Can seasonal soil N mineralisation trends be leveraged to enhance pasture growth?

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HIGHLIGHTS
• We compare plant, soil and nutrient outputs of APSIM, DayCent and DairyMod.
• We examined whether seasonal N fertilisation influenced mineralisation.
• No model was consistently more reliable in simulating measured variables.
• Seasonal climates had more influence on mineralisation than tactical N application.
• Sensitivity of N mineralisation to fertiliser was generally greatest in DayCent.

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Abstract

Background: Soil N mineralisation is the process by which organic N is converted into plant-available forms, while soil N immobilisation is the transformation of inorganic soil N into organic matter and microbial biomass, thereafter becoming bio-unavailable to plants. Mechanistic models can be used to explore the contribution of mineralised or immobilised N to pasture growth through simulation of plant, soil and environment interactions driven by management.

Purpose: Our objectives were (1) to compare the performance of three agro-ecosystems models (APSIM, DayCent and DairyMod) in simulating soil N, pasture biomass and soil water using the same experimental data in three diverse environments (2), to determine if tactical application of N fertiliser in different seasons could be used to leverage seasonal trends in N mineralisation to influence pasture growth and (3), to explore the sensitivity of N mineralisation to changes in N fertilisation, cutting frequency and irrigation rate.

Abbreviations: A.G., aboveground biomass; AP, Agricultural Production Systems Simulator (APSIM); B.G., belowground biomass; BIOM, microbial biomass pool; C, soil carbon; DC, daily time-step version of the CENTURY biogeochemical model (DayCent); DM, biophysical simulation model of the dairy pasture system (DairyMod); FOM, fresh organic matter pool; HF, high frequency irrigation treatment; HGR, herbage growth rate; HUM, humic pool; INERT, inert pool; LF, low frequency irrigation treatment; MB, mean bias; MPE, mean prediction error; N, nitrogen; N2O, nitrous oxide; NH4, ammonium; NO3, nitrate; NOx, oxide forms of nitrogen; NSW, New South Wales; P, phosphorus; QLD, Queensland; R², coefficient of determination; RMSE, root mean square error; SoilN, the soil N and C module in APSIM; S, sulfur; VR, variance ratio; VIC, Victoria; VWC, volumetric water content.

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1. Introduction

Intensive pasture-based systems are generally associated with high stocking rates, high synthetic N fertilisation, and as a corollary, high nitrogen (N) loading per unit area (Chang-Fung-Martel et al., 2017; Rawnsley et al., 2019). Such loading may lead to losses via nitrate (NO₃⁻) leaching or gaseous emissions such as nitrous oxide (N₂O), which can result in adverse environmental implications such as eutrophication and global warming, respectively (Coskun et al., 2017; Harrison et al., 2011; Harrison et al., 2014a). Several physical, chemical and biological factors influence the fate of N inputs, which may be converted into oxide forms of nitrogen (N₃⁻), or ammonium (NH₄⁺) or transformed into a plant unavailable form within soil organic matter (immobilisation). At the same time, soil organic N may be released (mineralised) into plant-available mineral N (McNeill and Unkovich, 2007). The ongoing exchange between mineral N and organic materials, and subsequent release of immobilised N back into the soluble mineral N pool is known as the “mineralisation-immobilisation turnover”. While it is known that soil N mineralisation trends vary seasonally in line with temperature and soil moisture (Ji et al., 2014; McGarity and Myers, 1973; Contosta et al., 2011; Harrison et al., 2018), the extent to which long-term trends in seasonal mineralisation/immobilisation can be manipulated by tactical (seasonal) application of N and the implications of this interplay for pasture growth are yet unknown.

Because soil N cycling is a function of many abiotic and biotic factors (e.g. climate, soil N status, soil moisture, soil texture, organic matter, clay content etc.), dynamic, mechanistic models are essential tools for integrating such variables, providing insight into long-term relationships under manifold genotype by environment by management interactions (Alococ et al., 2014; Harrison et al., 2014a; Ho et al., 2014). Three contemporary models that allow N cycling in holistic pasture-based grazing systems include APSIM (Keating et al., 2003), DairyMod (Johnson, 2016) and DayCent (Del Grosso et al., 2008). DayCent is the most complex of the three models, as it was developed for the purpose of simulating carbon (C) and N fluxes in terrestrial ecosystems. The APSIM module used for simulating N mineralisation (SoIiN) has intermediate complexity, with soil organic matter pools mainly being based on measurable parameters, such as water-soluble carbohydrates and acid detergent lignin (Bell et al., 2015; Pembleton et al., 2016). The N mineralisation in DairyMod is more simplistic, being simulated as a function of the N mass in the slow and fast turnover pools, amount of biomass and respiration rate. Previous work comparing C and N cycling in biogeochemical models to measured data has shown that while simulated N cycling across models were similar, simulated N gas fluxes and soil N pools were quite different (Frolking et al., 1998). Other work validating the SoIiN module of APSIM (Sharif et al., 2011) has shown that APSIM underestimated soil mineral N, leaching and mineralisation. However, we are unaware of any studies that explicitly compare the ability of APSIM, DairyMod and DayCent in simulating soil N and pasture biomass using the same experimental datasets. Collectively these results call for (1) a comparison of APSIM, DayCent and DairyMod using the same measured data and across climatic zones and (2), deeper understanding of the reasons that drive differences in soil mineral N (e.g. soil N status, biomass and soil water content). These clear gaps in the literature are part of the novelty and necessity of this study. These objectives will allow insight into (1) whether model sophistication is related to improved ability to simulate soil N, pasture biomass and/or soil water, (2) whether tactical application of inorganic N in different seasons can be used to influence soil N mineralisation and pasture growth, and (3) how biophysical drivers of mineralisation processes in different models relate to real experimental data measured in the field. For instance, if one model is found to be more reliable than another in simulating soil N, these results could be used to improve the algorithms of other models in simulating soil N.

