



## Modelling nitrous oxide and carbon dioxide emission from soil in an incubation experiment

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### ABSTRACT

Nitrous oxide (N<sub>2</sub>O), one of the primary green house gases (GHG), is an important contributor to the radiative forcing and chemistry of the atmosphere. Nitrous oxide emissions from soil are mainly due to denitrification. In this paper, we test sub-modules in the APSIM and DAYCENT models to simulate denitrification. The models were tested by comparison of predicted and measured N<sub>2</sub>O emission from an incubation experiment using 8.2 L soil cores. The N gas sub-modules in DAYCENT were based on the leaky pipe metaphor, that is, total N gas emissions are proportional to N cycling and gas diffusivity in the soil determines the relative amounts of N gas species emitted. The same approach was added to APSIM to enable simulation of N<sub>2</sub>O emission. The soil monoliths were irrigated three times during a two-week period and set on tension tables to control the suction at the base of each core. The results show that APSIM underestimates denitrification, whereas DAYCENT better predicted N<sub>2</sub>O emission from denitrification. In contrast, predictions of CO<sub>2</sub> emissions were better from APSIM than DAYCENT. Modification to the temperature response for denitrification in APSIM improved the simulation significantly. The use of multiple soil layers in the simulations improved predictions, especially at low soil moisture content. Under these conditions, the layered approach better captures the impact of soil moisture distribution. Reducing the time step to hourly improve the prediction of N<sub>2</sub>O peaks and the daily total emissions, but there were still temporal mismatches between simulated and observed values. The denitrification algorithms in DAYCENT, combined with APSIM simulated CO<sub>2</sub>, together with an hourly time step and a layered approach, produced the best results. These results highlight the need for improvement to the APSIM denitrification sub-model.

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### 1. Introduction

Nitrous oxide (N<sub>2</sub>O) is one of the major greenhouse gases (GHG) that cause global warming. It is a long-lived trace gas in the atmosphere and plays an important role in ozone depletion (Prather et al., 1994; Rodhe, 1990). One molecule of N<sub>2</sub>O has 310 times greater impact on the warming potential than a molecule carbon dioxide (CO<sub>2</sub>), and has a residence time of about 120 years in the atmosphere (Albritton et al., 1995; Olivier et al., 1998; Prather et al., 1994). The concentration of N<sub>2</sub>O in the atmosphere has increased from ~270 ppb in the pre-industrial period to ~319 ppb by 2005 (IPCC, 2007). Nitrous oxide contributes about 5% of global warming potential in the GHG assessments (Rodhe, 1990). The IPCC report (2007) and other studies (Bouwman et al., 1995; Prather et al., 1994) indicate that the increase in N<sub>2</sub>O concentration is mainly attributed to soil-atmosphere exchange from agriculture areas. Improved understanding of the

processes that produce N<sub>2</sub>O and accurate prediction of the flux from agricultural soils is needed to provide the scientific basis for development of mitigation strategies.

Nitrous oxide emissions from agricultural soils occur during nitrification and denitrification (Davidson, 1991; del Grosso et al., 2000a; Firestone and Davidson, 1989; Li et al., 1992; Parton et al., 1996; Sahrawat and Keeney, 1986). Nitrification is the biological process that occurs under aerobic conditions (Bremner and Blackmer, 1978) and oxidises ammonium (NH<sub>4</sub>) to nitrate (NO<sub>3</sub>). During nitrification, a small proportion of the nitrogen is lost as N<sub>2</sub>O (Conrad, 1996; Firestone and Davidson, 1989). The rate of nitrification is controlled by NH<sub>4</sub> concentration, soil pH, temperature, water content, and available soluble carbon. The maximum rate occurs in aerobic soils with moderate water content (Goreau et al., 1980; Hasegawa et al., 1999; Keating et al., 2001; Li et al., 1992; Parton et al., 1996).

In contrast, denitrification is a microbial process that occurs under anaerobic or oxygen-restricted conditions where the microbes reduce the NO<sub>3</sub> to gaseous N. The N oxides (NO<sub>3</sub>, NO<sub>2</sub>, NO, or N<sub>2</sub>O) are used as the terminal electron acceptors. It is a process of the dissimilatory

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reduction of  $\text{NO}_3^-$  (or nitrite,  $\text{NO}_2^-$ ) to gaseous products including nitric oxide (NO),  $\text{N}_2\text{O}$ , and  $\text{N}_2$  (Heinen, 2006; Knowles, 1981; Paul and Clark, 1989; Williams et al., 1992). During denitrification, the relative yields of  $\text{N}_2$  and  $\text{N}_2\text{O}$  are a function of the  $\text{NO}_3^-$  concentration and intensity of the reducing conditions with more  $\text{N}_2$  being produced under highly reduced conditions (Parton et al., 1996; Ye et al., 1994). The ratio of  $\text{N}_2:\text{N}_2\text{O}$  is positively correlated with the amount of soluble carbon and water-filled-pore space (WFPS – reflecting  $\text{O}_2$  availability in soil), but inversely related to  $\text{NO}_3^-$  concentration (Parton et al., 1996; Weier et al., 1993). Quantification of  $\text{N}_2\text{O}$  emissions from denitrification has proved to be difficult because of variations in soil texture, soil water content, biological properties, and substrate levels ( $\text{NO}_3^-$  and soluble carbon), which regulate  $\text{N}_2\text{O}$  production (Li et al., 1992).

Different approaches have been used to predict  $\text{N}_2\text{O}$  emissions from nitrification and denitrification. Statistical approaches were used in some early studies based on data from laboratory incubation experiments (Focht, 1974; Parton et al., 1996; Weier et al., 1993). Later, mechanistic models were developed to simulate the physical and biological processes that control nitrification and denitrification rates. These approaches have increased understanding of relationships between these rates, soil moisture, soil texture, diffusion, soluble carbon and N oxides. These models include DNDC (Li et al., 1992; Li et al., 2000), DAYCENT (Parton et al., 1996; Parton et al., 2001) and APSIM (Keating et al., 2001). The DNDC model is the most detailed in process description; it simulates the dynamics of the microbial denitrifier population. Further, it has been coupled with geographical information systems (Kiese et al., 2005) to estimate  $\text{N}_2\text{O}$  emissions from catchments (Kiese et al., 2005; Li et al., 2005a). The DAYCENT model is relatively simple and widely used (Chen et al., 2008). APSIM is able to simulate both the nitrification and denitrification processes. It has been recently tested for simulations of  $\text{N}_2\text{O}$  emissions by optimising the denitrification rate and incorporating  $\text{N}_2:\text{N}_2\text{O}$  equations of del Grosso et al. (2000a,b) into APSIM (Huth et al., 2010; Thorburn et al., 2010). With the exception of DNDC, most models run on a daily time step. Thus, they do not simulate the dynamics of  $\text{N}_2\text{O}$  emissions at hourly or finer time steps. However, peak  $\text{N}_2\text{O}$  emissions are observed to occur within 1 or 2 h, particularly in light textured well drained soils because of the rapid change in soil moisture. The relative merit of using hourly or daily time steps for simulating  $\text{N}_2\text{O}$  emissions is not well documented. In the current models,  $\text{N}_2\text{O}$  productions from a soil profile are predicted using: (i) a single soil layer (DAYCENT; Parton et al., 1996), (ii) by summation of  $\text{N}_2\text{O}$  production from multiple soil layers (APSIM; Thorburn et al., 2010), (iii) considering the contributions from each soil layer based on process understanding (DNDC, Li et al., 2000) or (iv) empirical equations (FASSAT, Hanson et al., 2000). The comparison of these approaches and the contributions from each layer to the total flux have not been analysed in detail.

The objectives of this paper were to: (i) test the algorithms used in DAYCENT and APSIM for simulating denitrification in terms of  $\text{N}_2\text{O}$  emissions against data obtained in an incubation experiment, (ii) investigate possible ways of improving APSIM for simulation of gaseous loss of nitrogen, and (iii) explore whether the use of multiple layered and hourly time step simulations lead to better  $\text{N}_2\text{O}$  simulations.

