

Contribution of the cotton irrigation network to farm nitrous oxide emissions

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Abstract. Nitrous oxide (N₂O) is a potent greenhouse gas, and agriculture is the dominant source of N₂O-N emissions. The Australian cotton industry requires high inputs of N to maintain high lint quality and yields; however, over-fertilisation with N is symptomatic of the industry. Up to 3.5% of N fertiliser applied is lost directly from cotton fields as N₂O gas. Excess N may also be lost via erosion, deep-drainage, leaching and runoff, and may subsequently form indirect N₂O emissions. The estimate by the Intergovernmental Panel on Climate Change (IPCC) suggests that 0.0025 kg N₂O-N is produced indirectly from groundwater and surface drainage for each kg N lost via runoff and leaching, although this estimate carries a large degree of uncertainty. This study is the first to address the lack of indirect N₂O emission data from irrigated cotton-farming systems. Indirect emissions were determined from total N concentrations in irrigation runoff by using the IPCC emission factor and from measurements of dissolved N₂O during the first four irrigations (October–December 2013). Total indirect N₂O emissions from the surface of the irrigation network over 3 months when estimated by the dissolved-N₂O method were 0.503 ± 0.339 kg ha⁻¹. By contrast, N₂O emissions estimated by the IPCC methodology were 0.843 ± 0.022 kg ha⁻¹ irrigation surface area. Over the same period of measurement, direct land-surface emissions were 1.44 kg N₂O-N ha⁻¹ field. Despite relatively high emissions per surface area, the irrigation network is only a minor component of the total farm area, and indirect emissions from the irrigation system contribute ~2.4–4% of the total N₂O emissions and <0.02% of the applied N fertiliser.

Additional keywords: furrow irrigation, N₂O emissions, nitrogen use efficiency (NUE), runoff.

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Introduction

In Australia, irrigated cotton is a high-yielding system that requires nitrogen (N) fertiliser inputs to maintain the quality and quantity of yields. Over-fertilisation with N does occur. Comparisons between the internal N-use efficiency (kg lint kg⁻¹ crop N uptake) from commercial crops and cotton grown under optimum N rates demonstrate that during 2009–12 the industry over-fertilised by ~49 kg N ha⁻¹ in 2011 (Rochester 2011) and 25 kg N ha⁻¹ in 2012 (Rochester 2012). Several growers over-fertilised by 80–90 kg N ha⁻¹ (Rochester *et al.* 2009; Rochester 2011, 2012). A consequence of the excess N is increased production of the greenhouse gas nitrous oxide (N₂O).

Nitrous oxide is a potent greenhouse gas with a 100-year warming potential 298 times that of carbon dioxide (Butterbach-Bahl *et al.* 2013). The N₂O molecule is produced as an intermediate compound from two main processes, nitrification and denitrification (Butterbach-Bahl *et al.* 2013). Rates of N₂O emission are controlled by various environmental factors including soil porosity, temperature, microbial community, pH and availability of mineral N e.g. (Eichner 1990; Bouwman 1994; Butterbach-Bahl *et al.* 2013). Emissions

of N₂O resulting from fertiliser use and manure management comprise 26–35% of total emissions (Syakila and Kroeze 2011), and increased applications of N fertiliser are positively related to direct N₂O emissions (Bouwman 1996; Hinton *et al.* 2015; Rochester 2003). For cotton, the relationship between N rate and N₂O emissions is exponential, with 1.1–3.5% N applied subsequently emitted as N₂O at N rates of 280–320 kg N ha⁻¹ (Grace *et al.* 2016).

Excess N may also be leached (Benjamin *et al.* 1998) or lost as runoff into the irrigation system (Mchugh *et al.* 2008). A study of furrow-irrigated cotton in Emerald, Queensland, Australia, with application of 250 kg N ha⁻¹, showed average N runoff to be 18.8 and 11.3 kg N ha⁻¹ for 2001–02 and 2002–03, respectively (Mchugh *et al.* 2008). In furrow-irrigated maize production systems in Iran, nitrate (NO₃⁻) runoff ranged from 26 to 70 N ha⁻¹ after application of 60 kg N ha⁻¹ (Ebrahimian *et al.* 2012). Nitrogen species lost via runoff may subsequently undergo denitrification to form N₂O in the water column or drain sediments.

Emissions of N₂O that occur as a result of the transformation of N species lost from the field (e.g. via volatilisation, runoff and leaching) or movement of dissolved N₂O from the field

are termed 'indirect N_2O emissions' (Reay *et al.* 2005; IPCC 2006). Indirect emissions are thought to be 29–67% of the magnitude of direct emissions (Reay *et al.* 2003; Syakila and Kroeze 2011; Outram and Hiscock 2012). Current estimates from the Intergovernmental Panel on Climate Change (IPCC) suggest that for each kg N lost via runoff or leaching, 0.0025 kg N_2O -N may be produced (emission factor, $\text{EF}_{5\text{g}} = 0.0025$) but the range of uncertainty is large at 0.0005 to 0.025 (IPCC 2006). Based on the NO_3 -N losses reported by Mchugh *et al.* (2008), we might estimate that ~ 0.028 – 0.047 kg N_2O -N ha^{-1} would be produced from furrow-irrigated cotton via indirect emissions. Harrison and Matson (2003) have shown with direct measurement that average emissions of 0.04 N_2O -N kg ha^{-1} day $^{-1}$ can occur within furrow-irrigated wheat production in Mexico.