Here, we first calibrated APSIM, DairyMod and DayCent against temporally measured soil N, soil water, N₂O emissions and plant production, then validated each model using an independent dataset. In doing this, we aimed to gain better insight as to why or why not a given model simulated soil N well through concurrent examination of related model variables. All models were parameterised and validated using measurements from treatments collected from field experiments conducted under three different climates in southern and eastern Australia.

Past work with DairyMod has shown that N mineralisation rates in temperate, irrigated pasture-based systems are higher in summer and lowest in winter, reflecting trends in ambient temperatures and pasture growth (Harrison et al., 2017; Harrison et al., 2019a). However, the extent to which such trends can be manipulated by tactical N application is yet unknown. Our second aim was thus to determine whether tactical N application could be used to manipulate long-term trends in N mineralisation. A positive answer to this aim may suggest that N could be applied tactically through ‘loading the system’ that could later benefit pasture growth when environmental conditions became conducive to mineralisation. To conduct this study, we sourced experimental field data from three diverse environments. We then parameterised and validated APSIM, DairyMod and DayCent using these datasets. Using the validated models, we conducted scenario analyses by evaluating the impacts of seasonal N application on long-term trends in pasture biomass, soil water and soil N. We also performed an analysis in which the sensitivity of N mineralisation/immobilisation to either N fertilisation, irrigation or cutting frequency was examined. For consistency, sections are ordered alphabetically by model (APSIM, DairyMod and DayCent) and by site name (Casino, Camden and Noorat) throughout the manuscript.

2. Materials and methods

2.1. General approach

To compare simulated outputs from APSIM, DairyMod and DayCent in a variety of soil types and prevailing climatic conditions, we sourced
experimental data from sites spread across the Eastern seaboard of Australia. Field experiments were located in environments ranging from sub-topical with either (1) uniformly distributed seasonal rainfall (Camden, NSW) or (2) summer-dominant rainfall (Casino, NSW), to the cool temperate, (3) winter-dominant rainfall zone of southern Victoria (Noorat). Descriptions of field experiments below are provided for background only: experimental details for the Camden, Casino and Noorat trials are available in Dougherty et al. (2016), Mumford et al. (2019), and Kelly (2014), respectively. Following description of the model parameterisation and validation process, we detail the scenario analyses used to explore how the tactical application of N influenced long-term soil N cycling and mineralisation trends. The experimental procedure is shown in Fig. 1.

2.2. Experimental data: study sites and measurements

2.2.1. Camden

The Camden site was located 50 km SW of Sydney, Australia (34.1°, 150.7°E). Average annual rainfall over the last forty years at Camden was 750 mm (range 257–1261 mm), with 33% occurring during the summer months (December–February). Average annual minimum temperature occurred in July (with monthly average temperature of 10 °C), while average annual maximum temperature occurred in January (monthly average temperature of 23 °C) (Table S1). The soil at the site was a Eutrophic Red Chromosol (Isbell, 1997, Table S2). Each plot was fertilised, irrigated and harvested. Botanical composition was dominated by annual ryegrass (Lolium rigidum) and kikuyu (Cenchrus clandestinum). In these environments, kikuyu actively grows from mid-December through to March/April, at which point it is oversown with ryegrass. In the current experiment, ryegrass was harvested at the three-leaf stage and kikuyu was harvested at the three- or four-leaf stage. Treatments consisted of applying synthetic N at a rate of 46 kg N ha$^{-1}$ or 25 kg N ha$^{-1}$ immediately after every harvest in spring and autumn, and every other harvest in summer and winter. Irrigation was applied over summer as required. Pasture yield was estimated by collecting and composting pasture that was cut to a height of 5 cm from four quadrats per plot. Further details of pasture harvests, irrigation and fertiliser timing for each treatment are given in Table 1.

2.2.2. Casino

The experimental site was located at Casino, NSW, Australia (28.8°S, 152.9°E). Average annual rainfall over the last forty years was 1080 mm (range 528–1772 mm) with 38% occurring during the summer. Average annual maximum temperatures occur in February (31 °C), while average annual minimum daily temperatures occur in July (7 °C) (Table S1). The site soil was a black Vertosol (Isbell, 1997) with a clay content of 44% (increasing to 59% at depth) and a water holding capacity of 82 mm in the top 50 cm (Table S1). In line with regional practices, kikuyu pasture was mulched heavily in late April (autumn) and oversown with annual ryegrass drilled at a rate of 30 kg ha$^{-1}$ with 10 kg N ha$^{-1}$ as urea. The experiment included two irrigation treatments: a ‘high frequency’ (HF) irrigation treatment conducted using regular irrigation intervals (4–7 days) with low amounts (11–33 mm),...
Table 1