## 2. Material and methods

### 2.1. The incubation experiment

An incubation experiment was carried out in the laboratory in 1997 for 14 days using soil collected from improved pasture at the northern side of Wagga Wagga, Australia (35.153°S, 147.472°E). The soil was a Red Kandosol (Isbell, 1996), or Typic Haploxeralf (Soil Survey Staff, 1992) typically a sandy or loamy A horizon (~0.4 to 0.5 m thick) overlying a light to medium clay B horizon. The soil is well

drained as shown by saturated hydraulic conductivities of 850 and 35 mm/day at 0.3 and 1.0 m depths, respectively (Snow et al., 1999). Soil carbon (2.25%) and nitrogen (0.17%) values (Table 1) in the surface 0.05 m were low and the soil was acidic ( $\text{pH} \leq 5.3$ ) with exchangeable Al present on the cation exchange sites.

Five undisturbed soil cores (225 mm diameter, 200 mm length) were taken using large sleeves with a reinforced cutting edge (McKenzie and Cresswell, 2002; McKenzie and Jacquier, 1997) (see Figure 3 in McKenzie and Jacquier, 1997). The inner ring creates an air filled annulus that was filled with Vaseline heated slightly above melting point (about 50 °C) and injected into the gap with a grease gun. The base of the cores was prepared by carefully removing the surface with a small scalpel to create a freshly broken surface, which was then cleaned using a vacuum cleaner. The cores were lowered onto ceramic plates that were mounted in Perspex base made to fit the outside diameter of the PVC core (approximately 250 mm internal diameter), resulting in a tight seal between the outside of the core and the ceramic plate. A small amount of fine-grain contact material (diatomaceous earth) was added to the ceramic plates to improve the contact between the base of the soil core and the ceramic plate (Cresswell, 2002). The outer PVC side of the cores was sealed to the Perspex holder using silicon sealant.

Water potentials of –10 cm (–13.33 kPa, 1 cm = 1.33 kPa), –25 cm (–33.325 kPa), –50 cm (–66.65 kPa), –75 cm (–99.975 kPa) and –100 cm (–133.3 kPa) of water were applied respectively to the base of the five individual cores using hanging columns of water to control the tension at the base of the cores (Cresswell, 2002). Micro-tensiometers and soil solution samplers (22 mm diameter), and small Time Domain Reflectometry (TDR) probes (35 mm diameter) were installed horizontally in each core at 30, 90 and 140 mm below the soil surface. Water treatments of the soil cores were run two weeks before the experiment to calibrate TDR. Tension was measured using water filled manometers. Soil water contents were recorded every 15 min, and soil solutions were collected several times per day following irrigation and then at increasing time intervals to measure  $\text{NO}_3^-$  concentration.

Irrigation of the cores was carried out three times during the experimental period using a drip infiltrometer filled with gauge 18 hypodermic needles (McKenzie and Jacquier, 1997). The irrigant was effluent collected from Wagga (Falkiner and Smith, 1997; Smith et al., 1998) spiked with potassium bromide and  $^{15}\text{N}$  potassium nitrate. Between 607 and 746  $\text{cm}^3$  of solutions was added to the soil cores with a  $\text{NO}_3^-$ -N concentration of 210  $\mu\text{g N cm}^{-3}$ .

During the experiment, temperature was held constant at 25 °C. Evaporation (E) from the soil cores was measured at about 3–4 hour intervals following irrigation events and then at increasing time intervals as the change in weight of the cores using a 15 kg (repeatability of 0.2 g) balance.

Fluxes of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  were measured several times each 24 hour period by placing a cover over the core, sealing the cover to the PVC core using a large rubber band and with drawing two 10  $\text{cm}^3$  gas samples from the headspace at 0, 10, and 20 min. The gas flux was calculated as the initial linear rate of concentration change (Galbally et al., 2008). The headspace volume of the covers was  $2604 \pm 90 \text{ cm}^3$ . Nitrous oxide analyses were made on a HP5890 Series 1 (Hewlett Packard, USA) gas chromatograph, fitted with an electron capture detector (ECD) that was operated at 400 °C. Samples were injected via a 10-port Valco gas sampling valve fitted with a 3  $\text{cm}^3$  gas loop held at

**Table 1**  
Soil bulk density, soil pH and initial soil organic carbon, total N content.

Soil depth	Soil organic carbon	Total N	Soil bulk density	pH
	% (weight)	% (weight)	$\text{g cm}^{-3}$	–
3 cm	2.25	0.17	1.38	5.3
9 cm	0.90	0.065	1.60	4.1
14 cm	0.46	0.035	1.54	4.1

80 °C. The gas chromatographic separation was achieved using two packed columns (0.32 cm outside diameter) containing Porapak QS, and operated at 65 °C. The two columns were arranged in a back-flush arrangement. Carbon dioxide concentrations were measured using Licor CO<sub>2</sub>/H<sub>2</sub>O gas analyser. The CO<sub>2</sub> and N<sub>2</sub>O measurement systems were calibrated undertaken, and standards run during each measurement period.

## 2.2. Modelling of nitrification and denitrification in APSIM

The Agricultural Production Systems Simulator (APSIM; Keating et al., 2001) is a process-oriented model that has modules for the simulation of plant and soil processes. The APSIM-SoilN module (Probert et al., 1998; Thorburn et al., 2010) simulates the dynamics of both carbon and nitrogen. A detailed description of the module is given at <http://www.apsim.info/Wiki/SoilN.ashx>. In SoilN, soil organic matter is divided into four pools: a fresh organic matter pool (FOM) including roots and incorporated crop residue, a BIOM pool representing the more labile soil microbial biomass and microbial products, a HUM pool comprising the humic fraction of soil organic matter, and an inert pool (INERT) that does not decompose. Decomposition of the BIOM, HUM and FOM pools are treated as first-order decay processes with the rate being modified by soil temperature and moisture and the C:N ratio for the FOM pool. Carbon dioxide (CO<sub>2</sub>) production is calculated as a constant fraction of the carbon undergoing decomposition of FOM, HUM, and BIOM pools. The CO<sub>2</sub> emission from the soils is calculated as the sum of CO<sub>2</sub> production in the soil layers. Flows between different pools are calculated in terms of carbon, and the corresponding nitrogen flows depend on the C:N ratio of the receiving pool. Mineralisation and immobilisation of N is determined as the balance between the release of N during decomposition and immobilisation during microbial synthesis and humification. Vertical movement of inorganic N in the soil profile is controlled by the water movement as simulated by the soil water balance model.

In APSIM, nitrification depends on four main factors: the substrate NH<sub>4</sub> concentration, oxygen, soil moisture, soil pH and soil temperature. Impact of oxygen availability and soil water on biological activity is simulated using a soil moisture factor, which has a value of 1.0 if soil moisture is between the middle range and the drained upper limit. It decreases linearly to zero when soil moisture drops to lower limit (too dry) or increases to saturation (lack of oxygen supply). The model also assumes that the optimal pH for the biological processes is between 6 and 8, and the process stops at pH of 9 and 4.5. Unlike CERES (Godwin and Jones, 1991), there is no provision for the potential rate of nitrification to change with time to represent a changing microbial population. APSIM also use a more sensitive temperature function than that in the CERES model to account for the combined effects on both biological and physical processes.

In the model, the denitrification rate is controlled by available NO<sub>3</sub> in the soil, active carbon, soil aeration, and temperature. Active carbon is related to the carbon concentration of humic and fresh organic pools. Soil aeration is simulated with a soil moisture factor that increases from 0.0 at drained upper limit to 1.0 at saturation water content (anaerobic condition). The model assumes a wider temperature range than that for nitrification.

APSIM did not calculate N<sub>2</sub>O emission in its earlier versions. Recently, the ratio of N<sub>2</sub> to N<sub>2</sub>O from del Grosso et al. (2000a,b) for N gas emitted during denitrification, and a constant fraction of nitrification were introduced to simulate N<sub>2</sub>O emissions (Thorburn et al., 2010).

## 2.3. Modelling of nitrification, denitrification and N<sub>2</sub>O emission in DAYCENT

Detailed description of DAYCENT can be found in Parton et al. (1996) and Parton et al. (2001). Briefly, nitrification is controlled by soil NH<sub>4</sub> concentration, soil moisture, temperature and pH. It is

linked to the daily net N mineralisation from organic matter decomposition. In addition, it uses the water filled pore space (WFPS) to normalise the effect of soil moisture and texture. It links the optimal temperature to the average maximum monthly air temperature for the warmest month of the year to account for the higher temperature optimum at warmer environments. It assumes no reduction in the nitrification rate at high pH. Nitrous oxide emissions during nitrification are estimated as a proportion of the nitrification rate.