Indirect N_2O emissions may be a significant component of the total N_2O emissions for Australian cotton systems. However, indirect N_2O fluxes from agriculture have not been measured in Australia. Current estimates for indirect emissions rely on the use of IPCC emission factors with high levels of uncertainty. The aims of this study are to quantify indirect N_2O losses and to compare indirect with direct N_2O emissions, in an Australian furrow-irrigated cotton-farming system.

Materials and methods

Site description and sampling regime

The research was conducted at the Australian Cotton Research Institute (ACRI) at Narrabri, NSW, Australia ($30^\circ 19' \text{S}$ $149^\circ 46' \text{E}$). ACRI is located at the geographic centre of cotton production in Australia. The soil at this site is a high shrink–swell medium grey clay overlying brown clay and is classified as a fine, thermic, montmorillonitic Typic Haplustert (Soil Survey Staff 2010). Cotton is grown at ACRI by using furrow irrigation, and on average, the irrigation network contains water 100 days each year. The irrigation network comprises storage ponds, supply channels, head (supply) and tail ditches for each field, furrows through the field, main tail drains and return channels (which return water to the storage ponds) (Fig. 1). Prior to the irrigation season, water is transferred from the river or groundwater source to supply channels, and then to head ditches. Water is then supplied to the irrigation furrows via siphon from the head ditches. Once the water has transited the field, it empties into the tail ditch and runs off into the main tail drains. The return channel takes the water back to a pump that lifts the water either into the storage ponds or back into the head ditch. The cycling of water around the irrigation network occurs within a 12-h period, and the return water is stored until required for a subsequent irrigation.

Water sampling and measurements were made at ACRI during the 2013–14 Australian cotton season. Samples were taken over 1-week periods in October, November and December 2013. These are the first 3 months of the season and they coincide with land preparation, sowing and fertilising; active growth phase and complete uptake of the fertiliser N by cotton crop; and the final crop irrigation. The blocks, field drains, channels and storage ponds throughout the irrigation network were sampled in triplicate on an *ad hoc* basis coinciding with the farm irrigation schedule for the sampling period (Fig. 1).

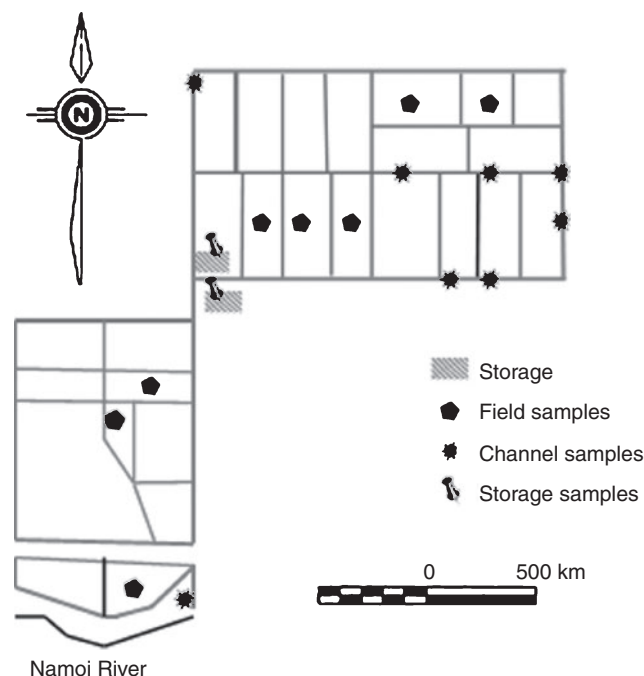


Fig. 1. Location of water samples taken throughout the cotton farm irrigation system of the Australian Cotton Research Institute, Myall Vale, NSW, during the first 3 months of the 2013–14 cotton season. Field water samples were collected at both the tail and head ditches of each field.