| Treatment | Parameterisation | Validation |
|-----------|------------------|------------|
| Camden (NSW) | 46 kg N ha⁻¹ urea treatment | 25 kg N ha⁻¹ urea treatment |
| | Fertiliser dates: 15 Sep 2012–29 Nov 2013 (14 applications) | Fertiliser dates: 13 Nov 2013–18 Dec 2014 (8 applications) |
| | Irrigation dates (mm): 3 Dec 2012–31 Jan 2014 (11, 22 or 33 mm; 33 applications in total) | Irrigation dates as for parameterisation treatment |
| | Pasture harvest dates: 8 Nov 2012–15 Apr 2014 (16 pasture harvests). | Pasture harvest dates: 1 Nov 2013–18 Dec 2014 (9 harvests) |
| Casino (NSW) | High-frequency irrigation treatment | Low-frequency irrigation treatment |
| | Fertiliser dates: 25 Apr 2015–25 Apr 2016 with 10–26 kg N ha⁻¹ as urea (19 applications). | Fertiliser dates and rates as for high-frequency irrigation treatment |
| | Irrigation dates (mm): 3 Jun 2015–11 Mar 2016 (4–17 mm; 23 irrigation days). | Irrigation dates (mm): 3 Jun 2015–22 Mar 2016 (10–94 mm; 16 irrigations) |
| | Pasture harvest dates: 25 Jun 2015–10 May 2016 (21 harvests) | Pasture harvest dates as for high-frequency irrigation treatment |
| Noorat (VIC) | 50 kg N ha⁻¹ urea treatment | 0 kg N ha⁻¹ treatment |
| | Fertiliser application dates: 19 Jul 2012–21 Aug 2014 (6 applications) | No fertiliser |
| | No irrigation | No irrigation |
| | Pasture harvest dates: 22 Aug 2012–11 Nov 2014 (12 harvests) | Pasture harvest dates as for 50 kg N ha⁻¹ treatment |

* Dates and rates of individual fertiliser and irrigation applications are provided in Supplementary Information 3 (Table S3).

while the ‘low frequency’ (LF) treatment was conducted by watering at two-four weeks intervals (see Tables 1, 2 and S3). Both treatments were fertilised with urea at rates ranging between 10 and 26 kg N ha⁻¹ per application (Table S3). Pasture harvests were conducted by mowing plots to a height of 5 cm with clippings removed from the plots. Further experimental details are outlined in Mumford et al. (2019).

2.2.3. Noorat

The Noorat field site was located at the Glenormiston College Campus (38.2°S; 143.0°E) in south west Victoria, Australia. Average annual rainfall over the last forty years at Noorat was 764 mm (range 399–1010 mm); rainfall primarily occurs during winter (33% between June and August) and only 16% in summer. Average annual minimum temperatures occur in July (9 °C), while average annual maximum daily temperatures occur in February (19 °C) (Table S2). The site soil was a black Dermosol (Isbell, 1997; Table S1). Botanical composition consisted of predominantly perennial ryegrass (Lolium perenne) and white clover (Trifolium repens). Urea was applied at a rate of 50 kg N ha⁻¹ after every second defoliation until the end of the growing season each year (100 kg N ha⁻¹ yr⁻¹; Table 1). Further background to the Noorat experiment is provided in Kelly (2014).

2.3. Overview of each model

2.3.1. APSIM

The Agricultural Production Systems SIMulator (APSIM v7.10 r4158, Holzworth et al., 2014) is a framework with task-oriented modules that simulate biophysical processes in farming systems (Keating et al., 2003). The APSIM SoilN and SurfaceOM modules simulate dynamics of N and C on a daily time-step in separate soil layers (Vogeler et al., 2013). APSIM has mainly been developed to simulate biological and physical processes in farming systems, initially with emphasis on cropping systems, and more recently also for pasture systems (Giltrap et al., 2015; Li et al., 2011). The SoilN module in APSIM is derived from CERES (Probert et al., 1998), being able to simulate mineralisation, immobilisation, nitrification, denitrification and urea hydrolysis. Soil organic matter is divided into three pools, a fast decomposing (BIOM), an intermediate (HUM), and a stable pool (INERT). Unlike DayCent, which couples the passive pool of organic C with the slow and active pools, the INERT pool in APSIM is uncoupled from that of other soil decomposition processes (Krull et al., 2003). SoilN assumes that synthesis of stable soil organic matter is predominantly through formation of BIOM, though some C may be transferred directly to the more stable pool (HUM). The model further assumes that BIOM and HUM have constant C:N ratios (Nguyen, 2016). Nitrogen mineralisation or immobilisation is determined as the balance between release of N during decomposition and immobilisation during microbial formation and humification (Archontoulis et al., 2014). Where there is inadequate mineral N to meet an immobilisation demand (e.g. high C:N of FOM), decomposition is limited by the N available to be immobilised (Nguyen, 2016).

2.3.2. DairyMod

Unlike the separation of pools for undecomposed soil organic matter and soil microbes in DayCent and APSIM, DairyMod (Johnson, 2016; Johnson et al., 2008) combines the fresh organic matter and decomposing enzymes into a single “fast” pool (Moore et al., 2014). DairyMod assumes that the supply of organic matter to the surface pool is from litter (dead plant material) and dung (Johnson, 2016). There are three soil organic matter pools (in addition to surface litter, dung and live roots): fast turnover (particulate organic matter) and slow turnover (humus) and inert. Decay characteristics of the fast pool are related to the digestibility of the inputs so that litter and dead roots from less digestible pastures will decay at a slower rate than more digestible inputs (Johnson, 2016). The organic matter and N sub-routine models in DairyMod are relatively simple compared with those in APSIM and DayCent. The only parameters required in DairyMod are the decay rate constants for the fast and slow pools (proportional decay per unit time), efficiency of decay (proportion of C respired during decay), and the transfer rate from the fast to slow pool (Johnson, 2016). The N concentration of the inputs are also required, with N content of soil organic matter pools calculated dynamically in the model.

