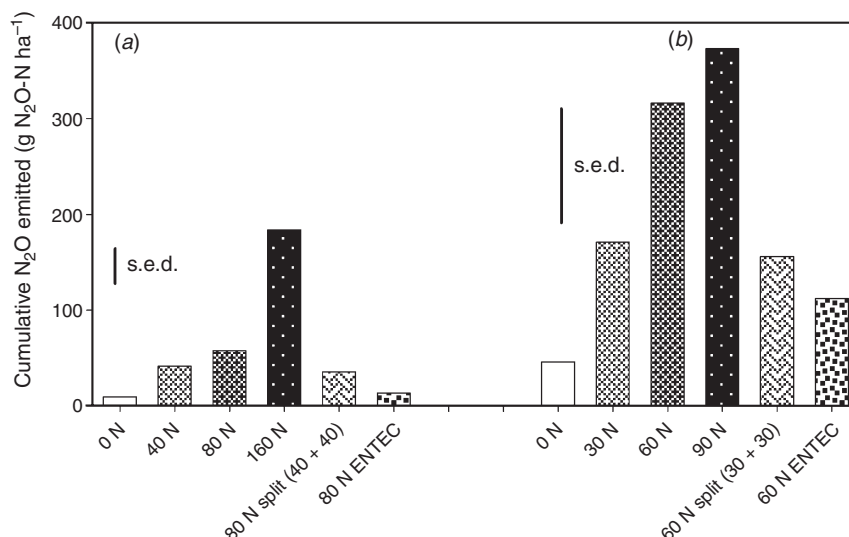


Fig. 7. Cumulative N₂O emitted in (a) Expt 4 and (b) Expt 5. Data are means of four replicates. $P < 0.001$ (Expt 4) and $P = 0.11$ (Expt 5). Standard error of difference (s.e.d.) shown for each experiment. Treatments refer to kg N ha⁻¹ as standard urea applied at sowing or as a split application, or DMPP-coated urea (ENTEC) applied at sowing.

soil in each experiment, with ranges of 242–435 g CH₄-C ha⁻¹ for Expts 1–3, and 181–366 g CH₄-C ha⁻¹ for Expts 4–5 (Fig. 8). There were no significant N fertiliser treatment effects on CH₄ uptake in any experiment.

N₂O emission factors

The similarity between EF_{crop} and EF_{year} in Expts 1 and 2 reflects the particular environmental conditions of these experiments, with N₂O emissions primarily occurring during early crop growth (Table 4). In Expt 4, the EF for the treatment with DMPP-coated urea at 80 kg N ha⁻¹ was significantly less than for the corresponding N rate of urea applied all at sowing (80 kg N ha⁻¹), whereas the EF for the treatment with split N (40 + 40 kg N ha⁻¹) was statistically between the these two treatments.

The EI values reflected significant effects of N fertiliser applications in Expts 1 and 4, with more N₂O emitted per t grain when N fertiliser was applied in Expt 1 because of the seasonal conditions. However, in Expt 4, the inefficiency of the highest N rate was demonstrated by a higher EI than all other treatments (Table 4). The treatments with DMPP-coated urea in both Expts 4 and 5 had lower EIs than the equivalent N rates with ordinary urea, although these differences were not statistically significant.

Non-CO₂ GHG balance

The non-CO₂ GHG balance for the crop period varied from 10 to 150 kg CO₂-e ha⁻¹ across Expts 1–3, and from 15 to 181 kg CO₂-e ha⁻¹ for the full year (Table 5). The influence of CH₄ uptake in offsetting N₂O emissions differed between experiments and treatments. In CO₂-e terms, CH₄ uptake offset 8–11% of the N₂O emitted from the 80 kg N ha⁻¹ treatment in Expts 1 and 2, and 39–56% of the N₂O from the nil N treatment. In Expt 3, fertiliser N addition did not

significantly affect the 9% of N₂O emissions offset by the CH₄ uptake.