Dissolved nitrate, organic nitrogen and nitrous oxide in the irrigation network

Electrical conductivity (EC), pH and temperature of the water were measured *in situ* with a WP-81 field meter (TPS, Brendale, Qld). Samples were filtered ($0.45 \mu\text{m}$) and analysed for NO_3 -N, total ammonia N (TAN) and total dissolved N (DTN). Total N (TN) was determined on unfiltered samples; $\text{N} > 0.45 \mu\text{m}$ equates to $\text{TN} - \text{DTN}$. Nitrate-N and TAN were measured by the cadmium reduction method (Method 4500 Nitrate) and automated phenate method (Method 4500 Ammonia G), respectively (Rice *et al.* 2012). Samples of TN and DTN were digested by using the persulfate method (Method 4500-N) and the NO_3 -N concentration in the digest was measured using the cadmium reduction method (Rice *et al.* 2012). Dissolved organic N (DON) was determined by subtracting mineral N (NO_3 -N and TAN) from TDN. The calculated DON values, except for six samples (mean -0.2 , standard error 0.03) were always > 0 . After sampling, water samples were stored at 4°C , and analysed within 4–7 days of collection. The detection limit of the NO_3 -N and TAN analysis was 0.02 mg N L^{-1} .

Dissolved N_2O ($\text{N}_2\text{O-N}_\text{d}$) concentrations were determined by using the headspace equilibrium technique (Weiss and Price 1980; Roper *et al.* 2013). Briefly, during field sample collection, a 6-mL unfiltered water sample was injected into an evacuated 12-mL Exetainer (Labco, Lampeter, UK) and stored at 2 – 4°C , then returned and analysed in the laboratory within 4–7 days of collection. Harrison and Matson (2003) showed that after 12–48 h there is limited consumption or production of N_2O . However, at the longer storage times used in this study, some consumption or production of N_2O may have occurred

but it is expected to be limited because at temperatures $<4^{\circ}\text{C}$ denitrification is limited (Nowicki 1994). Prior to analysis, samples were allowed to warm to room temperature ($\sim 25^{\circ}\text{C}$) and 10 mL of helium was injected into each Exetainer. The N_2O concentration of the headspace was then measured with a GC-2014 fitted with an electron capture detector (Shimadzu, Kyoto, Japan). The temperature of the laboratory was recorded during sample analysis by an EL-USB-2 data logger (Lascar Electronics, Whiteparish, UK) and used to calculate the $\text{N}_2\text{O}-\text{N}_\text{d}$ concentration in the analysed water sample, using the approach of Weiss and Price (1980) and Roper *et al.* (2013).

Nitrous oxide emissions: direct (terrestrial cropping area) and indirect (irrigation network) emissions

To enable the comparison of the direct and indirect emissions, the report fluxes are relative to the source. Thus, the direct emissions are the function of area (ha) of land surface and the indirect emissions are in terms of area of irrigation network.

Direct (terrestrial cropping area) N_2O emissions

Direct (or terrestrial) N_2O emissions were calculated from the equation of Macdonald *et al.* (2015):

$$\text{N}_2\text{O}-\text{N} \text{ (kg N}_2\text{O ha}^{-1}\text{)} = 0.891 \times e^{(0.005x)} \quad (1)$$

where x is the fertiliser rate, and in this case the average rate was 200 kg N ha^{-1} .

Indirect (irrigation network) N_2O emissions

The N_2O flux from the irrigation network surface (13 ha) was calculated using (i) dissolved N_2O concentrations (Cole and Caraco 2001; Clough *et al.* 2007) and (ii) IPCC emission factors (IPCC 2006).

(i) *Dissolved N_2O method.* Indirect N_2O fluxes ($\text{N}_2\text{O}-\text{N}_\text{df}$) were estimated from $\text{N}_2\text{O}-\text{N}_\text{d}$ concentrations according to Eqn 2:

$$\begin{aligned} \text{N}_2\text{O}-\text{N}_\text{df} \text{ (}\mu\text{mol m}^{-2} \text{ day}^{-1}\text{)} \\ = k_{\text{total}} \times (\text{N}_2\text{O}-\text{N}_\text{d(water)} - \text{N}_2\text{O}-\text{N}_\text{d(eq)}) \end{aligned} \quad (2)$$

where $\text{N}_2\text{O}-\text{N}_\text{d(water)}$ ($\mu\text{mol m}^{-3}$) is the measured concentration of N_2O in the water, $\text{N}_2\text{O}-\text{N}_\text{d(eq)}$ ($\mu\text{mol m}^{-3}$) is the concentration the water would have if it were in equilibrium with the atmosphere N_2O concentration, and k is the gas transfer coefficient (m s^{-1}) (Cole and Caraco 2001; Clough *et al.* 2007).

The gas transfer coefficient, k_{total} , was calculated as the sum of the transfer velocities attributed to wind ($k_{\text{wind}} \text{ m s}^{-1}$) and water ($k_{\text{water}} \text{ m s}^{-1}$) speed, and these were calculated using Eqns 3 and 4 (Clough *et al.* 2007; Wanninkhof 1992):

$$k_{\text{wind}} = 0.31 u_{10}^2 \left(\frac{Sc}{660} \right)^{0.5} \quad (3)$$

$$k_{\text{water}} = \sqrt{\frac{DU}{h}} \quad (4)$$

where u_{10} (m s^{-1}) is the wind speed at 10 m above the height of the water body; Sc (dimensionless) is the Schmidt number for N_2O ; D ($\text{m}^2 \text{ s}^{-1}$) is the temperature- and salinity-dependent

diffusion coefficient of N_2O in water; U (m s^{-1}) is the velocity of water, which was measured using an OTT Flow Meter (OTT, Kempton, Germany); and h (m) is the average depth of the water body. Where water speed was unavailable, k_{wind} was used instead of k_{total} .