2.3.3. DayCent

DayCent is the daily time-step version of the CENTURY biogeochemical model (Parton et al., 1998; Del Grosso et al., 2008). The model was developed to link to atmospheric models and to better estimate ecosystems trace gas fluxes (Parton et al., 1998). Flows of C and N between soil organic matter pools in DayCent are controlled by the size of the pools, C:N ratios and abiotic water/temperature factors. N gas fluxes from nitrification and denitrification are driven by soil NH₄ and NO₃ water content, temperature, soil texture, and labile C availability (Parton et al., 2001; Table S4). Soil organic matter is divided into active, slow, and passive pools, each having different decomposition rates. Above- and below-ground non-woody plant residues and organic animal excreta are partitioned into structural and metabolic pools as a function of the lignin

Table 2

| Treatment | Apr–Sep (mm) | Oct, Nov, Mar (mm) | Dec–Feb (mm) | N° of irrigation events | Cumulative total (mm) |
|-----------|-------------|--------------------|-------------|------------------------|----------------------|
| High frequency | 11 | 14 | 18 | 22 | 293 |
| Low frequency | 55 | 71 | 94 | 13 | 505 |
to N ratio in the residue (Parton et al., 1998). As the lignin:N ratio increases, more residue is partitioned to the structural pools, which have much slower decay rates than the metabolic pools (Harman and Parton, 2018). The active soil pool is influenced by soil texture but the active surface pool is not. The slow surface and soil pools include resistant plant material derived from the structural pool; both slow pools have turnover times ranging from years to more than a decade (Del Grosso et al., 2011). The passive pool is very resistant to decomposition, with turnover times of 300–1000 years (Del Grosso et al., 2008). The concentration of decomposition products (C, N, P and S) entering the passive pool from the active and slow soil pools increases with increasing clay content.

2.4. Model parameterisation and validation

Treatments used for parameterisation and validation are shown in Table 1, while soil characteristics including soil organic carbon are shown in Table S2. For each site, patched point climate data were obtained from the QLD Government (https://legacy.longpaddock.qld.gov.au/silo/). Each file contained daily values of solar radiation, maximum and minimum temperature, rainfall and evapotranspiration. Parameterisation for Camden, Casino and Noorat was conducted using the 46 kg N ha$^{-1}$ treatment, the HF treatment and the 50 kg N ha$^{-1}$ treatment, respectively, while the 25 kg N ha$^{-1}$, LF and 0 kg N ha$^{-1}$ treatments were used for validation (Tables 1 and 2). Each model was parameterised against measurements of soil volumetric water content, soil NH$_4^+$ and NO$_3^-$, seasonal cumulative N$_2$O emissions and shoot biomass production. The obtained parameterisation was validated using measurements from treatments shown in Table 1. For DayCent, parameterisation was performed by adjusting nine parameter classes controlling crop development and one parameter controlling N$_2$O emissions (Table S4). Parameterisation of each model was conducted first by adjusting parameters related to phenology (if any), second to equally to growth and to N cycling through iterative parameter adjustment to minimise the sum of squares residuals between observations and modelled values. Default and parameterised values are shown in Tables S4 and S5. Model evaluation statistics follow those outlined in Harrison et al. (2019b) including root mean square error (RMSE, ideal = 0, 0.10 = good, 0.1 = moderate, and > 0.2 = poor), coefficient of determination (R$^2$, range = 0–1, ideal = 1.0), mean bias (MB, the normalised difference between the observed and modelled mean; ideal = 0.0), variance ratio (VR, ratio of the variance of the observed data to that of the modelled data, ideal = 1.0; VR > 1.0 indicate greater variation in the actual data compared with the simulated data), mean prediction error (MPE, computed as the RMSE divided by the mean of the observed values. MPE values either <0.10, 0.10–0.20 or > 0.20 indicate good, moderate and poor model adequacy, respectively).

2.5. Scenario and sensitivity analyses: seasonal impacts of tactical N application on N cycling, pasture growth and mineralisation

Parameterised models were run using climate data from 1994 to 2019 to examine whether tactical N application could be used to influence seasonal trends in N mineralisation. At all sites pasture biomass was cut and removed at the end of month to a monthly residual biomass of 1000 kg DM ha$^{-1}$ (if there was less than 1000 kg ha$^{-1}$ at the end of the month, the models would not cut). In line with best management practice at Camden and Casino, 20 mm irrigation per week was applied from 1 June to 30 November. The first six years for each simulation were discarded to allow stabilisation of simulated values, thus results are shown for 20 years (2000–2019). Four N fertilisation treatments were conducted by applying 100 kg N ha$^{-1}$ per application on the first day of each season (1 Mar for autumn, 1 Jun for winter, 1 Sep for spring and 1 Dec for summer). A control scenario with no N fertilisation was also run. To determine the extent to which soil N status and N depletion influenced mineralisation, treatments were repeated with N only applied in the last ten years of the simulation (2009–2019, N$_{dep}$).