DAYCENT assumes that the total N gas loss from denitrification is controlled by labile carbon availability (e-donor), NO<sub>3</sub> concentration (e-acceptor) and oxygen (O<sub>2</sub>) availability (competing e-acceptor). It assumes that the process is controlled by the molecular species (NO<sub>3</sub>, or labile C) that is most limiting, and then attenuated by a multiplier that reflects O<sub>2</sub> availability. The O<sub>2</sub> status of soil is simulated as a function of WFPS and soil texture (del Grosso et al., 2000b; Parton et al., 1996; Parton et al., 2001). It is assumed there is no denitrification if WFPS is less than 40% for fine textured soils, <55% for medium textured soils and 60% for sandy soil. Total N gas flux increases exponentially with increasing WFPS in all soils. The availability of labile carbon is estimated from soil heterotrophic respiration (CO<sub>2</sub>), which is estimated using a maximum soil respiration rate (80 kg C ha<sup>-1</sup> d<sup>-1</sup>) modified by soil temperature and moisture factors. Nitrous oxide emission from denitrification is calculated based on the N<sub>2</sub> to N<sub>2</sub>O ratio of total denitrification. Further, it assumes that the proportion of N<sub>2</sub>O from denitrification decreases as the ratio of e-donor to e-acceptor increased. That is, a larger amount of N<sub>2</sub> is produced from NO<sub>3</sub> as the intensity of reduction increases under anaerobic conditions.

## 2.4. Simulation of the N<sub>2</sub>O emission in the incubation experiment using DAYCENT and APSIM

Nitrous oxide production was modelled at both daily and hourly time steps, with either a single or multiple soil layers, to investigate the effect of time step and layering on the simulation results. Three approaches were used for comparison purposes: i) the original DAYCENT model (DAYCENT), ii) the APSIM simulated denitrification rate together with the N<sub>2</sub> to N<sub>2</sub>O ratio from DAYCENT (APSIM\_D), iii) same as in i) but the CO<sub>2</sub> production from soil heterotrophic respiration was replaced by the CO<sub>2</sub> production from decomposition of soil organic matter in APSIM (DAYCENT\_A).

The simulations were conducted outside the APSIM framework by programming the modules with Visual Basic and running the simulations in Excel. The HUM and BIOM pools in APSIM were initialised based on measured soil organic carbon content. The proportion of organic carbon that is inert (F<sub>inert</sub>) and the proportion of non-inert C in BIOM pool (F<sub>biom</sub>) were set to 0.4 and 0.03 (Probert et al., 1998), respectively. Fresh organic matter contained in the soil was estimated based on previous crop type (legume pasture) and adjusted to match the first measured CO<sub>2</sub> flux from the soil in the 10 cm suction treatment.

Nitrous oxide and CO<sub>2</sub> release was modelled firstly using a single layer (0–20 cm soil), which is the default depth in DAYCENT for N<sub>2</sub>O simulation. In subsequent simulations, three soil layers (0–6, 6–12 and 12–20 cm) were used. Studies (Chatskikh et al., 2005; Davidson et al., 2000; Hanson et al., 2000; Perez et al., 2000) show that some of N<sub>2</sub>O will be reduced to N<sub>2</sub> as it diffuses through the soil. The relative contribution of N<sub>2</sub>O produced in each soil layer was estimated based on the central depth of the layers to the soil surface as according to Chatskikh et al. (2005):

$$f_{N_2O} = \max\left(0, \min\left(1.0, 1.008 - 0.0343Z_i - 3.1816Z_i^2\right)\right) \quad (1)$$

where  $f_{N_2O}$  is the contribution factor,  $Z$  is the depth of the centre of layer  $i$  from soil surface (m).

For multiple soil layer simulations, the surface  $N_2O$  emission from the 20 cm soil cylinder was calculated as the  $N_2O$  produced in each of the three layers multiplied by the contribution factor from Eq. (1). The relative contribution decreases with depth. A thicker layer at depth may locally produce more  $N_2O$ , but the contribution to surface emission is smaller.

The daily potential rates of nitrification and denitrification were transformed to hourly rates by dividing by 24 for simulations at hourly time step. The daily rates of soil organic matter decomposition for BIOM, FOM, and HUM pools were transformed to hourly rates using Eq. (2) because they are first order decay rates:

$$\ln(1.0-r) = \ln(1.0-R) / 24 \quad (2)$$

where  $r$  is the hourly rate, and  $R$  is the daily decomposition rate.

In the experiment, soil water content was monitored continuously. However, soil  $NO_3$  was measured intermittently. The observed soil water content (hourly basis) was used as input to the model. Nitrate-N contents in each soil layers were estimated for each hour based on water movement between the three layers in the soil cylinders (see below). The estimated hourly  $NO_3$ -N contents were used as input for the hourly modelling.

### 2.5. Calculation of $NO_3$ -N movement and drainage at the bottom of the cores

Drainage from the cylinder was calculated from the measured soil water content in the soil profile and evaporation (data not shown), for the purpose of estimating  $NO_3$ -N concentration in the soil at an hourly time-step and  $NO_3$ -N leaching from the soil cores. For each time step, the water balance is given as:

$$D = I - E + \sum_{i=1}^n V_i \times \Delta SW_i \quad (3)$$

where  $D$  is drainage at the base of the core ( $cm^3$ );  $I$  is the irrigation amount ( $cm^3$ );  $E$  is evaporation ( $cm^3$ );  $\Delta SW$  is the change of volumetric water content ( $cm^3 cm^{-3}$ ) in the soil profiles;  $V_i$  is volume of the soil in a layer ( $cm^3$ ).

Water movement was estimated based on the measured soil water content in the cylinder. Furthermore, we assumed that  $NO_3$ -N was mixed in the soil solution and the downwards flux was proportional to drainage, thus only convective transport was considered.

## 3. Results

### 3.1. Soil moisture and drainage

The dynamics of soil water contents at three layers in the soil cylinders are shown in Fig. 1(a-e). Water contents in the 0-6 cm surface soil layer were constantly higher than those in the 6-12 cm and 12-20 cm soil layers in the 10 cm suction treatments (Fig. 1a). In the other treatment, differences in water contents between layers were much smaller, especially in the 100 cm suction treatment (Fig. 1e).

The comparisons of the calculated versus the observed cumulative water drainage are presented in Fig. 1f-j. Two points were over-estimated at 10 cm and 25 cm suction water treatments (Fig. 1f and g) during the second irrigation (12 May), and two points were under-estimated between the second irrigation and the third irrigation in the 50 cm and 75 cm suction treatments (Fig. 1h and i). In general, drainage from the soil core was reasonably well estimated using the water balance method (mean  $r^2 = 0.8$ , ranges: 0.63-0.98). This gives us confidence in the estimation of nitrate movement in the soil core.

### 3.2. $NO_3$ and $NH_4$ concentration in soil solution

Fig. 2 shows the comparisons of the measured and simulated  $NO_3$  concentration in the soil solutions in the soil cylinders. Nitrate concentration increased with time because of the  $NO_3$ -N added in the irrigation water. There was a general agreement between the simulated and observed  $NO_3$  concentrations. However, after the third irrigation (15 May 1997), the  $NO_3$  concentrations were slightly underestimated in all cores, probably due to the assumption of full mixing of  $NO_3$  in water and the slight overestimation of drainage. The simulated  $NO_3$  concentrations were used in the simulation of denitrification.

Soil ammonium ( $NH_4$ ) in the 0-20 cm soil profiles ranged from 0.03 to 0.8  $\mu g N cm^{-3}$  throughout the experiment. The concentration decreased significantly after irrigation because no  $NH_4$ -N was applied (data not shown). Ammonium-N concentrations were very low during the experiment. The enrichment of the  $^{15}NO_3$  did not decrease significantly, showing limited mineralisation occurred during the experimental period (data not shown). Consequently, we conclude that the contribution of  $N_2O$  emissions from nitrification was considered to be almost zero and was neglected.

### 3.3. Soil heterotrophic respiration

The measured  $CO_2$  fluxes and the calculated water-filled-pore-space (WFPS) for all treatments are presented in Fig. 3. The  $CO_2$  fluxes were sensitive to the changes in WFPS, indicating that soil heterotrophic respiration is sensitive to changes in soil moisture. The observed  $CO_2$  fluxes ranged from 0.07 to 0.5  $g C m^{-2} h^{-1}$ ; the highest values were observed just after each irrigation.