Discussion

N₂O emissions in relation to rainfed grain production

Several studies have examined N₂O emissions from N-fertilised dryland wheat on cracking clay soils in Australia, with total yearly N₂O emissions ranging from 0.50 kg N₂O-N ha⁻¹ in western Victoria (Officer *et al.* 2008) to 0.90 kg N₂O-N ha⁻¹ in southern Queensland (Wang *et al.* 2011). By comparison, we measured 0.42 kg N₂O-N ha⁻¹ for N-fertilised wheat and 0.23 kg N₂O-N ha⁻¹ for N-fertilised barley. Our EF values for wheat (0.42% in Expt 1, 0.20% in Expt 2, 0.06% in Expt 4) and barley (–0.02% in Expt 3, 0.30% in Expt 5) were considerably lower than the 3-year average EF of 0.77% for no-till, stubble-retained wheat measured by Wang *et al.* (2011). However, they were generally higher than the 0.14% for N-fertilised, non-irrigated wheat in the study by Officer *et al.* (2008).

The dissimilarity in cumulative N₂O-N totals between Expts 1 and 2 is likely the result of differences in sampling frequency (Barton *et al.* 2015), with manual sampling occurring weekly on average during the first 2 months, and then every 12 days on average for the remainder of the year. Large but transient daily N₂O emission peaks occurring between sampling days in the first 2 months may therefore have been missed. Additionally, there may have been days when the flux at the designated time of sampling was not representative of the daily average flux rate. The high-frequency data from Expt 1 are the more robust measurement.

None of the experiments reported here experienced average rainfall in the first few months after sowing and N fertiliser application (Fig. 1). In 2010 (Expts 1 and 2), rainfall for several days after sowing resulted in conditions of high soil WFPS, which produced significant N₂O emissions from the