Sensitivity analyses were performed by perturbing each management variable in a piecemeal fashion using the N fertilisation treatment in summer as a case study. Sensitivity of model outputs were examined through modification to baseline nitrogen fertilisation levels, irrigation rates or cutting frequencies. Following Senapati et al. (2016), sensitivities of >0.1, 0.05–0.1 and < 0.05 were considered high, moderate and weak, respectively. Sensitivity treatments are shown in Table 3.

3. Results

3.1. Model inter-comparison

Simulated shoot biomass (Figs. 2-4 d-f) were within the range of observed yields; overall, the difference between sites was greater than the difference between models. For example, all models had high RMSE (700–900 kg DM ha$^{-1}$) for shoot biomass at Camden but the lowest RMSE at Casino (RMSE <400 kg DM ha$^{-1}$ Fig. 4g, h), RMSE of less than 400 kg DM ha$^{-1}$ were within the variability of observed cut yields, indicating adequate model performance. DairyMod generally had the lowest MB for shoot biomass, though there was large variability across sites. The variance ratio (VR, ratio of observed to simulated variance) for DayCent simulations of shoot biomass were generally greater than VR values for the other two models and overall R$^2$ values were low, ranging from 0.07 for DayCent at Camden to 0.59 for APSIM simulations at Noorat (Fig. 5h).

Volumetric water content (VWC) was reasonably simulated (Figs. 2a, 3a, 4a), albeit simulated values had a tendency for greater variability compared with observed VWC, particularly at Casino (Fig. 3a) and Noorat (Fig. 4a). The RMSE of all models for soil water content in the uppermost 10 cm were similar (Fig. 5a). Mean bias ranged between −0.04 and 0.04; in general MB for VWC for all models were reasonable. Variance ratio (VR) for VWC were between 0.75 and 1 (Fig. 5b, d, f), which indicates lower variation in modelled data compared with the observed data. R$^2$ values close to 1.0 suggest that all models simulated VWC relatively well (except for Casino, where R$^2$ values were very low).

Daily N$_2$O emissions were difficult to simulate (Figs. 2-4 g-i), however this was to be expected given that N$_2$O is a function of many other variables (soil N, rainfall, soil water content etc) and not all of these variables were identically matched by each model. However, N$_2$O emissions aggregated over the season were generally well simulated (Fig. 5m, n). Other than APSIM and DayCent simulations for Casino, cumulative N$_2$O emissions over the measurement period were well replicated.

In general, soil NH$_4^+$ was reasonably simulated (Figs. 2b, 3b, 4b). Across sites, there was a tendency for the models to underestimate NH$_4^+$ with the majority of MB being positive (Fig. 5i). DayCent produced the most reliable NH$_4^+$ simulations (Fig. 5i, j), having the lowest MB and VR. Soil NO$_3^-$ was well simulated at Noorat (Fig. 4c) and significantly underestimated by all models at Camden (Fig. 2c), though measured NO$_3^-$ at Camden may be questionable given that all models underestimated NO$_3^-$ at this site. RMSE for NH$_4^+$ ranged from 8 kg ha$^{-1}$ to 30 kg ha$^{-1}$, indicating reasonable ability in simulating NH$_4^+$ content.
considering the standard deviation of NH₄ ranged from 5 kg NH₄ ha⁻¹ to 20 kg NH₄ ha⁻¹ (Fig. 5e, f). For Casino and Noorat, DairyMod had higher VR for NH₄, suggesting that variability in modelled simulations was less than that for observations. RMSE values for NO₃ were generally higher than those for NH₄, but this was more reflection of the magnitude of the NO₃ data rather than greater model-measurement mismatch in the latter variable (Fig. 5g, h). VR for NO₃ of all models was generally greater than 1.0, suggesting lower variability in the modelled compared with the measured data.

3.2. Effects of tactical N application on long-term soil N cycling and N mineralisation trends

3.2.1. Camden

In the sub-tropical irrigated environment at Camden, the timing of N application had greater effects on pasture growth rates compared with immobilisation/mineralisation (Fig. 6). Without N fertilisation, pasture growth rates of DairyMod and DayCent were similar, however seasonal mineralisation of DayCent was higher than that from DairyMod (Fig. 6). N fertilisation in autumn, winter and summer had clear effects on pasture growth; in contrast, summer fertilisation (when moisture content was low) had inconsistent effects on growth rates across models. After either the winter or spring N fertilisation events, DayCent simulated levels of N₂O (peaks of 150–320 g N ha⁻¹) that were 7.5 times higher than the values observed from APSIM. This result may be partially attributed to greater nitrification rates in DayCent; even though NH₄ peaks following urea application were similar, NO₃ peaks from DayCent were higher than those from the other models. Both APSIM and DayCent exhibited clear immobilisation (negative mineralisation) trends when N fertiliser was applied, but such trends were less clear for DairyMod.

3.2.2. Casino

Under the irrigated sub-tropical environment at Casino, pasture growth responses to N applied in autumn, winter or spring for the three models were similar, although growth rates were generally higher for DayCent (Fig. 7). Despite similar NH₄ and NO₃ peaks for all models after N application, N₂O fluxes were greatest at Camden and Casino for DayCent, regardless of the timing of N application. Immobilisation in response to N application was simulated by APSIM and DayCent, with the troughs simulated by DayCent around a month later than those simulated by APSIM. While immobilisation was evident, there were no corresponding seasonal peaks in mineralisation, and as such
there was no clear association between mineralisation and pasture growth. These patterns suggest more gradual mineralisation that could not be discerned from background mineralisation rates.