Heterotrophic respiration predicted using the DAYCENT denitrification sub-module did not show this sensitivity. The predicted values were insensitive to changes in soil moisture (Fig. 4a-e). In contrast, the simulated  $CO_2$  release by APSIM model agreed well with the observed data, except that on some occasions the peak emissions were under estimated (Fig. 4a-e). Comparison of the simulated and observed time course of  $CO_2$  release show that the simulated peaks were 1-4.5 h ahead of what was measured (Table 2).

### 3.4. Nitrous oxide emissions from denitrification

The measured  $N_2O$  fluxes responded directly to changes in WFPS (Fig. 3f-j). This is consistent with other studies (Li et al., 1992; Linn and Doran, 1984; Weier et al., 1993). The highest  $N_2O$  fluxes were observed in 1-10 h after the peaks of WFPS (Table 2). The  $N_2O$  predictions using DAYCENT showed a very sensitive response to the changes of WFPS (Fig. 4f-j). Despite the poor prediction of  $CO_2$ , the DAYCENT model predicted the measured  $N_2O$  fluxes reasonably well using the hourly time step, with the exception of 10 cm and 75 cm suction treatments where the emissions were under predicted. This was most obvious before the second irrigation in 10 cm suction treatment (Fig. 4f-j, DAYCENT), mainly because of the low  $N_2O$  fraction at the higher WFPS.

When the APSIM simulated denitrification rate, together with the N gas ratio from DAYCENT was used,  $N_2O$  release was severely underestimated for all the treatments, and was zero for most of incubation time period (Fig. 5a-e, APSIM\_D). Assuming that the ratio of  $N_2O:N_2$  used in DAYCENT is correct (as shown in DAYCENT simulations in Fig. 5f-j), the underestimation of  $N_2O$  release must be a result of underestimation of the denitrification rate in APSIM.

Combining the APSIM-simulated  $CO_2$  release with the denitrification sub-module in (DAYCENT\_A) resulted in no significant difference in the simulated  $N_2O$  fluxes (Fig. 5f-i), implying that the  $N_2O$  release in the experiment was less regulated by carbon, but rather water. The agreement between observed and simulated  $N_2O$  release indicated reasonable performance of the DAYCENT approach.

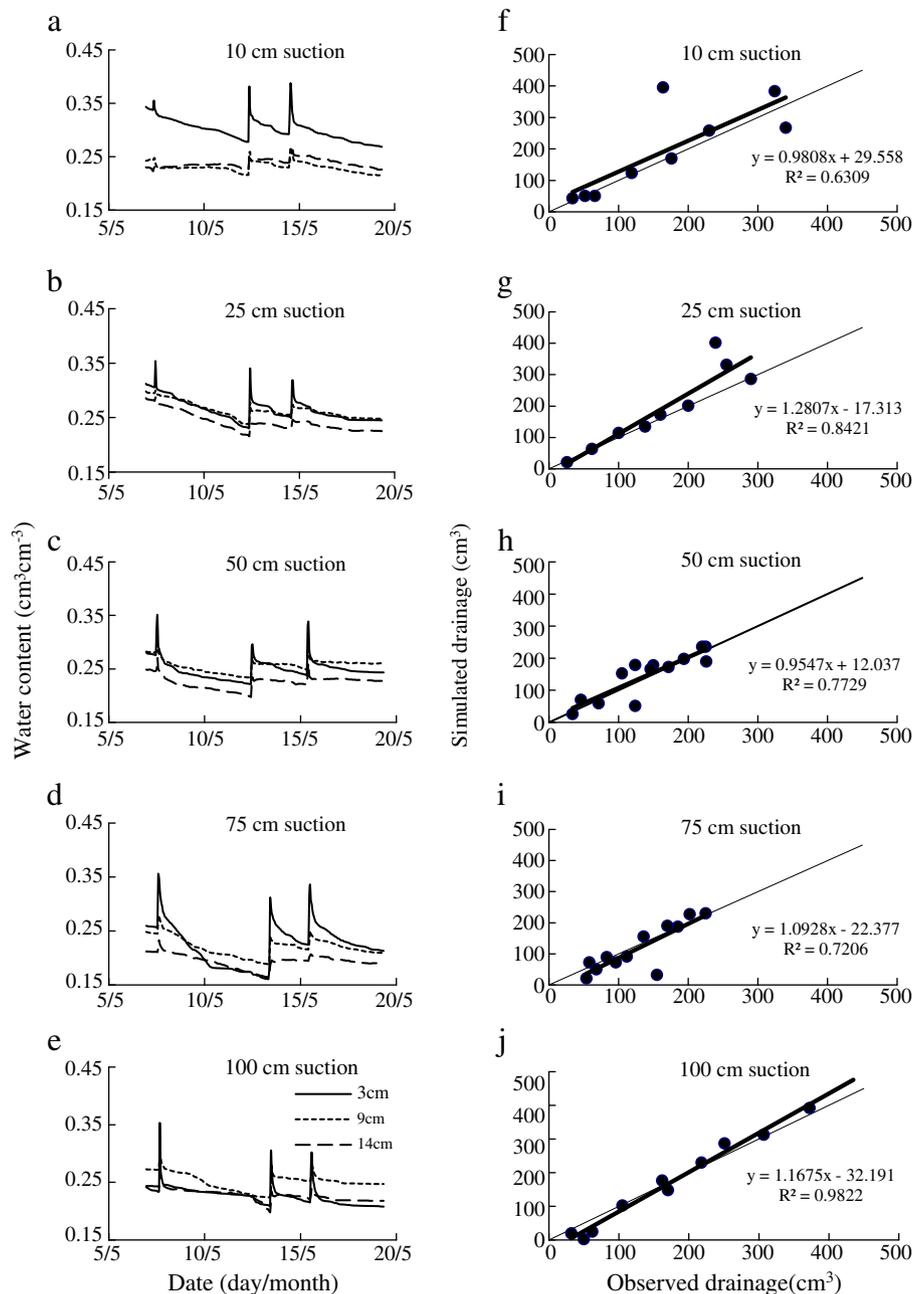
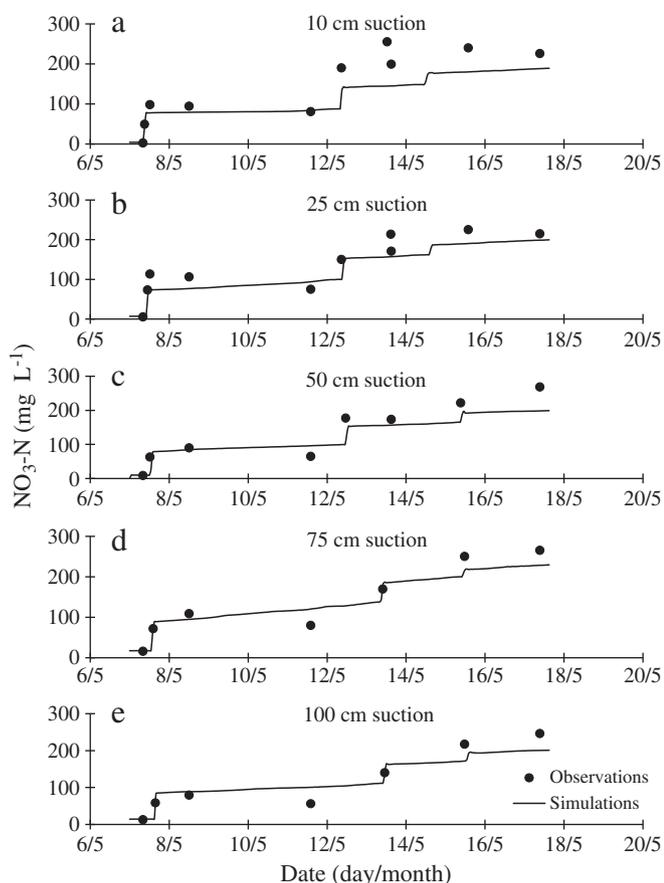


Fig. 1. Observed soil volumetric water content ( $\text{cm}^3 \text{cm}^{-3}$ ) (a–e) and comparison of observed and simulated cumulative drainage ( $\text{cm}^3$ ) (f–j) for 10, 25, 50, 75, and 100 cm suction treatments.