The wind speed at 10 m height was calculated from measured wind speeds (ACRI weather station) by using the logarithmic wind profile law (Eqn 5):

$$\frac{U_1}{U_2} = \ln\left(\frac{Z_1}{Z_2}\right) \div \ln\left(\frac{Z_2}{Z_0}\right) \quad (5)$$

where Z_0 is the 'effective roughness height', here assumed to be 0.001 m; and U_1 and U_2 (m s^{-1}) are the wind speeds at heights Z_1 and Z_2 , respectively (Kubik *et al.* 2011). Sc and D were calculated in R, using the package 'marelac', from measured water salinity and temperature and atmospheric pressure (R Development Core Team 2015; Soetaert *et al.* 2014).

The average daily $\text{N}_2\text{O}-\text{N}_\text{df}$ flux ($\text{kg N}_2\text{O}-\text{N m}^{-1} \text{ ha}^{-1}$) was calculated by using Eqn 2. During the irrigation season, the period for which the irrigation network contains tail water is ~ 15 days.

(ii) *IPCC EF_5 method.* The default IPCC emission factor for leaching and runoff (EF_5) of 0.0075 has three components: emission factors for groundwater and surface drainage ($\text{EF}_{5g}=0.0025$), rivers ($\text{EF}_{5r}=0.0025$) and estuaries ($\text{EF}_{5e}=0.0025$) (IPCC 2006). Given that water for cotton irrigation usually remains on site, the EF_{5g} was used to calculate the indirect emissions using Eqn 6:

$$\begin{aligned} \text{N}_2\text{O}-\text{N}_{\text{EF}5g} \text{ (kg N}_2\text{O}-\text{N ha}^{-1}\text{)} \\ = \overline{TN} \times v \times n \times \text{EF}_5 \div A \times B \end{aligned} \quad (6)$$

where \overline{TN} (mg L^{-1}) is the average concentration of TN in the tail and main tail drain water during each of the first four irrigations; v is the volume of water discharging into the field per irrigation (assumed to be $250\,000 \text{ L ha}^{-1}$, which is 25% efficiency of a 100-mm application); n is the number of irrigations within the month; and A is the surface area of the irrigation network (here 13 ha) and B the irrigation area (here 188 ha).

All indirect losses are reported on the water surface area and the direct emissions on the land surface area.

Data analyses

All analyses were performed in R (R Development Core Team 2015). Analyses of variance were used to examine influenced by location and sampling time on the measured parameters (EC, pH, TN, NO_3^- , and $\text{N}_2\text{O}-\text{N}_\text{d}$) using the model: water chemistry = location + sampling time.

Linear regression was used to determine (i) the relationship between N_2O concentration and the other water chemistry parameters, and (ii) the relationship between the two different methods used to calculate indirect N_2O emissions. Where data did not meet assumptions of equal variance, generalised least-squares procedures (in the 'nlme' package) were used as an alternative (Hay-Jahans 2011; Pinheiro *et al.* 2015).

Results

Water chemistry: EC, pH and nitrogen species in the irrigation network

There was a significant effect of location and month on the distribution of EC, pH, TN and NO₃-N of the water sampled (Tables 1–4). Values of EC, TN, NO₃-N, DTN and N > 0.45 µm all increased after the irrigation water transited the field. Conversely, the pH of the water decreased during the transit (Table 1). Throughout the season, the EC and concentrations of the different N species followed a similar pattern, with EC, TN,

NO₃-N, DTN and DON peaking during December (Table 2). The water chemistry of the tail water shows that the concentration of N in the DON fractions was often as large as the NO₃-N fraction (Tables 1 and 2). There was a positive correlation between EC and NO₃⁻ concentration of the discharge water ($P < 0.001$, $r^2 = 0.51$).

Dissolved N₂O-N concentration

The N₂O-N_d concentrations followed a similar pattern to that of the other N species with time of different sampling and

Table 1. Electrical conductivity (EC), pH, and concentrations of various nitrogen species and dissolved N₂O (mean ± standard error) in water samples collected at different locations throughout a cotton farm irrigation system at the Australian Cotton Research Institute, Myall Vale, NSW, during the 2013–14 cotton season

Parameters EC, pH, total N, NO₃-N, dissolved total N (DTN) and dissolved organic N (DON) showed significant differences between locations of sampling. No analysis was undertaken for NH₃