3.2.3. Noorat

Under the winter-dominant rainfed environment at Noorat, N applied either in autumn, winter or spring resulted in similar growth rates. N fertilisation in summer resulted in less consistent trends over the long-term (Fig. 8). In all seasons, N applied resulted in the greatest increase in NH$_4$ and NO$_3$ simulated by APSIM; NO$_3$ for APSIM was greater than that simulated by the other models. The VWC at 30 cm followed similar trends for all models, peaking in winter and declining in summer, however VWC for APSIM was always less than that for the other models (and DairyMod was always the highest). Trends in N$_2$O fluxes followed those in NO$_3$, with APSIM simulating the highest fluxes, while N$_2$O emissions simulated by DayCent and DairyMod were more aligned with the timing of N fertilisation. Immobilisation was only evident for DayCent when N was applied in winter or spring (and negligible in summer). Mineralisation trends for APSIM and DairyMod at Noorat were little affected by fertilisation and consequently did not have discernible effects on pasture growth rates (Fig. 8).

3.3. Sensitivity treatments: effects of N fertilisation, cutting frequency and irrigation rate on N mineralisation

Overall, soil NH$_4$, NO$_3$, and N$_2$O in APSIM were most sensitive to management perturbation at the irrigated sites of Camden and Casino, while the relative change of these variables for the rainfed site of Noorat was greatest for DayCent (Figs. S8.1, S8.2 and S8.3). At Camden (Fig. S8.1), N mineralisation was relatively insensitive to either N fertilisation or irrigation with an average relative change of less than 0.02. However, N mineralisation of APSIM was relatively sensitive to cutting frequency (between 0.09 and 0.25), likely because cutting in APSIM had relatively moderate effects on pasture growth rate, NH$_4$ and NO$_3$, particularly from late autumn through to early spring (May-Sep).

Similar effects of management on N mineralisation were observed at Casino (Fig. S8.2), albeit the sensitivity of all models was relatively lower than results observed for Camden (average relative change of N mineralisation of between 0.09 and 0.17). At the rainfed site of Noorat
N mineralisation simulated by DairyMod and APSIM were similarly relatively insensitive to fertilisation or cutting. In contrast, sensitivity of DayCent N mineralisation in later summer/autumn (Feb-May) was highly sensitive to N fertiliser due to higher relative effects on pasture growth rate, NH4 and NO3 in DayCent compared with the other models.

Across sites, there was little relationship in absolute terms between N mineralisation and root biomass, except for that simulated at Noorat by APSIM and DairyMod, where trends were similar (Fig. S8.4). The sensitivity analysis did not reveal a clear relationship between the relative change in root biomass in response to management and N mineralisation (Fig. S8.5, 8.6 and 8.7) although relative changes in root biomass to N fertiliser or cutting frequency simulated by DayCent at Noorat were greater than corresponding sensitivities of the other models (Fig. S8.7). At irrigated sites, DayCent and APSIM had comparable N mineralisation/immobilisation responses to management at Camden, while DayCent was most sensitive to management at Casino (Fig. S8.5 and 6). Overall, our results indicate that N mineralisation/immobilisation simulated by DayCent was more sensitive than APSIM or DairyMod to either changes in fertilisation, irrigation or cutting frequency. These changes were more apparent in the absence of irrigation (Noorat, see Fig. S8.3, S8.7), where effects of fertiliser and cutting frequency on pasture growth rates and mineral N have greater relative effect in DayCent compared to the other models.

4. Discussion
4.1. Model parameterisation and validation
4.1.1. Pasture production
Our first aim was to compare the performance of three agroecosystems models (APSIM, DayCent and DairyMod) in simulating soil N using the same experimental data collected in three diverse environments. However, given that soil N cycling is influenced by N source (synthetic N and atmospheric deposition), N sinks (i.e. pasture biomass), N status, soil moisture and other factors, small discrepancies in such variables between models have implications for the reliability of simulated mineral N (NO3 and NH4) as well as N loss pathways (e.g. N2O). To this end, we also compared the performance of the three models in simulating biomass, soil water and N2O emissions. While soil water and shoot biomass at some sites were adequately predicted (e.g. all three models at Casino and DayCent at Noorat), in some cases there were large differences between observed and simulated values (e.g. Fig. 3). In general, model-measurement errors were greater between sites than between models.

Using the principle of parsimony, we calibrated as few parameters as possible. Indeed, in all model parameterisation experiments, models will be somewhat biased towards their site of calibration. It is important to note that the conceptual design of this study and...
the agricultural systems under which we tested the three models are unique. In contrast to other work that has examined nitrogen cycling in cropping systems, we tested the ability of APSIM, DairyMod and DayCent under multi-species, pasture-based cutting experiments spread across the eastern seaboard of Australia. The combination of parameters calibrated and their difference to default levels illustrates the inherent diversity in soil biochemistry between cropping systems (the situations under which model parameters have mostly been developed) and polycultural pasture swards subjected to periodic defoliation. We call for future work to further contrast dynamic models in their ability to simulate N cycling in pasture-based systems.