Comparison of the temperature and soil moisture response functions of denitrification used in APSIM, DAYCENT and DNDC revealed significant differences between models in terms of temperature and soil moisture limitation on denitrification (Fig. 6). At the experiment temperature of 25 °C, DAYCENT and DNDC simulate a temperature factor of 1.0 (i.e., optimal temperature and no limitation to denitrification), while the APSIM approach gives a temperature factor of 0.3, leading to 70% reduction in denitrification as compared to DAYCENT and DNDC (Fig. 6a). Several other studies also indicated that denitrification reaches a maximum rate at a temperature around 25–35 °C (George and Antoine, 1982; Pfenning and McMahon, 1997; Saad and Conrad, 1993; Stanford et al., 1975). Furthermore, the moisture factor in APSIM, calculated based on soil water content,

drained upper limit and saturation water content, is also much lower than that calculated based on WFPS in DAYCENT (Fig. 6b). Other studies (Dobbie and Smith, 2001; Linn and Doran, 1984; Weier et al., 1993) showed that denitrification starts when WFPS reached 0.6 in loam soil, equivalent to a volumetric soil water content of 0.24 in our experiment. Based on this information, we modified the temperature and soil moisture response functions for denitrification as shown in Fig. 6 (APSIM\_modified).

Fig. 5 shows the simulation results using the modified APSIM denitrification routine (APSIM\_modified). The results are significantly improved through changes made to the temperature and soil moisture responses. They are similar to that simulated by the DAYCENT\_A approaches (see Fig. 5). However, the observed  $\text{N}_2\text{O}$



**Fig. 2.** Comparison of observed (Marks) and simulated (lines)  $\text{NO}_3$  concentration ( $\text{mg L}^{-1}$ ) in the soil solution for suction treatments of (a) 10 cm, (b) 25 cm, (c) 50 cm, (d) 75 cm, and (e) 100 cm.

emissions better agreed with the simulations using DAYCENT\_A than APSIM\_modified (Fig. 5).

### 3.5. Layered simulations on gas emissions

The results of the layered simulations showed that the sum of  $\text{CO}_2$  release from the three soil layers was generally lower and showed better agreement with the observations than that simulated using a single layer, except at high soil moisture (10 cm suction treatment; Fig. 7a–e). This may be attributed to better representation of soil water and soil properties with depth. The sum of  $\text{CO}_2$  fluxes also showed a more sensitive fluctuation with soil moisture as observed in the experimental data. Based on the simulation results, the surface layer (0–6 cm soil profiles) contributed the largest proportion to  $\text{CO}_2$  flux amount at high soil moisture (Fig. 7a). However, the contribution from the sub-layers increased at lower soil moisture contents (Fig. 7a–e).

The total  $\text{N}_2\text{O}$  loss for the layered simulations was higher than that simulated using a single layer during the periods of relative high soil moisture ( $\text{WFPS} > 0.65$ ), especially after irrigation (Fig. 7f–j). In addition, the layered simulation was able to predict the small  $\text{N}_2\text{O}$  fluxes at low soil moisture ( $\text{WFPS} < 0.6$ ), which the single layer approach was unable to predict (Fig. 7f–j). The contributions of the deeper soil layers to total  $\text{N}_2\text{O}$  emissions increased with decreasing soil moisture in the soil profiles, especially for the periods when surface soil moisture decreased rapidly (Fig. 7f–j). However, both approaches underestimated the  $\text{N}_2\text{O}$  fluxes under the 10 cm suction treatment (Fig. 7f).

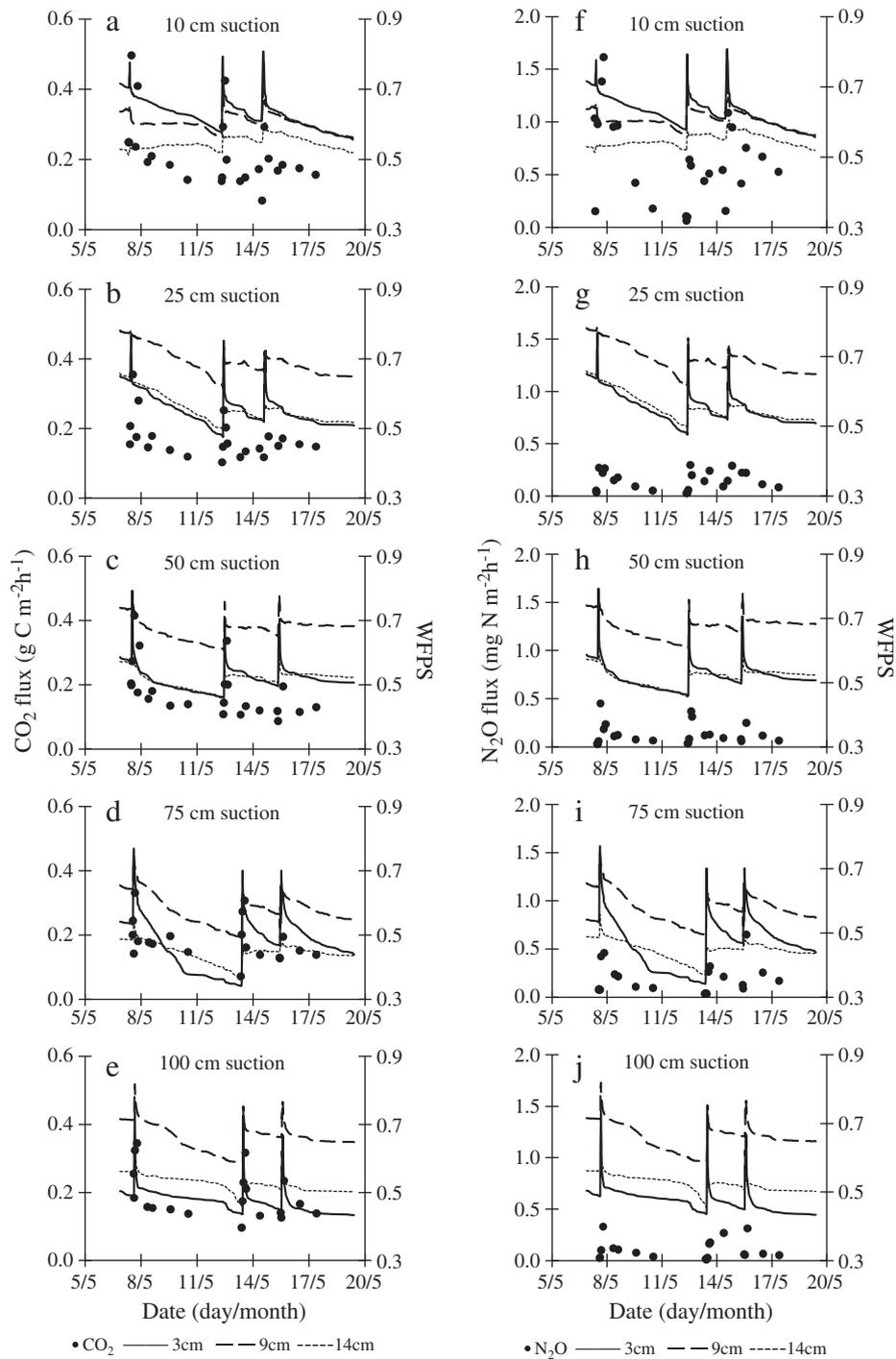
### 3.6. Simulations with hourly and daily time steps

The predictions of  $\text{N}_2\text{O}$  emissions using the DAYCENT\_A approach with hourly and daily time step are shown in Fig. 8. Nitrous oxide emissions simulated using the hourly time step were higher than that simulated with daily time steps, and agreed better with observations;  $\text{N}_2\text{O}$  emissions simulated using daily time step underestimated the measured data (Fig. 8a–e). In contrast, the DAYCENT\_A hourly approach generally simulated the measured data. These results show that simulations using a daily time step underestimated  $\text{N}_2\text{O}$  emissions, because of failure of the model to capture the effects of the rapid changes on soil moisture that occurred following irrigation. The  $\text{N}_2\text{O}$  emissions were underestimated by single layer with hourly time step with low soil moisture (Fig. 7f–j), implying that the single layer approach may underestimate  $\text{N}_2\text{O}$  emissions, especially when surface soil was very dry. However, the  $\text{N}_2\text{O}$  emissions were overestimated with multiple layers in some occasions because the  $\text{N}_2\text{O}$  emissions from deeper layers were overestimated (Figs. 7 and 8). Overall, predicted daily total  $\text{N}_2\text{O}$  emissions using the layered method and hourly time steps were better than the simulated values using a single soil layer and hourly time step. The use of multiple soil layers and an hourly time step may be better to predict  $\text{N}_2\text{O}$  emissions, especially under lower soil moisture conditions.