	EC (µS cm ⁻¹)	pH	Total N (mg L ⁻¹)	NO ₃ -N (mg L ⁻¹)	NH ₃ -N (µg L ⁻¹)	DTN	DON (mg L ⁻¹)	N > 0.45 µm	Dissolved N ₂ O-N (µg L ⁻¹)
Storage	622 ± 40.5 (n = 7)	8.67 ± 0.152 (n = 7)	4.82 ± 0.272 (n = 6)	2.42 ± 0.635 (n = 6)	–	4.19 ± 0.179 (n = 6)	2.39 ± 0.8 (n = 6)	0.625 ± 0.132 (n = 6)	0.73 ± 0.08 (n = 6)
Supply channel	479 ± 24.9 (n = 10)	8.74 ± 0.078 (n = 10)	1.15 ± 0.121 (n = 9)	0.895 ± 0.124 (n = 10)	–	1.12 ± 0.149 (n = 9)	0.373 ± 0.0821 (n = 9)	0.133 ± 0.0492 (n = 9)	0.395 ± 0.045 (n = 8)
Head	494 ± 19.9 (n = 17)	8.6 ± 0.041 (n = 17)	10.6 ± 4.14 (n = 16)	2.67 ± 1.02 (n = 16)	26.7 ± 13.6 (n = 13)	9.83 ± 4.43 (n = 13)	7.97 ± 3.8 (n = 16)	2.57 ± 0.881 (n = 16)	0.672 ± 0.095 (n = 16)
Tail	847 ± 94.9 (n = 22)	8.28 ± 0.0368 (n = 22)	30.4 ± 7.47 (n = 22)	14.9 ± 4.42 (n = 22)	40.1 ± 13.1 (n = 16)	28.3 ± 7.33 (n = 19)	15.6 ± 3.63 (n = 22)	5.85 ± 1.29 (n = 22)	2.15 ± 1.34 (n = 22)
Main tail drain	718 ± 20.8 (n = 3)	8.1 ± 0.04 (n = 3)	13.1 ± 0.251 (n = 2)	1.55 ± 0.0408 (n = 3)	–	–	11.5 ± 0.265 (n = 2)	12.5 ± 0.24 (n = 2)	2.07 ± 0.267 (n = 2)

Table 2. Electrical conductivity (EC), pH, and concentration of various nitrogen species and dissolved N₂O (mean ± standard error) in water samples collected at different sampling times across the cotton farm irrigation system at the Australian Cotton Research Institute, Myall Vale, NSW, during the 2013–14 cotton season

DTN, Dissolved total N; DON, dissolved organic N. All parameters showed significant differences between times of sampling, except NH₃-N for which no analysis was undertaken

	EC (µS cm ⁻¹)	pH	Total N (mg L ⁻¹)	NO ₃ -N (mg L ⁻¹)	NH ₃ -N (µg L ⁻¹)	DTN	DON (mg L ⁻¹)	N > 0.45 µm	Dissolved N ₂ O-N (µg L ⁻¹)
Oct. 13	656 ± 25.2 (n = 11)	8.32 ± 0.0881 (n = 11)	11.9 ± 1.56 (n = 8)	2.81 ± 0.593 (n = 10)	–	–	8.76 ± 1.39 (n = 8)	11.3 ± 1.48 (n = 8)	1.29 ± 0.183 (n = 8)
Nov. 13	546 ± 24.4 (n = 18)	8.73 ± 0.0647 (n = 18)	2.44 ± 0.423 (n = 18)	1.49 ± 0.3 (n = 18)	–	2.17 ± 0.359 (n = 18)	1.08 ± 0.347 (n = 18)	0.319 ± 0.0722 (n = 18)	0.556 ± 0.059 (n = 17)
Dec. 13	709 ± 78.9 (n = 30)	8.4 ± 0.04 (n = 30)	26.4 ± 6.17 (n = 29)	11.9 ± 3.53 (n = 29)	34.1 ± 9.36 (n = 29)	22.8 ± 5.3 (n = 29)	14.5 ± 3.39 (n = 29)	3.57 ± 0.867 (n = 29)	1.72 ± 1.02 (n = 29)

Table 3. Pair-wise comparisons, using Tukey's HSD, for water chemistry components between each of the irrigation network locations sampled at Australian Cotton Research Institute, Myall Vale, NSW

EC, Electrical conductivity; TN, total nitrogen; DTN, dissolved total N; DON, dissolved organic N; N45, N > 0.45 µm. Components shown are significantly different between each pair of locations. DTN measurements were not available for the main tail drain

	Storage	Supply channel	Head	Tail
Supply channel	TN, DTN, N45	–	–	–
Head	N45	N45	–	–
Tail	TN, DTN, DON, N45	EC, pH, TN, NO ₃ -N, DTN, DON, N45	pH, EC, N45	–
Main tail drain	TN, DON, N45	EC, pH, TN, NO ₃ -N, DON, N45	pH, EC, N45	N45

locations, but concentrations were highly variable. Differences in $\text{N}_2\text{O}-\text{N}_\text{d}$ concentration due to location were not significant (Tables 1 and 3) despite $\text{N}_2\text{O}-\text{N}_\text{d}$ concentrations tending to increase in the tail ditch and the main tail drain. Average concentrations of $\text{N}_2\text{O}-\text{N}_\text{d}$ ranged from $0.395 \pm 0.045 \mu\text{g L}^{-1}$ (supply channel) to $2.15 \pm 1.34 \mu\text{g L}^{-1}$ (tail drain) in the irrigation network for the 3 months of measurement.