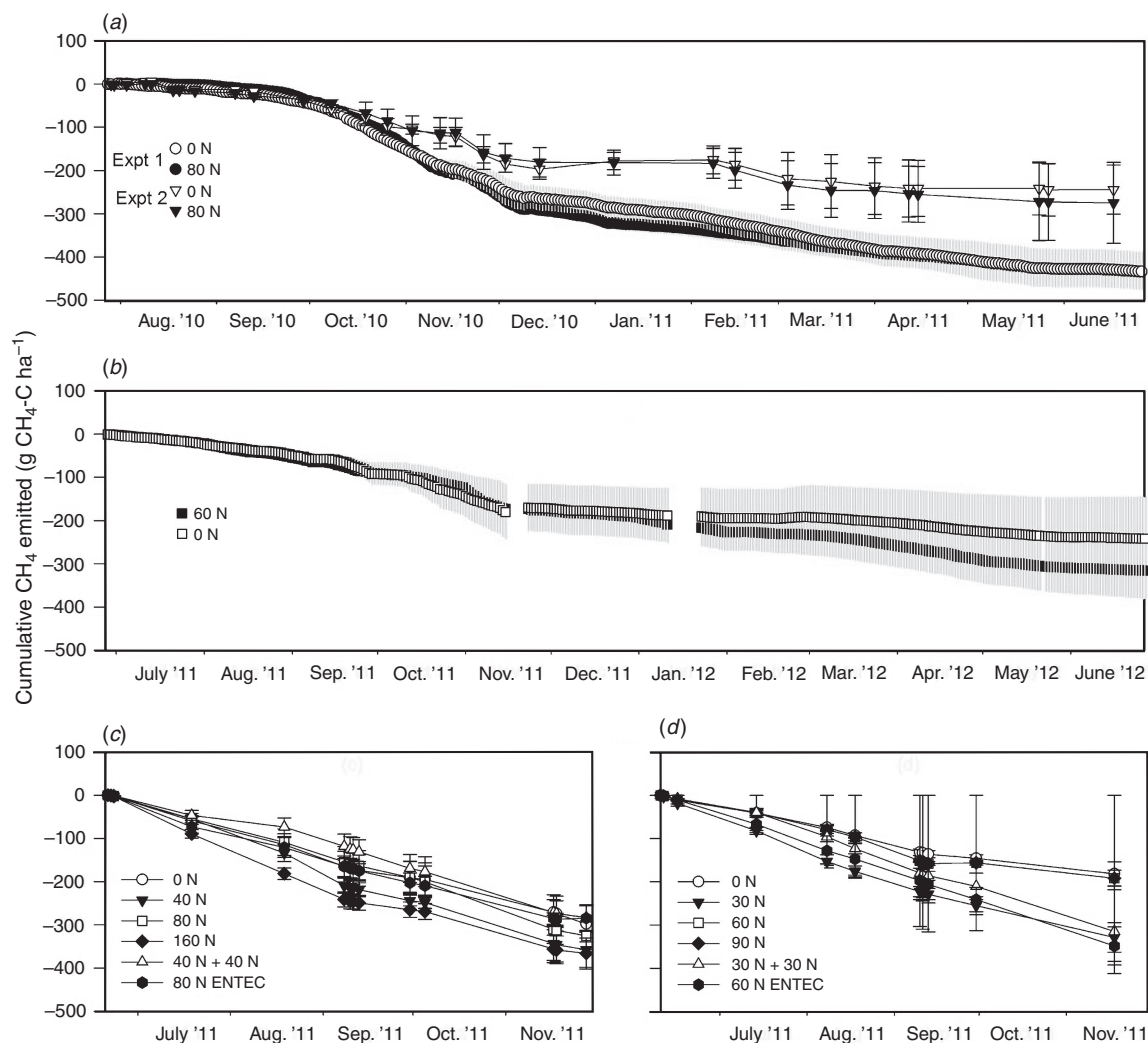


Fig. 8. Cumulative CH₄ emitted in (a) Expts 1 and 2, (b) Expt 3, (c) Expt 4, and (d) Expt 5. Data are means (\pm standard error) of three (Expts 1–3) or four (Expts 4 and 5) replicates. Treatments refer to kg N ha⁻¹ as standard urea applied at sowing or as a split application, or DMPP-coated urea (ENTEC) applied at sowing.

N-fertilised treatment. Soil sampling conducted 1 month after sowing found less mineral N in the soil than would be expected from the amount added in fertiliser, indicating substantial N loss from the surface soil through denitrification and nitrate leaching. Because the N-fertilised soil did not affect post-harvest N₂O emissions, the critical period for N₂O loss was the first 2–3 months after application of N fertiliser (Scheer *et al.* 2016).

By contrast, the N fertiliser applied at the 2011 sowing remained largely intact as soil mineral N for the next 2 months due to below-average moisture conditions (Fig. 1). Resumption of average, though not intense, rainfall during September led to rapid plant uptake of the soil mineral N (Fig. 2). Above-average rainfall in November temporarily increased N₂O emissions but by then soil nitrate concentration was low (Fig. 2a), so N₂O losses were small. As in 2010, there was minimal mineral N remaining post-harvest and no N-fertiliser treatment effect on crop residue N to cause any lasting treatment effects on post-harvest N₂O emissions. Therefore, the risk of early N₂O loss

after fertiliser N application was not realised in 2011 because of the dry conditions. Consequently, the measured EF was effectively nil.

Clearly, N₂O emissions associated with fertiliser N applications for a particular site will very much depend on the seasonal rainfall conditions. Predicting emissions by using readily available information such as soil texture, rainfall and temperature profile will produce more accurate inventory results. In the meantime, the currently prescribed EF of 0.2% appears reasonable (Shcherbak and Grace 2014; Commonwealth of Australia 2015a).

N₂O mitigation options for rainfed cereal cropping

Application of N fertiliser in excess of crop requirements can lead to exponentially increased N₂O emissions, as seen in Expts 4 and 5, and in many international studies (Scherbak *et al.* 2014). Even at optimum rates, emissions can still be substantial, so alternative strategies for N application need to be considered.