## 4. Discussion

The incubation experiment provided data on  $\text{CO}_2$  and  $\text{N}_2\text{O}$  emissions, which were used to evaluate the APSIM and DAYCENT models for the simulation of soil heterotrophic respiration and  $\text{N}_2\text{O}$  emissions due to denitrification. The good agreement between predicted and measured  $\text{CO}_2$  from APSIM indicated that this model could reasonably simulate  $\text{CO}_2$  fluxes from soil organic matter (SOM) decomposition (Fig. 4a–e). However, the DAYCENT approach failed to capture the dynamics of  $\text{CO}_2$  release as affected by the variations of soil moisture (Fig. 4a–e). In APSIM,  $\text{CO}_2$  emission from SOM decomposition increases with soil water content; it reaches a maximum at DUL, and then decreases. In many cases, the value of  $\text{WFPS}$  was about 0.70 when soil moisture reached DUL for the loam soil (Fang et al., 2006; Liu, 1989; Ratliff et al., 1983; Ritchie, 1981), and some studies showed that soil heterotrophic respiration was the largest when  $\text{WFPS}$  is about 0.7 (Grant and Rochette, 1994; Li et al., 2006; Wildung et al., 1975). This is consistent with the results in our incubation experiments and the APSIM simulation results. In DAYCENT, the optimal  $\text{WFPS}$  for maximum soil heterotrophic respiration for loam soil is around 0.6 (Figure 2a in Parton et al., 1996.), which is lower than the value of 0.7 as discussed above.

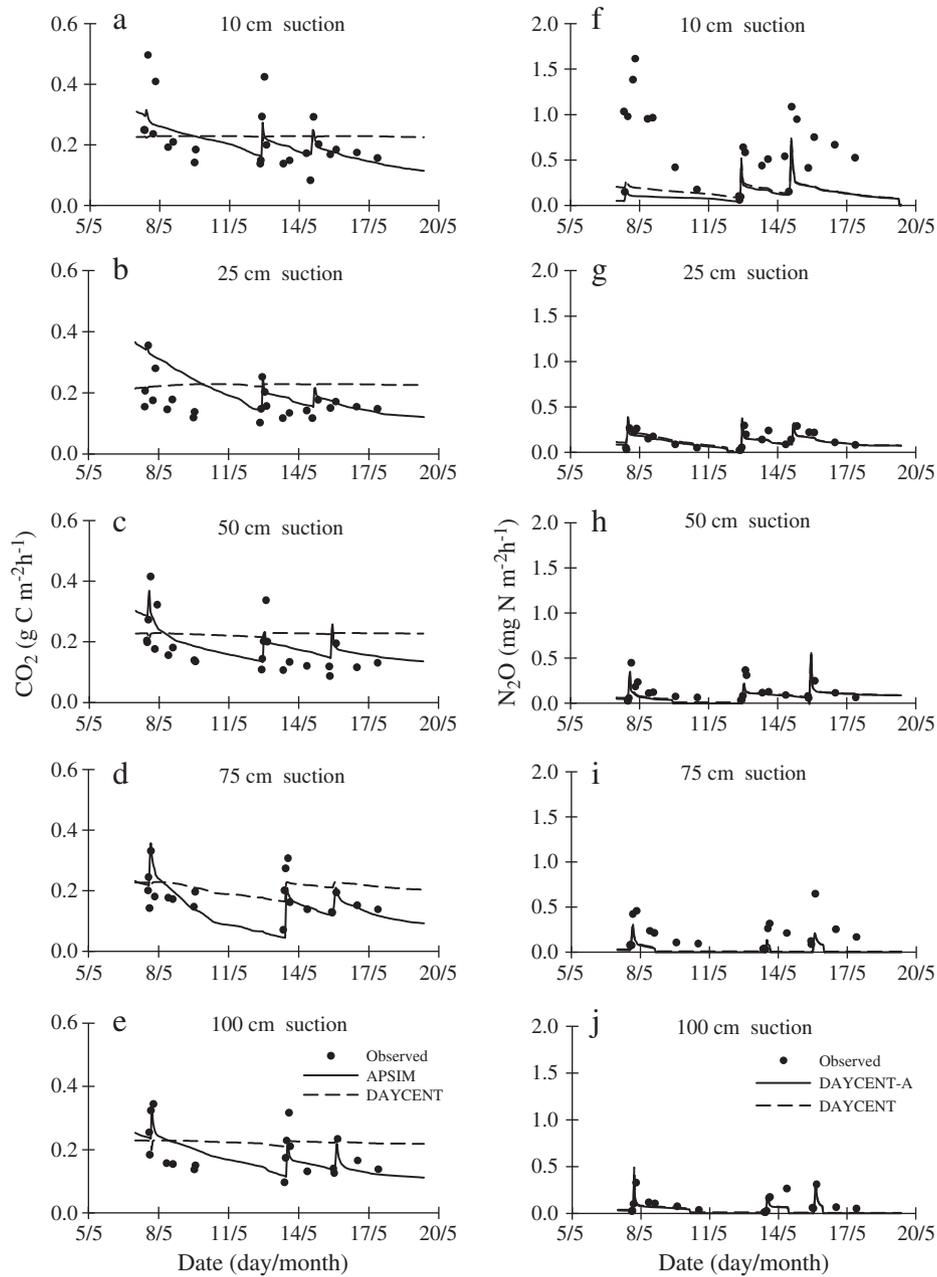
The significant underestimation of  $\text{N}_2\text{O}$  fluxes by the APSIM approaches indicates that APSIM underestimates denitrification, an observation that is consistent with the findings of Huth et al. (2010) and Thorburn et al. (2010). A comparison of the responses of denitrification to  $\text{NO}_3$ , carbon, temperature and water conditions indicated that the response of denitrification rate to soil temperature and moisture were the two primary factors leading to the underestimation of denitrification (Fig. 5). The growth of denitrifiers is assumed not to be limited in DNDC when the temperature is above 22.5 °C (Li et al., 2000). In DAYCENT, denitrification rate reaches a maximum when the temperature is above 20 °C (Parton et al., 1996; Parton et al., 2001). Other studies also showed that denitrification increased significantly as the temperature increases above 10 °C, and reached more than 60% of its maximum value at 25 °C (Craswell, 1978; de Klein and van Logtestijn, 1996; Pfenning and McMahon, 1997; Saad and Conrad, 1993; Stanford et al., 1975), and only increased slightly above 35 °C (Stanford et al., 1975). The improved simulation of  $\text{N}_2\text{O}$  release through modification to APSIM based on above mentioned data indicates a need to modify the temperature response of denitrification in APSIM.



**Fig. 3.** Carbon dioxide and  $\text{N}_2\text{O}$  fluxes (dots) measured in the experiment and calculated hourly WFPS (lines) for suction treatments of (a, f) 10 cm, (b, g) 25 cm, (c, h) 50 cm, (d, i) 75 cm, and (e, j) 100 cm.

There might also be problems in the soil moisture response of denitrification in APSIM. Previous studies showed that WFPS was around 0.70 for most loam soils when soil water content reached DUL. Denitrification could occur at water contents below DUL because of anaerobic microsites, and occur at WFPS ranging from 0.55 to 0.90 (de Klein and van Logtestijn, 1996; Dobbie and Smith, 2001; Linn and Doran, 1984; Weier et al., 1993). In soils with high clay content, denitrification may occur at WFPS around 0.40 (Li et al., 2005b; Mosier et al., 1996; Parton et al., 1996; Robertson et al., 1993).