We also found that the algorithms used to model the transition between kikuyu and annual ryegrass in DairyMod are perhaps overly simplistic. In DairyMod, the transition between species is defined by the user based on fixed dates; in reality this would be determined by environmental cues, such as daylength and temperature, and these variables change between years. Such need to fix transitions between pasture species in this way may partly explain some of the seasonal mismatch between DairyMod simulations and those measured at Casino and Camden. However, DairyMod had the lowest MB and RMSE for biomass across sites. Further work using more environments and management conditions is necessary to determine whether DairyMod simulates pasture growth more reliably than the other models. Indeed,
while the pasture component of each model has received significant validation and testing individually (Bell et al., 2013; Cullen et al., 2014; Harrison et al., 2014b; Harrison et al., 2016a; Harrison et al., 2017; Harrison et al., 2018; Necpállova et al., 2015), few authors have compared all three models in the same study. Among these, Ehrhardt et al. (2018) assessed uncertainties in the three models but did not delineate and/or highlight the strengths and weaknesses of the three models studied here.

4.1.2. Soil NO₃, NH₄ dynamics and N₂O emissions

Model-measurement residuals for mineral N were generally greater between sites than between models, e.g. simulated soil NO₃ at Camden were consistently underestimated by all models (Fig. 4c). This indicates that either (1) field measurements of mineral N and N₂O required more replication, (2) models were poorly parameterised, (3) the process-bases for subroutines used in all models contain assumptions that did not hold in these environments, or (4) combinations of the above. It is possible that field conditions for nitrification at Camden were atypical given that the magnitude of NO₃ was reasonably well simulated at Casino and Camden. DairyMod was more reliable than DayCent and APSIM in simulating trends in NO₃ and NH₄, though this was primarily caused by the lower temporal variability of mineral N from DairyMod (this result was also supported by low relative change to management - see Supplementary Information 8). This result accords with observations of Harrison et al. (2018), who showed that NO₃ from DairyMod was generally more reliable than that from APSIM for Camden and Noorat, because the temporal NO₃ oscillations from DairyMod tended to be lower (and more in line with measured temporal NO₃ flux) than that from APSIM. These insights underscore the difficulty in attempting to simulate complex, dynamic biophysical systems with multiple interacting variables such as those typically seen in rainfed multispecies pasture experiments. Such complexity are key reasons why we parameterised three models using data from three independent sites.

In some cases, relationships between soil N₂O with soil water and/or mineral N measured in the field were difficult to discern, although there were clear peaks of N₂O when water content became saturating (Figs. 2-4 j-l). For the models used here, N₂O emissions are calculated as a function of water-filled pore space (WFPS; the volumetric water content relative to saturation), such that peaks of N₂O are sensitive to the WFPS value at which denitrification begins (between drained

Fig. 6. Modelled average pasture growth rates (HGR, kg DM ha⁻¹ d⁻¹), VWC (volumetric water content, cm³ cm⁻³), N₂O emissions (g N ha⁻¹ per week), NH₄ (ammonium, kg N ha⁻¹ per week at 10 cm depth), NO₃ (nitrates, kg N ha⁻¹ per week at 30 cm depth) and N mineralisation (kg N ha⁻¹ per week) across the N fertilisation treatments (autumn, winter, spring and summer) over 2000–2019 at Camden, Australia. Simulations were conducted with APSIM (red dashed lines), DairyMod (black dash-dotted lines) and DayCent (grey dotted lines).
upper limit and saturation), as well as NO$_3$ concentration. The models examined here may have overestimated the sensitivity of N$_2$O to soil N and/or water, whereas factors such as clay content, soil temperature or mineralisation of soil organic matter perhaps should have been given more weight in driving N$_2$O. Such differences underscore a key challenge in reliably simulating N$_2$O emissions in multi-species pasture field experiments. If either simulated VWC, NO$_3$ or NH$_4$ do not match measured values, simulated N$_2$O may also be in error (e.g. APSIM simulations for Camden). Even if soil water and soil N are well predicted, it is possible that simulated N$_2$O may still not match measured values due to other biotic factors such as changes in microbial mass (Risch et al., 2019) or field sampling regime (Ehrhardt et al., 2018; Meier et al., 2020). To limit such uncertainties in simulating N$_2$O, future modelling intercomparisons should examine soil N in each model by first stipulating inputs wherein model inputs for climate data, soil water content, biomass and soil C over time all match observed data. These conditions would provide more control over simulated NO$_3$, NH$_4$ and thus insight into N$_2$O emissions from the model vs those measured in the field (Ehrhardt et al., 2018; Sandor et al., 2016).

An illustration of the effects of treatment versus seasonal variation in mineral N is shown for Noorat in Fig. S7.1. Urea N applied in September 2013 had very little effect on mineral N, whereas N application in June 2014 had larger effects. While such perturbations were well simulated by each model, nitrification of NH$_4$ to NO$_3$ was not well simulated, indicating a need to investigate parameters governing this process and perhaps biophysical processes implicit to model algorithms. This trend was consistent across sites: while the amplitude of NH$_4$ was reasonably simulated at most sites, in general NO$_3$ was poorly simulated, suggesting greater emphasis may need to be placed in understanding and modelling of nitrification in irrigated and pasture-based systems with and without N fertilisation.