Table 4. N₂O emissions factor (EF, %) and N₂O emissions intensity (EI, g N₂O-N t⁻¹ grain) for each experiment

EF_{crop}, N₂O emitted during crop growth divided by N added as urea × 100; EF_{year}, N₂O emitted in the year since N addition divided by N added as urea × 100; EI_{crop}, N₂O emitted during crop growth divided by grain produced. *P*-values for comparison between treatments within experiments and standard errors of difference (s.e.d.) are also presented

	N fertiliser (urea) (kg N ha ⁻¹)	EF _{crop}	EF _{year}	EI _{crop}
<i>Expt 1</i>				
2010–11	0	–	–	13
	80	0.38	0.42	115
<i>P</i>				0.00
s.e.d.				13
<i>Expt 2</i>				
2010–11	0	–	–	12
	80	0.20	0.20	66
<i>P</i>				0.08
s.e.d.				16
<i>Expt 3</i>				
2011–12	0	–	–	21
	60	0.01	–0.02	20
<i>P</i>				0.88
s.e.d.				14
<i>Expt 4</i>				
2011	0	–	–	2
	40	0.08	–	8
	80	0.06	–	10
	160	0.11	–	35
	40+40 split	0.03	–	7
	80 DMPP-coated	0.01	–	3
<i>P</i>		0.20		0.01
s.e.d.		0.04		6.6
<i>Expt 5</i>				
2011	0	–	–	17
	30	0.42	–	53
	60	0.45	–	95
	90	0.36	–	98
	30+30 split	0.18	–	40
	60 DMPP-coated	0.11	–	29
<i>P</i>		0.64		0.17
s.e.d.		0.28		36

Results from Expts 1 and 2 and from a study of N-fertilised canola at the same site (Schwenke *et al.* 2015) indicated that application of fertiliser N at sowing led to significantly higher N₂O emissions for up to several months before crop growth depleted the pool of soil mineral N derived from fertiliser. Expts 4 and 5 explored two potential strategies to reduce this pool of soil mineral N. The strategies were (i) splitting the optimal N fertiliser 50:50 between application at sowing and topdressing at mid-tillering, and (ii) applying DMPP-coated urea at sowing at the optimal N fertiliser rate. These experiments coincided with abnormally dry conditions in 2011 where denitrification or leaching losses were minimal during the critical post-sowing period, so the full potential of these strategies could not be assessed within this study.

Cereal N uptake typically proceeds very slowly until tillering begins, and then increases rapidly to a maximum N

uptake rate during the jointing stage. Therefore, it is logical to delay some or all of the N fertiliser application until late tillering. Splitting the N application for cereal production has been found to increase grain yield, grain protein and fertiliser N recovery in many studies (IAEA 2000). Split N application is practised in many cereal-growing regions worldwide; however, it is rare in the study region. This is because <20% of the annual rainfall (600–800 mm) occurs in winter, winter rainfall events are highly variable with coefficients of variation of 46–80% (Webb *et al.* 1997), and forecast rain fronts during winter may not eventuate into sufficient rainfall for the crop to utilise the applied N (Doyle and Shapland 1991; Herridge 2011). Other studies of effects of split N application on N₂O emissions have shown mixed results, depending on the timing of significant rainfall events in relation to N application (Weier 1999; Burton *et al.* 2008; Venterea and Coulter 2015), or the total N rate applied (Allen *et al.* 2008; Zebarth *et al.* 2008). Expts 4 and 5 in this study showed apparent reductions in emissions of 38–51% compared with a single N application at sowing, although grain yield was also reduced in Expt 4. Further field research is needed into the impacts of split N application on N₂O emissions from rainfed cereal crops in Australia.

The application of DMPP-coated urea fertiliser (ENTEC) at sowing to delay nitrification has been reported in several cropping experiments (Weiske *et al.* 2001; Liu *et al.* 2013; De Antoni Migliorati *et al.* 2014; Scheer *et al.* 2014; Scheer *et al.* 2016). All studies showed that this treatment significantly reduced nitrate production from fertiliser and consequently reduced seasonal N₂O emissions by 38–75% compared with standard urea, with deviations in effectiveness linked to soil moisture and temperature conditions (Chen *et al.* 2010; Menéndez *et al.* 2012). In our study, DMPP-coated urea reduced cumulative N₂O emissions in Expts 4 and 5 by 65–75% compared with standard urea when both were applied at the same N rate at sowing. Our soil mineral N and N₂O results also indicated good potential for these strategies to influence the outcome in a wetter season, but the 2011 season did not see waterlogging that would have caused potentially yield-reducing soil N loss through denitrification. Further field research is needed to quantify the impact of nitrification inhibition as a practical mitigation option in unusually wet cropping seasons.