However, APSIM assumes that denitrification does not begin until the soil moisture reaches DUL. This is another reason for the underestimation of denitrification by APSIM. The impact of soil moisture is one of the most difficult aspects involved in the modelling of denitrification. For example, Heinen (2006) showed a large number of different relationships between denitrification rate and soil moisture content. The higher WFPS values in coarser soils likely demonstrate that pore size distribution is important in the formation of anaerobic conditions where denitrification can occur. While WFPS is not directly



**Fig. 4.** Comparisons of observed and simulated CO<sub>2</sub> flux (g C m<sup>-2</sup> h<sup>-1</sup>) using APSIM and DAYCENT approaches (a–e), and comparisons of observed and simulated N<sub>2</sub>O emissions (μg N m<sup>-2</sup> h<sup>-1</sup>) using DAYCENT and DAYCENT combined with APSIM simulated CO<sub>2</sub> (DAYCENT-A) (f–j).

proportional to the diffusion of gases that regulate denitrification, further studies are needed to better define soil moisture thresholds that regulate the denitrification rate.

The studies of Huth et al. (2010) and Thorburn et al. (2010) also report underestimation of denitrification by APSIM. Thorburn et al. (2010) investigated the problem by optimising the effect of soil moisture on denitrification rate, and the value of denitrification coefficient based on field measurements from a sugarcane fields. However, no modification of the temperature response on denitrification was explored. They concluded that increasing the denitrification rate was one way to improve the simulations of denitrification. This modification was subsequently shown to provide good predictions of field measured N balances in grain production (Huth et al., 2010). The values predicted using their method was very close with the values calculated using APSIM\_modified (data not shown). Our

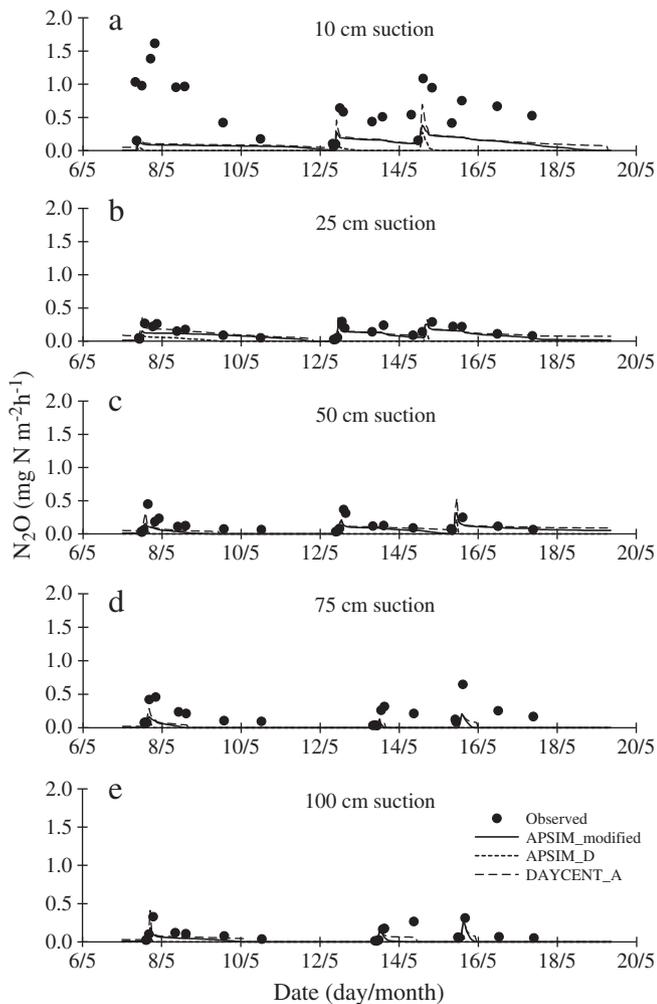
results show that simulations of N<sub>2</sub>O emissions in APSIM can be improved through modification of response functions. However, further studies are needed to verify which modifications are justified.

The time step at which the model runs is also important for simulation accuracy, especially for the processes that change quickly over short time periods (Hoogenboom, 1999). The comparisons of simulated daily N<sub>2</sub>O emissions based either on hourly or daily time steps showed that the daily time step always underestimated the N<sub>2</sub>O emissions in our experiment. Our experimental results, and others studies (Bowman and Focht, 1974; Bronson and Fillery, 1998; George and Antoine, 1982; Pfenning and McMahon, 1997; Smith et al., 1998; Stanford et al., 1975; Weier et al., 1993), show that denitrification is very sensitive to changes in soil water content (or WFPS). Following irrigation or rain, soil moisture may change significantly within a

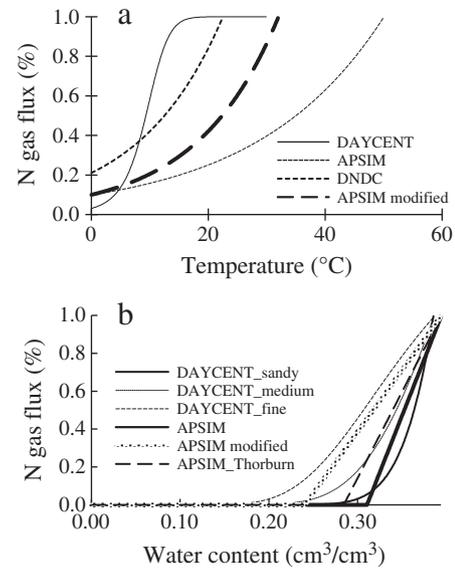
**Table 2**  
Time lags (minutes) between WFPS peaks and peak of gas emissions.

Irrigations		Lags (minutes)		
		1	2	3
10 cm suction	WFPS	59	50	120
	N <sub>2</sub> O	600	175	60
	CO <sub>2</sub>	130	175	60
25 cm suction	WFPS	60	55	105
	N <sub>2</sub> O	130	175	255
	CO <sub>2</sub>	130	15	255
50 cm suction	WFPS	58	60	110
	N <sub>2</sub> O	155	240	275
	CO <sub>2</sub>	155	240	275
75 cm suction	WFPS	65	66	105
	N <sub>2</sub> O	320	270	145
	CO <sub>2</sub>	85	270	145
100 cm suction	WFPS	60	60	105
	N <sub>2</sub> O	170	155	105
	CO <sub>2</sub>	170	155	105

short period (<1 day), especially in dry environments and permeable soils. Under these conditions, the N<sub>2</sub>O emission is likely to be severely underestimated because of the inability to capture the emission peaks if the daily time step is used. However, in situations where water content only changes slowly during a day, a daily time step may be sufficient.