Indirect N_2O emissions

Dissolved N_2O method. The cumulative $\text{N}_2\text{O}-\text{N}$ loss from the irrigation water surface during the first four irrigations between October and December 2013 was $0.503 \pm 0.338 \text{ kg ha}^{-1}$ (Table 5).

IPCC EF_5 method. Average total N concentrations for water sourced from tail ditches and main tail drains over the four irrigations was $28.96 \pm 6.903 \text{ mg L}^{-1}$. This corresponded to a cumulative $\text{N}_2\text{O}-\text{N}$ emission of $0.843 \pm 0.022 \text{ kg ha}^{-1}$ from the irrigation water surface, representing a field leaching loss of $23.31 \pm 0.61 \text{ kg N ha}^{-1}$ during the first four irrigations between October and December 2013 (Table 5).

There was a strong, positive linear relationship between monthly N_2O fluxes calculated by using the IPCC EF_5 and dissolved N_2O methods ($P < 0.05$, $R^2 = 0.99$). However, the disparity between the two methods increased with higher N_2O emissions, and total N_2O emissions estimated using the IPCC method were 46% higher than under the dissolved method.

Land-surface direct $\text{N}_2\text{O}-\text{N}$ emissions

During the cotton season, direct emissions of $\text{N}_2\text{O}-\text{N}$ from the land surface were, on average, $16 \text{ g N}_2\text{O}-\text{N ha}^{-1} \text{ day}^{-1}$ (Macdonald *et al.* 2015). The cumulative direct $\text{N}_2\text{O}-\text{N}$

Table 4. Pair-wise comparisons, using Tukey HSD, for water chemistry components between each of the different sampling times at Australian Cotton Research Institute, Myall Vale, NSW

EC, Electrical conductivity; TN, total nitrogen; DTN, dissolved total N; DON, dissolved organic N; N45, $\text{N} > 0.45 \mu\text{m}$. Components shown are significantly different between each pair of sampling times. DTN measurements were available only for November 2013 and December 2013 sampling events

	Oct. 13	Nov. 13
Nov. 13	EC, pH, TN, DON, N45, N_2O	–
Dec. 13	TN, NO_3-N , N45	EC, pH, TN, NO_3-N , DTN, DON, N45

Table 5. Total indirect $\text{N}_2\text{O}-\text{N}$ emissions (kg ha^{-1} irrigation water surface, 13 ha) from Australian Cotton Research Institute, Myall Vale, NSW

Estimates based on average concentrations of total nitrogen and dissolved N_2O in runoff water in tail and main tail drains only (mean \pm standard error)

	Dissolved $\text{N}_2\text{O}-\text{N}$ flux	IPCC $\text{N}_2\text{O}-\text{N}$ flux
Oct. 2013	0.062 ± 0.034	0.130 ± 0.002
Nov. 2013	0.012 ± 0.009	0.014 ± 0.001
Dec. 2013	0.429 ± 0.337	0.699 ± 0.022
Cumulative N_2O emissions	0.503 ± 0.339	0.843 ± 0.022

emission off the entire cotton farm over the season (150 days) was $2.42 \text{ kg N}_2\text{O}-\text{N ha}^{-1}$. During the period of indirect measurements (90 days), the direct $\text{N}_2\text{O}-\text{N}$ emissions off the cotton farm were 1.45 kg ha^{-1} .

Discussion

Electrical conductivity, pH, dissolved nitrate and organic nitrogen in the irrigation network

The water chemistry of the irrigation water was modified during its transit through the cotton field (Table 1). Nitrate and DON were the main components of TN present in the irrigation water, and both N species were lost from the cotton field (Table 1). The measured NO_3-N concentrations are similar to those from studies within the Australian cotton industry (Mchugh *et al.* 2008; Weaver *et al.* 2013) and other irrigated cropping systems (Harrison *et al.* 2005). Salt and other nutrients accumulate as a result of evaporation from the furrow surface (Noborio *et al.* 1996) and are remobilised during the first flush at the beginning of an irrigation. Irrigated furrows were less saline than non-irrigated furrows, suggesting that movement of water from irrigated to skip furrows transits through the adjacent hill, removing salts and N, which are then lost via runoff (Fig. 2). The differences in the N concentrations between the sampling events (Table 2) are likely due to the mineralisation or organic N within the hill releasing ammonium and NO_3-N , which can be mobilised by the irrigation water.