CH₄ uptake associated with rainfed grain production

Methane uptake rather than emission dominated CH₄ fluxes in this study, with the rate of uptake negatively correlated with soil moisture; that is, dry soil absorbed more CH₄. Daily CH₄ fluxes were within the ranges for CH₄ emission and uptake recorded for other Australian rainfed grain-cropping experiments (Barton *et al.* 2010, 2013; Wang *et al.* 2011). The annual cumulative CH₄-C uptake in this study ranged from 242 to 435 g CH₄-C ha⁻¹ year⁻¹ (Table 5), which was comparable to the 301–539 g CH₄-C ha⁻¹ year⁻¹ uptake measured in a semi-arid sandy soil (Barton *et al.* 2013). However, other Australian grain-cropping studies have reported either no net CH₄ uptake (Barton *et al.* 2010), or net CH₄ emissions of 75–150 g CH₄-C ha⁻¹ year⁻¹ (Wang *et al.* 2011).

There is evidence in the literature for the inhibition of soil CH₄ uptake by applied N fertiliser (Dalal *et al.* 2008),

Table 5. Cumulative N₂O, CH₄ and non-CO₂ greenhouse gas (GHG) balance for crop and full-year periods in Expts 1–3

Values are presented as N₂O, CH₄ or CO₂ equivalents (CO₂-e) per ha. *P*-values for comparison between treatments within experiments and standard errors of difference (s.e.d.) are also presented

N rate (kg ha ⁻¹)	Cumulative N ₂ O		Crop period Cumulative CH ₄		Non-CO ₂ GHG (kg CO ₂ -e)	Crop period + post-crop fallow				Non-CO ₂ GHG (kg CO ₂ -e)
	(g N ₂ O-N)	(kg CO ₂ -e)	(g CH ₄ -C)	(kg CO ₂ -e)		Cumulative N ₂ O (g N ₂ O-N)	Cumulative N ₂ O (kg CO ₂ -e)	Cumulative CH ₄ (g CH ₄ -C)	Cumulative CH ₄ (kg CO ₂ -e)	
Expt 1										
0	39	18	-266	-9	10	80	38	-434	-15	23
80	340	159	-292	-10	150	417	196	-435	-15	181
<i>P</i>	0.00	0.00	0.72	0.72	0.00	0.00	0.00	0.52	0.52	0.00
s.e.d.	40	19	31	1.0	19	51	24	47	1.6	25
Expt 2										
0	39	18	-181	-6	12	48	23	-244	-8	15
80	197	92	-197	-7	86	210	98	-275	-9	90
<i>P</i>	0.13	0.13	0.77	0.77	0.12	0.12	0.12	0.84	0.84	0.15
s.e.d.	62	29	49	1.6	28	62	29	132	4.4	33
Expt 3										
0	73	34	-178	-6	28	247	115	-242	-8	107
60	80	38	-184	-6	32	232	109	-316	-11	98
<i>P</i>	0.96	0.96	0.88	0.88	0.96	0.94	0.94	0.76	0.76	0.93
s.e.d.	50	23	48	1.6	22	115	54	101	3.4	52

but we found no such effects in our experiments. Likewise, Wang *et al.* (2011), with a similar soil type (Black Vertosol) and subtropical climate, also found no effect of long-term (38-year) N fertiliser addition on CH₄ fluxes during 3 years of continuous monitoring. In Expt 5, one sampling period indicated enhanced CH₄ uptake from soils fertilised with DMPP-coated urea compared with soils fertilised with standard urea at the same N rate. Weiske *et al.* (2001) found that DMPP-coated ammonium sulfate nitrate stimulated annual soil CH₄ uptake by an average of 28% during a 3-year study in Germany, with the treatment differences in 2 years lasting for several months after fertiliser application. Given the consistent and significant overall trend for soil CH₄ uptake observed in this study, further field or laboratory studies should be targeted to isolate the effects of potentially influencing factors such as N fertiliser rate, weed management (herbicides, tillage operations), fertiliser type, and fertiliser inhibitors.