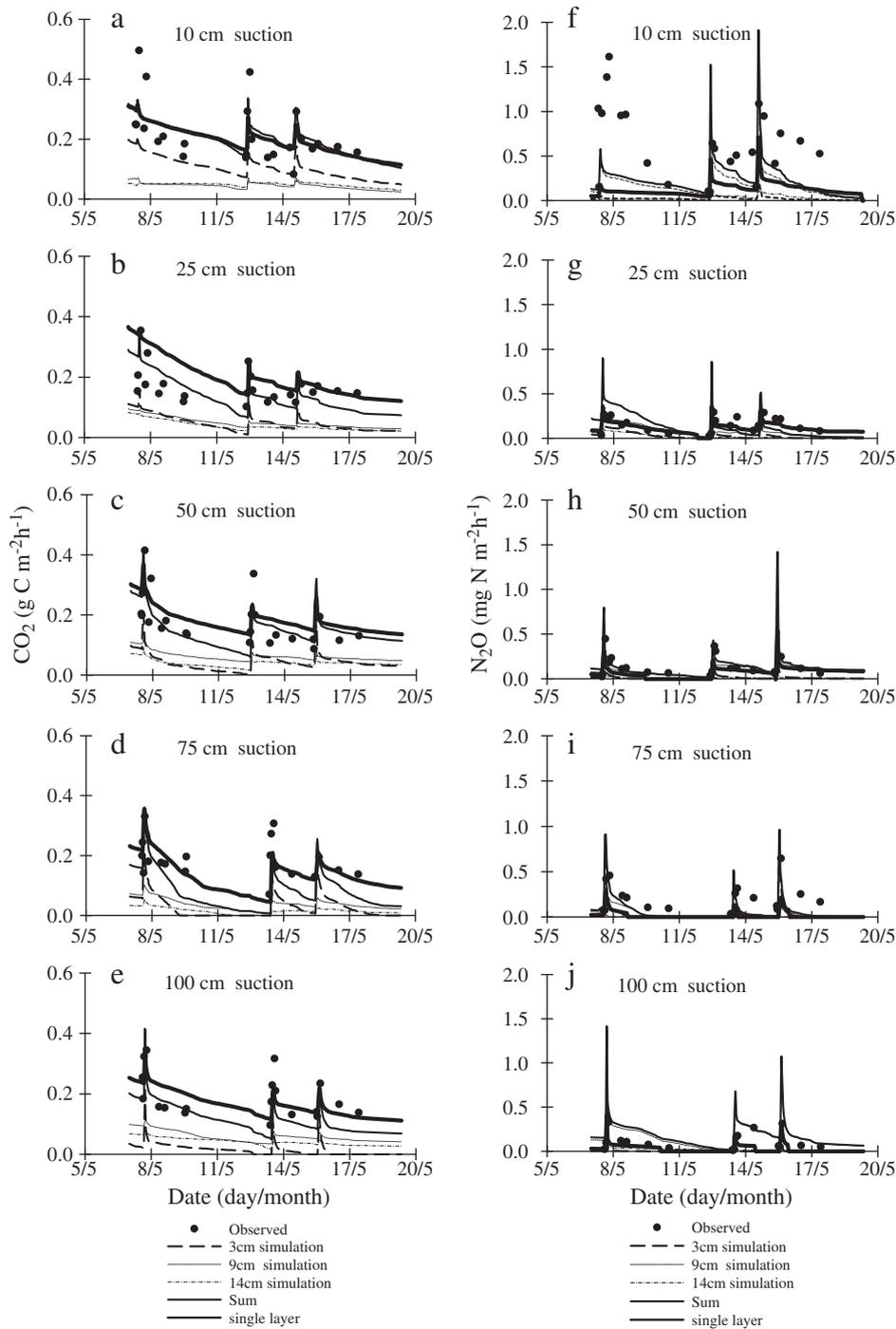
**Fig. 5.** Comparison of observed and simulated N<sub>2</sub>O fluxes ( $\mu\text{g N m}^{-2} \text{h}^{-1}$ ) using APSIM incorporating the N gas ratio from DAYCENT (DAYCENT\_D) and modified APSIM denitrification routines.



**Fig. 6.** The effect of temperature on denitrification rate used in APSIM, DAYCENT, and DNDC models (a), and the effect of water content on denitrification used in APSIM and DAYCENT (b).

The temporal mismatch of predicted and observed N<sub>2</sub>O emissions, especially the emission peaks (Table 2, Fig. 5), leads to low correlation between simulated and observed values. This mismatch results from the inability of models to capture the detailed processes involved which may be attributed to three reasons, as follows. (1) Denitrification is a multi-step biochemical process, and each step is controlled by individual enzymes, which are sequential and substrate dependent (Paul and Clark, 1989). (2) Each step is driven by a number of variables including soil environmental factors such as temperature, moisture, pH, and substrate concentration (Craswell, 1978; Knowles, 1981; Paul and Clark, 1989; Ye et al., 1994), and there is a time lag between the production of each intermediate substrate and its consumption by the next enzyme (Paul, 2006). (3) Gas diffusion in the soil profile is another contributing factor to the lag. Perez et al. (2000) showed that the time for gases at 1 m soil depth to diffuse to the surface was less than 1 h, based on the hypothesis that the soil gas profile and the surface fluxes are in the steady state on the timescale and the soil is uniform. The dynamics and activities of enzymes for each step during denitrification are difficult to predict. Furthermore, the time of gas diffusion is no more than 1 h within simulated depth (<1.0 m) in the soil profiles. Therefore, models assumed that N<sub>2</sub>O emissions changes immediately with the environmental factor. The observations in our experiment and the findings of others (Li et al., 1992; Parton et al., 1996; Parton et al., 2001; Smith and Tiedje, 1979; Tiedje, 1978) showed that there were 1–10 hours lags between the gas emissions and the peaks of soil moisture or WFPS (Table 2). In spite of the temporal mismatch, the use of the hourly time step can correctly predict the daily total emissions in most cases.

Questions remain how thick a single soil layer should be and whether a multiple layer approaches should be used for N<sub>2</sub>O emission modelling. Our results show that a layered approach improved simulations during relatively dry periods (WFPS < 0.6 for loam soil), and were able to show the relative contribution of each layer to total gas emissions under varying soil water contents (Fig. 7). Under drier conditions, significant heterogeneity of anaerobic conditions can be related to soil texture and the distribution of water in the soil profile. In the single-layer approach, averaging of soil moisture and other factors may lead to underestimation of anaerobic microsites and subsequently denitrification. A multiple layer approach can capture



**Fig. 7.** Comparison of observed and simulated CO<sub>2</sub> fluxes by APSIM using single layer and multiple layers approach (a–e), and comparisons of observed and simulated N<sub>2</sub>O fluxes (μg N m<sup>-2</sup> h<sup>-1</sup>) by DAYCENT combined with APSIM simulated CO<sub>2</sub> using single layer and multiple layers approach (f–j).

the impact of the heterogeneity of soil moisture distribution, and improve simulations in deeper wet layers. Further studies are needed to quantify under which condition the results of the single or multi-layer approach differ most.

**5. Conclusion**

The APSIM decomposition approach could capture the dynamics of CO<sub>2</sub> release from SOM, and the DAYCENT approach could predict the N<sub>2</sub>O emissions reasonably in the incubation experiment. APSIM underestimated N<sub>2</sub>O emissions suggesting that predicted rates of denitrification were likely too low. Modification to the temperature

response improved the simulation significantly. The combination of DAYCENT denitrification and APSIM decomposition approaches with hourly time step and the multiple layered approaches seems to lead to the best results as compared with the N<sub>2</sub>O measurement in the experiment. This highlights the needs of improvements in both models.

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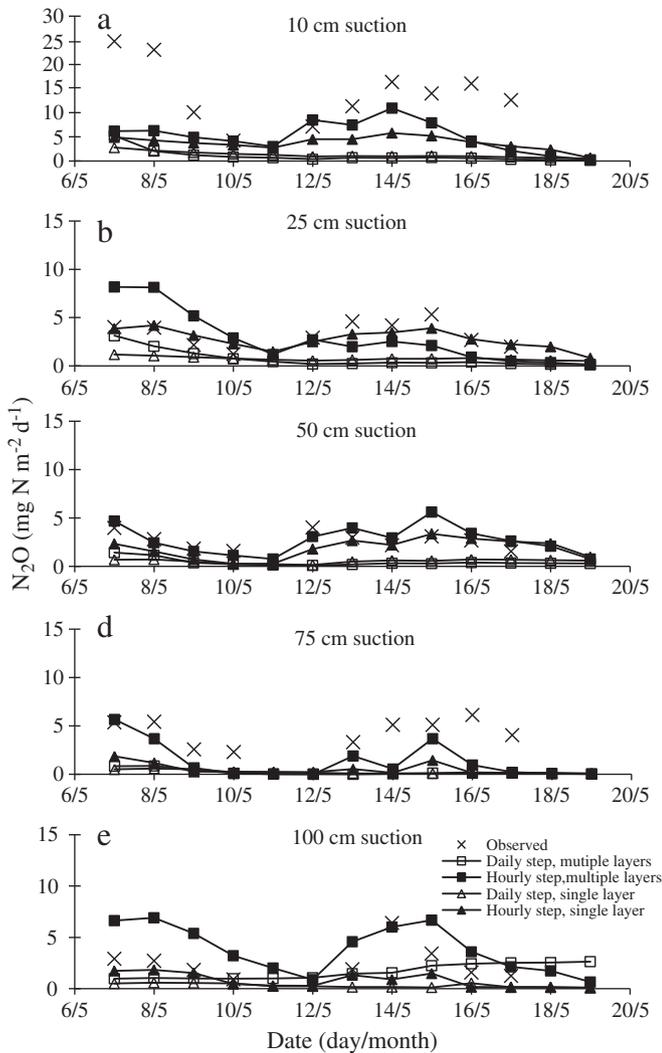


Fig. 8. Comparison of simulated  $N_2O$  fluxes ( $\mu\text{g N m}^{-2} \text{d}^{-1}$ ) using DAYCENT combined with APSIM simulated  $CO_2$ , hourly and daily time steps and single and multiple layers.

author of this paper to conduct the research in CSIRO Land and Water, Australia.

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