Further, we observed significant variation in the water N concentration during irrigation and between irrigations. The soil physical and moisture characteristics also vary within each furrow and mound, and as a result, the irrigation water and dissolved N compounds will transit through the soil at different rates. It is evident from the measured concentrations that the flux of the DON pool must be as important as the NO_3-N in the measured furrow-irrigated system (Tables 1 and 2). The DON is being sourced from the mound as the water passes through from the irrigated furrow to the skip furrow. DON, like NO_3-N , can undergo transformation and conversion into $\text{N}_2\text{O}-\text{N}_\text{d}$ in the water column and on the sediment surfaces (Nevison 2000; Tiedje *et al.* 1982). All N species lost into the irrigation system can potentially undergo subsequent transformations to form $\text{N}_2\text{O}-\text{N}_\text{d}$ within the water column and drain sediments (Nevison 2000; Harrison and Matson 2003).

Dissolved $\text{N}_2\text{O}-\text{N}$

The $\text{N}_2\text{O}-\text{N}_\text{d}$ in irrigation water may be sourced from N_2O produced within the field, or from subsequent denitrification or nitrification reactions in the water column. Irrigated cotton fields provide optimal conditions for denitrification, including microbial available carbon, nitrate and anaerobic environment. The much lower $\text{N}_2\text{O}-\text{N}_\text{d}$ concentrations in our study than in other studies (Harrison *et al.* 2005; Outram and Hiscock 2012) are likely due to fields being irrigated when there is a 75-mm water deficit in the soil profile. At such water contents, the formation of N_2O in the surface soil would be negligible (Weier *et al.* 1993; Davidson *et al.* 2000), and the measured terrestrial atmospheric flux rates in cotton systems at these soil moistures are small relative to those after emissions that occur when irrigation has ceased (Mahmood *et al.* 2008; Scheer *et al.*

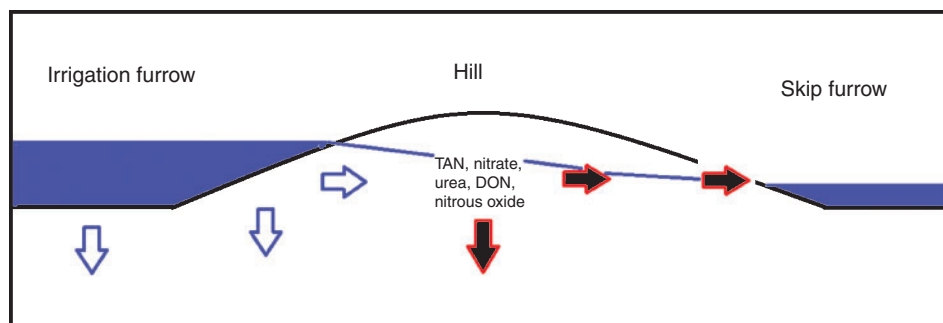


Fig. 2. A schematic showing the movement of water without (white fill arrows) and with (black fill arrows) fertiliser nitrogen compounds from the hill to the skip furrow. TAN, Total ammonia N; DON, dissolved organic N.

2013). There is no pool of N_2O -N to move from the soil during the irrigation, and typically denitrification and N_2O -N emissions occur 1–2 days after the irrigation has ceased. Further, our site is in a semi-arid, irrigated cropping region of Australia, whereas many of the other indirect emissions studies were conducted in areas of higher rainfall (Outram and Hiscock 2012; Risk *et al.* 2013; Kaushal *et al.* 2014), which are more conducive to shallow groundwater fluxes of N_2O - N_d .

There was no relationship between N_2O - N_d and the other N components. This is in contrast to several studies that have demonstrated a relationship between N_2O - N_d and NO_3 -N concentrations (Harrison and Matson 2003; Reay *et al.* 2005; Beaulieu *et al.* 2009, 2011; Warneke *et al.* 2011) or NH_4 -N concentrations (Xia *et al.* 2013). Water in the cotton irrigation system is transient, only retained for a short period, due to the cessation of irrigation once mounds are ‘wet up’ and short field lengths (<500 m). There is also no lateral groundwater discharge into the canals.

Runoff from the cotton field at the ACRI experimental farm is negligible within 12 h of the start of the irrigation; however, on commercial farms, field irrigations occur over longer periods, due to the field length exceeding 1000 m. An increase in contact time between water and the soil surface could maximise N_2O - N_d production from TN in the irrigation tail water. Further indirect N_2O emissions, resulting from N loading in the irrigation water, may continue downstream (e.g. in storage ponds) and as the irrigation networks dry down, neither of which were measured in this study.