4.2. Effects of tactical N application on seasonal trends in N mineralisation

4.2.1. N$_2$O emissions

Across sites, relatively high NH$_4$ at Noorat may be explained by high clay content and soil organic matter at this site, which together increase sorption of organic N and NH$_4$ (Nieder et al., 2011). In general, high N$_2$O
emissions due to denitrification are observed in high clay soils with high levels of soil moisture, pH of 7–7.5, temperature between 15 and 35 °C, high soil organic matter content and high N levels (Saleh-Lakha et al., 2009; Zhu et al., 2013; Meier et al., 2020). While many of these factors were present at Noorat, with models simulating low denitrification rates and the lowest N2O emissions across the three sites (Figs. 6, 7 and 8), mainly due to relatively low soil moisture content.

Simulated N2O emissions at Casino and Camden by DayCent were relatively close to measured values, with peaks of 29–57 and 21–47 g N ha⁻¹ d⁻¹, respectively. In contrast, N2O emissions at Camden and Casino were underestimated by APSIM and DairyMod (Figs. 6 and 7). It is possible that low denitrification rate to soil temperature and moisture were the two primary factors leading to such underestimation in APSIM, similar to the result found by Xing et al. (2011). This assumption is supported by evidence obtained from the sensitivity analysis, where more irrigation was not accompanied by higher N2O levels (Figs. S8.1 and 2). Our results are partially in line with previous work by Harrison et al. (2018), who found relatively low N2O emissions at Casino and Camden with DairyMod.

4.2.2. Mineralisation

Across sites, mineralisation rates were more influenced by seasonal conditions than by tactical N application, as evidenced by comparing seasonal N mineralisation of each control with treatments where N was applied seasonally. While NH4, NO3 and pasture growth clearly responded in all models to applied urea, implications of N application for seasonal mineralisation rates and consequent pasture growth rates were less clear. Similarly, while N immobilisation in response to N fertilisation was evident in DayCent and APSIM, no immediate immobilisation in response to N application was evident in DairyMod. Our results indicate that while seasonal variation in N mineralisation does occur in fertilised pastured-based systems, this mineralisation cannot be distinguished from background immobilisation-mineralisation cycling that occurs daily. Rainfed pastures in Southeast Australia are generally dormant in December due to lack of soil moisture (Harrison et al., 2014c; Harrison et al., 2016b; Harrison et al., 2017), so application of N during this period would not be expected to benefit plant growth. This result was reflected in the long-term pasture growth at Noorat (Fig. 8). However, depending on seasonal conditions and soil C:N ratios,
it is likely that a greater fraction of N applied in December may be immobilised and later mineralised in the subsequent year. From our simulations, the re-mineralised N may be quickly depleted by plant uptake and result in increased summer pasture growth (Fig. 8), without affecting the overall N mineralisation levels. Similarly, the stored soil N in subtropical pastures can subsequently be rapidly re-mineralised and lost under wet and warm summer conditions (Rowlings et al., 2016), particularly when soil N content is high (Lobos Ortega et al., 2016).

In temperate regions, pasture growth is lower in winter due to growth-limiting temperatures. Our APSIM and DayCent simulation showed that when N was applied during winter (1st June), N mineralisation was lower and large amounts of N were immobilised compared with applying N in other seasons when temperature was greater (Figs. 6, 7 and 8). Ledgard et al. (1989) reported similar results, suggesting that trends were caused by a larger microbial N component when N was applied during early winter compared to an early spring application. Ledgard et al. (1989) intimated that availability of soil N when N was applied during early winter compared to an early spring application could be used to leverage seasonal trends in N mineralisation by models such as APSIM, DayCent and DairyMod in simulating soil N, pasture biomass and greenhouse gas emissions.

5. Conclusions

The objectives of this study were (1) to compare the performance of APSIM, DayCent and DairyMod in simulating soil N, pasture biomass and soil water and (2), to determine if tactical application of N fertiliser in different seasons could be used to leverage seasonal trends in N mineralisation to influence pasture growth. Despite considerable variability in the sophistication of each model, we did not find evidence for any one model more reliably reproducing measured data than other models. Differences in simulated soil NO3 and NH4 were often greater across sites than between models, indicating that each model was appropriate for simulating soil NO3 and NH4. Overall, our results suggest that each model is appropriate for simulating soil NO3 and NH4.

To further dissect the effect of N fertiliser, irrigation or cutting frequency on N mineralisation/immobilisation, sensitivity analyses were conducted (Supplementary Information 8). In general, these showed that N mineralisation/immobilisation simulated by DayCent was more sensitive than APSIM or DairyMod to either changes in fertilisation, irrigation or cutting frequency. These changes were more apparent in the absence of irrigation (site of Noorat, see Fig. S8.3, S8.7), where effects of fertiliser and cutting frequency on pasture growth rates and mineral N have greater relative effect in DayCent compared to the other models. It was also shown that while fertiliser, irrigation and cutting had intuitive effects on root biomass (e.g. greater addition of fertiliser also increased root biomass), clear relationships between the relative change in root biomass and the relative change in N mineralisation/immobilisation were absent. Our results suggest that biological, chemical and physical processes responsible for immobilisation/mineralisation in DayCent as a function of soil moisture as well as other driving variables (soil temperature, mineral N etc) were more sensitive to fertiliser and cutting frequency compared with the other models. The extent to which mineralisation or immobilisation eventuates as a function of such driving variables is an area that deserves further research.

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Declaration of competing interest

Nil.
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