Net non-CO₂ GHG emissions

Rainfed grain-cropping systems have mostly been evaluated for their impacts on N₂O emissions, with CH₄ and CO₂ fluxes not always measured or reported. Barton *et al.* (2013) found that cumulative CH₄ uptake increased with lime application in a wheat–wheat rotation, but they did not offset this against N₂O emitted from the same treatments and did not report CO₂ fluxes. Cumulatively, the beneficial effects of CH₄ uptake by the soils in this study offset the environmentally harmful effects of the N₂O emitted by 9–56%, with proportionally greater offsets occurring in the non-N fertilised plots that had lower N₂O emissions. Wang *et al.* (2011) found no treatment effects on CH₄ flux and no clear trends towards either net CH₄ emission or consumption, but they did include the CH₄ flux data in a net GHG evaluation of their experimental treatments.

The net soil CO₂ flux associated with cropping can also be considered when conducting a net GHG evaluation of

soil–plant management options. However, the chambers used in this study necessarily included growing plants (to capture N₂O emitted in transpiration); therefore, CO₂ flux measured in the chambers was a product of plant photosynthesis and plant–soil respiration. Although these data can be indicative of soil microbial activity (Barton *et al.* 2010), the inclusion of plant respiration precludes it from use in GHG balance calculations, as does the difficulty in accounting for the C added back into the soil as plant residues and exudates.

An alternative means of including CO₂ flux in a net GHG balance is to use an indirect estimate derived from long-term changes in soil organic C (SOC) stocks. For example, Wang *et al.* (2011) used 40 years of SOC data to calculate the net annual CO₂ fluxes from continuous wheat production on a subtropical Black Vertosol. They found a near-neutral response (9 ± 196 kg CO₂-e ha⁻¹ year⁻¹) in plots of continuous wheat under no-till, stubble-retained and N-fertilised conditions, compared with 284 ± 75 kg CO₂-e ha⁻¹ year⁻¹ lost by the same system with no N fertiliser. Such a difference potentially outweighs the negative impacts of N₂O emissions from N-fertiliser use when calculating the net GHG balance. We have not used CO₂ fluxes in our calculations because comparative CO₂ flux data do not exist for the no-till, stubble-retained, grain-legume–N-fertilised cereal cropping systems studied here. However, nearby long-term studies have found that SOC was stable over time in a cultivated, grain-legume–nil-N wheat rotation (Blair and Crocker 2000; Blair *et al.* 2006) after an initial decline (Holford *et al.* 1998), and potentially increasing in N-fertilised cereal–legume rotations with no-till and stubble retention (Young *et al.* 2005).

Conclusions

For a winter cereal crop, the critical period to target for strategic mitigation of N₂O emissions is between application of the N fertiliser at sowing and the period of rapid N uptake by the

growing crop after the onset of tillering. Although this risk period is present each year, actual N₂O losses are realised only when rainfall intensity raises soil WFPS and denitrification activity increases. Possible management options to reduce N₂O losses need further field investigation, with split applications of fertiliser N and urea coated with a nitrification inhibitor (DMPP) showing promise. The cereal crops studied here showed no post-harvest carry-over of the N applied at sowing; therefore, mineralisation of N-fertilised crop residues is unlikely to create further risk of N₂O losses, as was the case with N-rich legumes and canola (Schwenke *et al.* 2015).

Methane uptake in this production system was largely unaffected by N-fertiliser use or application strategy, but was found to vary in response to soil WFPS. Although the uptake of CH₄ by soil benefits the overall GHG balance for a cropping paddock, its contribution relative to N₂O emissions is generally small in an N-fertilised situation. However, where N₂O emissions are low in drier cropping seasons, CH₄ uptake can almost completely offset the negative environmental effects of N₂O emitted during a dryland cereal crop.

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