Indirect N_2O -N emissions: N_2O - N_df and N_2O - N_EF5g

There was a strong positive relationship between the two methods used to calculate monthly N_2O flux. Although both methods gave estimates of N_2O emissions within the same order of magnitude, the IPCC method returned an emission rate 65% higher than that calculated by the dissolved N_2O method. Differences between the dissolved N_2O and IPCC methods may have occurred through the dissolved N_2O method underestimating amounts of N_2O -N produced from the water surface. Alternatively, there are uncertainties associated with the current IPCC EFs for indirect emissions. Although the current EFs have been reduced from previous estimates owing to large discrepancies between measured and IPCC estimated fluxes (Nevison 2000; Reay *et al.* 2005; Clough *et al.* 2007), the

range of uncertainty for EF₅ is still large, from 0.0005 to 0.025 (IPCC 2006).

European measurements form much of the basis for the IPCC EFs (Reay *et al.* 2012). Use of local emission factors, or models that account for local climatic conditions, soil characteristics and land management, will then reduce the uncertainty in flux estimates (Reay *et al.* 2012). A definite need exists to quantify and understand better the processes controlling indirect N_2O emissions within the Australian cotton industry. This, in turn, will provide a better platform for policy decisions and discussions of potential mitigation strategies.

Magnitude of indirect emissions

The irrigation network area on a typical irrigated cotton farm may represent only 6.5% of the farm area. Despite having a flux rate per hectare comparable to that of the direct land-surface emissions, at the farm scale, the indirect emissions are a minor component of the N_2O inventory. The indirect emissions estimated by both methods, from the whole farm, were ~2.4–4% of the magnitude of direct land-surface emissions and <0.02% of the fertiliser applied (260 kg ha^{-1}) to the farm. These are similar to the values reported by Harrison *et al.* (2005) for furrow-irrigated wheat production in Mexico.

Sampling and measurement of indirect emissions

A key issue in the determination of indirect emissions on a per-hectare basis is the accurate quantification of the fate of the water within the irrigation network. The tail water in semi-arid, irrigated cotton systems is typically recirculated and re-used on-farm. Tail water is returned to the farm storage, stored briefly (24 h), and mixed with river or groundwater and returned to the fields for the next field irrigation. The duration and location of the tail water storage will change during each day of the irrigation period depending on farm watering requirements. We have assumed that the indirect emission is mainly sourced from the tail water because of the N loading from the field and is equally spread across the irrigation network.

In this study, point measurements of N components and N_2O occurred only during the period of an irrigation (<12 h), and they were concentrated at the cotton field. During this time, N that has been leached from the fields may be transformed into N_2O , NO_x or N_2 in the storage ponds and either emitted or assimilated in the water column or in the drain sediments.

In addition, although many studies of indirect emissions have focused on the emissions of N_2O from the water surface, there may be significant N_2O emissions from the sediments once the canals are drained. Sediments can sequester $\text{NO}_3\text{-N}$ from the water column (García-García and Gómez 2009), which can lead to significantly higher indirect emissions if irrigation water is allowed to pond and is not re-used. The complexity of these biogeochemical pathways would explain the large uncertainties associated with estimating N_2O emissions by using $\text{N}_2\text{O-N}_\text{d}$ concentrations.

Reducing indirect N_2O emissions

The key to reducing indirect $\text{N}_2\text{O-N}$ emissions from cotton irrigation networks is to control the N supply to the irrigation water. Improvements in the efficiency of water and N use would reduce the export of total N and, hence, lower the potential for indirect and N_2 emissions.

Indirect $\text{N}_2\text{O-N}$ emissions may be reduced by maximising the use of plant-available N already present in the water. The tail water contains large amounts of dissolved N, which could be used to fertilise adjacent fields. Reducing water return-times to the field is likely to increase the amounts of N that can be re-used; however, a better understanding is required of the rates of transformation for optimisation of N recycling in the cotton irrigation network.

Conclusions

Estimates of N_2O emissions from the surface waters of a cotton irrigation network are now possible. The concentrations of $\text{N}_2\text{O-N}_\text{d}$ and $\text{N}_2\text{O-N}_{\text{EF5g}}$ are 0.503 ± 0.338 and 0.843 ± 0.022 kg ha^{-1} irrigation surface, respectively, over 90 days. Overall, the indirect emissions from the surface of the irrigation network are not a significant component of the N_2O inventory for Australian cotton systems, because the irrigation network covers only a small area relative to the entire land surface of the farm. The measurement of indirect emissions from irrigated cotton production is not straightforward, owing to the *ad hoc* re-use and storage of water. Additional N_2O emissions are likely to occur downstream of the field within storages and main tail drains during the irrigation season and as the channels dry down. Nitrogen fertilisation due to the re-use of drainage water and subsequent field $\text{N}_2\text{O-N}$ emission could also contribute to indirect emissions. Overall, the IPCC EF_{5g} and the dissolved N_2O indirect flux estimation methods were in agreement, and the EF_{5g} could be used to estimate indirect fluxes provided local calibration was undertaken. The irrigation network is a prime mitigation target for minimising losses of dissolved N components via denitrification. Rapid re-use of N-enriched tail water, reducing N loss via runoff, and improving efficiency of water and N use are potential methods to reduce N losses.

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